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Welcome

Dear colleagues,

Welcome to the 20th edition of the International Symposium "The environment and the industry" to be held in Bucharest on September 28-29, 2017.

The symposium is aiming to bring together scientists, professors, consultants representing research and educational organizations, economic units, environmental authorities from all over the world in order to exchange their results, propose potential solutions to environmental issues and contribute to the integration of environmental dimension in the decision making process.

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HYBRID SONOLYSIS APPLICATION AS POLISHING STEP FOR REMOVAL OF THMS GENERATED FROM THE DRINKING WATER TREATMENT

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Abstract

Trihalomethanes (THMs) are organic compounds (with toxicity potential) generated during the classical treatment flow of drinking water as a result of reaction between natural organic matter (always present in drinking waters resources) and chlorine, which is the most disinfection reagent on a broad scale, in drinking water treatment plants. Ultrasonic treatment can be feasible for THMs removal for small or medium drinking water treatment plants.

This paper emphasyzes the possiblity to use sonolysis (chemical oxidation based on active radicals generated during cavitation process) as polishing step in drinking water treatment flow for trihalomethanes (THMs - trichloromethane, tribromomethane and bromodichloromethane) removal (initial concentrations over the admitted limit - 100 μg THM/l).

Four sonolysis systems were tested for synthetic and real surface treated water: direct sonolysis (US), US + H_2O_2, US + H_2O_2 + Fe (Fenton sonolysis), US + H_2O_2 + Fe + UV (low pressure mercury lamp $\lambda = 250 - 400$ nm). The variation domains of the main process parameters were as following: THMs concentrations 310 ÷ 3615 μg/L, sonolysis time 1 ÷ 60 min., ultrasonic energy $2x10^6$ J - $8x10^6$ J, ultrasonic amplitude 20 ÷ 80%, oxidant dose 0.6 ÷ 2.1 g H_2O_2/L, catalyst dose 0.25 ÷ 2 mg Fe^{2+}/L.

Experimental results showed the evolution of THMs removal depending on sonolysis system: direct sonolysis (US) 56% < sonolysis and hidrogen peroxide (US + H_2O_2) 59% < foto Fenton sonolysis (US + H_2O_2 + Fe + UV) 63% < Fenton sonolysis (US + H_2O_2 + Fe) 73% emphasizing that bromoform are more difficult to remove compared to other.

Keywords: *cavitation, drinking water, direct sonolysis, hybrid sonolysis, THMs*

Introduction

Ultrasonic radiation is a vibration of an elastic medium (water, gases, solids) having over 16 kHz frequency with many application in medicine, industry, biology as well as in water/wastewater treatment (Ashokkumar 2011).

Since 1990s ultrasound has been widely used in water and wastewater treatment processes as an emerging advanced oxidation process (AOP) technology, applicable for a wide range of contaminants with various initial concentrations (Mahammumi & Adewuyi 2010).

Generation, combination and recombination of free radicals, very reactive, able to degrade pollutants from water are the base of aqueous solutions sonochemistry (Ashokkumar 2011; Mahammumi & Adewuyi 2010; Naddeo & Belgiornao 2007).

Scientifically research in this field proved that direct sonolysis is efficient for advanced degradation of organic pollutants in water. Ultrasounds become more efficient in both pollutants degradation and economical if sonolyse is associated with other classical and AOPs methods for water treatment: US + H_2O_2, US + H_2O_2 + Fe, US + O_3, US + UV, US + electrochemical oxidation, US + adsorption (Joseph et al. 2009).

Natural organic matter from drinking water sources reacts with chlorine generating THMs. Over the limit of 100 μg/L THMs became toxic for human so, should be avoided their generation and diminished the concentrations below admitted limit if their formation cannot be prevented (Shemmer & Narkis 2005; Stefanescu et al. 2015).

Chlorine is still the most efficient and economical disinfectant having remanence in drinking water pipes. Because of this last reason chlorine cannot be totally replaced by ozone or/and UV radiation in the drinking water treatment plants.

Sonolysis could be an alternative option for THMs advanced removal from drinking water.

Experimental

This paper emphasizes the possibility to use sonolysis (chemical oxidation based on active radicals generated during cavitation process) as polishing step in drinking water treatment flow for trihalomethanes (THMs) removal (concentrations over the admitted limit - 100 μg THM/L).

Fig. 1 and Fig. 2 show the ultrasonic reactor (SONICS Vibracell 500) and photolytic reactor (Haereus) respectively which are used in sonolysis and hybrid sonolysis tests.

Figure 1. Ultrasonic reactor

Figure 2. UV Reactor

Preliminary experimental tests were performed on synthetic water (deionized water and THMs dosage: trichloromethane, tribromomethane and bromodichloromethane) in order to establish the influence of THMs initial concentration, type of sonolyse system, ultrasonic irradiation time, ultrasonic energy and amplitude. Ultrasonic frequency was constant - 20 kHz.

Four sonolysis systems were tested both for synthetic water and real surface treated water: direct sonolysis US, US + H_2O_2, US + H_2O_2 + Fe (Fenton sonolysis), US + H_2O_2 + Fe + UV (low pressure mercury lamp $\lambda = 250 - 400$ nm).

The variation domains of the main process parameters were as following: THMs concentrations 310 ÷ 3615 µg/L, sonolysis time 1 ÷ 60 min., ultrasonic energy $2x10^6$ J - $8x10^6$ J, ultrasonic amplitude 20 ÷ 80%, oxidant dose 0.6 ÷ 2.1 g H_2O_2/L, catalyst dose 0.25 ÷ 2 mg Fe^{2+}/L.

Results and Discussion

Sonolysis of synthetic solutions with THMs content

Experimental tests were performed for synthetic solutions with $CHCl_3$, $CHBr_3$, $CHBrCl_2$ in the following concentrations domain: $CHCl_3$ = 131 – 1536 µg/L, $CHBr_3$= 71 – 827 µg/L, $CHBrCl_2$ = 108 – 1252 µg/L, TTHMs (Total THMs) = 310 – 3615 µg/L. Sonolysis time was 1 ÷ 60 min. Ultrasonic energy field varied in the range of 2 ÷ 8 x 10^6 Joule and waves amplitudes were between 25 ÷ 80%.

The influence of the above mentioned experimental parameters was determinated (Tables 1 - 4).

Residual concentrations of THMs species were measured and removal efficiencies were calculated for each one and for total content (Tables 1 - 4 and Figures 3 - 5) .

Regarding *the influence of ultrasonic irradiation time*, sonolysis time between 30 – 60 min. leads to total residual THMs ≤ 100 µg/L (below admitted limit).

Fig. 3 shows that 78% is maximum removal efficiency of total THMs and $CHCl_3$ is the most removable THM (86% for 60 min. irradiation time).

Table 1. The influence of sonolysis time to remanent THMs concentrations

Sample	Time, min	Residual THMs concentrations, µg/L			Residual ΣTHMs concentrations, µg/L
		$CHCl_3$	$CHBr_3$	$CHBrCl_2$	
T1	1	94	49	73	216
T2	5	90	51	77	218
T3	15	58	50	53	161
T4	30	31	37	32	100
T5	45	29	33	28	90
T6	60	14	23	15	52

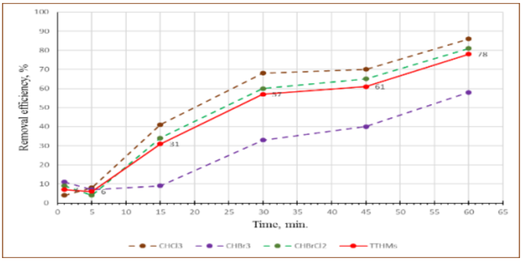

Figure 3. The influence of sonolysis time to THMs removal efficiencies

Concerning *the influence of initial THMs concentration*, for the same irradiation time, energy and amplitude the lowest residual THMs concentration was for sample C1 having THMs initial concentration 310 µg/L. Over this initial value the sonolysis process is not efficient in the selected operational conditions.

Table 2. The influence of initial THMs concentrations on residual organic content

Sample	Initial THMs concentrations, µg/L			Initial ΣTHMs conc., µg/L	Residual THMs concentrations, µg/L			Residual ΣTHMs conc., µg/L
	$CHCl_3$	$CHBr_3$	$CHBrCl_2$		$CHCl_3$	$CHBr_3$	$CHBrCl_2$	
C1	131	71	108	310	12.9	23.9	12.5	49.3
C2	237	135	196	568	52.5	84.9	57.2	194.6
C3	607	307	468	1382	144	147	133	424
C4	1048	531	820	2399	165	225	162	552
C5	1536	827	1252	3615	294	387	295	976
Time = 60 min, Energy = 4 x 10^6J, Amplitude = 25%								

The lowest value of total THMs residual content was determined for the highest value of ultrasonic energy (sample E4).

Regarding *the influence of ultrasonic energy*. Maximum efficiency for total THMs removal was 91% and bromoform has the lower value – 86%.

Table 3. The influence of ultrasonic energy to residual THMs content

Sample	Energy, J	Residual THMs concentrations, µg/L			Residual ΣTHMs concentrations, µg/L
		$CHCl_3$	$CHBr_3$	$CHBrCl_2$	
E1	$2x10^6$	26.3	35.5	25.4	87.2
E2	$4x10^6$	12.9	23.9	12.5	49.3
E3	$6x10^6$	11.3	17.4	10.4	39.1
E4	$8x10^6$	9.7	10.2	6.9	26.8
ΣTHMs = 310 µg/L ($CHCl_3$ = 131 µg/L, $CHBr_3$ = 71 µg/L, $CHBrCl_2$ = 108 µg/L), Time = 60 min., Amplitude = 25%					

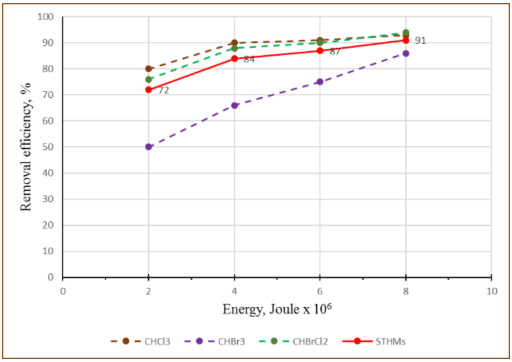

Figure 4. The influence of ultrasonic energy to THMs removal efficiencies

From the point of view of *the influence of ultrasonic waves amplitude*, the increase of ultrasonic amplitude has not a significant influence on residual THMs concentrations, which were in the domain of 26 – 30 µg/L.

Table 4. The influence of ultrasonic waves amplitude on residual THMs concentrations

Sample	Amplitude, %	Residual THMs concentrations, µg/L			Residual ΣTHMs concentrations, µg/L
		$CHCl_3$	$CHBr_3$	$CHBrCl_2$	
A1	25	9.7	10.2	6.9	26.8
A2	40	9.9	11	7.2	28.1
A3	60	8.9	9.7	7.5	26.1
A4	80	10.5	11.8	8.1	30.4
ΣTHMs = 310 µg/L ($CHCl_3$ = 131 µg/L, $CHBr_3$ = 71 µg/L, $CHBrCl_2$ = 108 µg/L), Time = 60 min., Energy = 8x10^6 J					

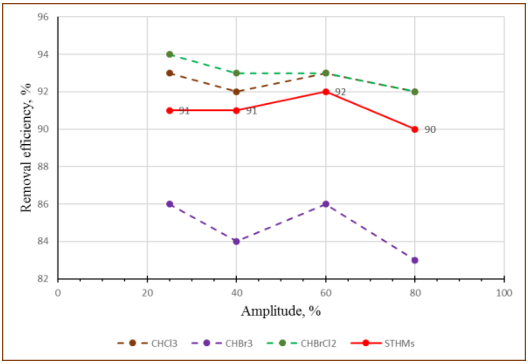

Figure 5. The influence of ultrasonic amplitude to removal efficiency of THMs

This tests confirm that bromoform had the lower removal efficiency (83% for the maximum amplitude of 80%).

Sonolysis of real drinking water with THMs content

In case of real drinking water which was pretreated by coagulation – flocculation (2 mg Al/L dose, 10 minutes stirring), flocculation with a flocculant based on starch and acrylamide (containing silver) 0.1% d.wt., 2 mL/L dose, TTHMs content was ~350 µg/L. These reagent doses and reaction times were established to be optimal based on previous research experiments (only the reaction time was halved).

The best results for the sonolysis tests were obtained in the following experimental conditions (Table 5):

- *direct sonolysis*: pH 7, time 30 min., energy 8x10^6 J, amplitude 25%;
- *hybrid sonolysis* US + H_2O_2: similar with direct sonolysis + 1,7 g H_2O_2/L;
- *hybrid sonolysis* US + H_2O_2 + Fe: similar with previous system + 1 mg Fe/L;
- *hybrid sonolysis* US + H_2O_2 + Fe + UV: pH 7, sonolysis time 30 min., UV irradiation time 30 min., 1,7 g H_2O_2/L, 1 mg Fe/L, energy 8x10^6 J, amplitude 25%, iron catalyst

and oxidant have put together in the photolytic reactor, after direct sonolysis phase.

Table 5. THMs removal efficiencies in different sonolysis systems

No.	Sonolysis system	ηTHM, %			ηTTHM, %
		$CHCl_3$	$CHBr_3$	$CHBrCl_2$	
1	US	70	48	65	56
2	US+H_2O_2	70	51	66	59
3	US+H_2O_2+Fe	82	67	80	73
4	US+H_2O_2+Fe+UV	63	66	59	63

Conclusions

Experimental results showed the evolution of THMs removal depending on sonolysis system: direct sonolysis (US) 56% < sonolysis and hidrogen peroxide (US + H_2O_2) 59% < foto Fenton sonolysis (US + H_2O_2 + Fe + UV) 63% < Fenton sonolysis (US + H_2O_2 + Fe) 73% emphasizing that bromoform are more difficult to remove compared to other.

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INDUSTRIAL WASTE Fe-Al COAGULATION AGENT UTILIZATION FOR WASTEWATER TREATMENT

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Abstract

This study shows the wastewater efficient treatment process resulted with Fe-Al complex coagulation agent obtained from industrial waste. Coagulation agent prezented 24.5 - 28.0 $g \cdot L^{-1}$ Fe and 16.0 - 17.5 $g \cdot L^{-1}$ Al content. pH coagulation agent is in the range pH=1-2. The wastewater with high degree *i.e.* chemical oxygen demand (COD) = 25,000-30,000 mg $O_2 \cdot L^{-1}$, Total organic carbon (TOC) = 3,600 - 4,000mg $C \cdot L^{-1}$, dry matter = 9.55 - 10.45 $g \cdot L^{-1}$, etc. is resulted from printing house. Treated water samples with the optimal dose of coagulation agent based on iron-aluminium salts obtained from industrial waste prezented similar TOC and dry matter reduction efficiencies with samples treated with the optimal dose of ferric chloride. COD reduction efficiency in treated water samples with the optimal dose of coagulation agent based on iron-aluminium salts it was 10% greater *vs*. reduction efficiency obtained from samples water treated with classic coagulation agent, $FeCl_3$. The advantage of the complex Fe-Al coagulation agent obtained from industrial waste was that it can be used for some wastewater of printing house in lower optimal dose, by 30%, *vs.* ferric chloride, coagulation agent. The complex Fe-Al coagulation agent obtained from industrial waste cost is much less than that of classical coagulation agents.

Keywords: *COD and TOC reduction efficiencies, Fe-Al complex coagulation agent, wastewater of printing house*

Introduction

The main pollutants in wastewater resulting from the production of printing agents and their use in packaging, textiles etc. are fine suspension and colloidal systems *i.e.* acrylic soluble compounds, compounds with chromospheres groups, alcohols, etc. Printing agents also contain dozens of additives, such as stabilizers, anti-foaming agents, blocking agents, surfactants, preservatives, etc. Coagulation of this type of wastewater involves processes of destabilization of fine particles and colloidal systems. In first step with subsequent union in large aggregates, mass transfer processes, adsorption processes of some organic/inorganic chemical species on the aggregates formed, etc. (Wu et al. 2002; Zhao et al. 2005; Ding et al. 2011). The coagulation process relates at increases effect of removing soluble substances by co precipitation and/or sweep coagulation (O'Melia 1980; Amirtharajah & O'Melia 1990; Letterman et al. 1999). Sweep flock is achieved by adding an excess of coagulant to the water that becomes saturated and the coagulant precipitates. The importance of the coagulation stage in a wastewater purification process results in the water cleaning effect, respectively, of the amount of pollutant removed from this water. Process efficiency is determined through conventional global parameters by characterization of raw and treated water: colour, turbidity, suspensions, organic matter expressed by demand chemical oxygen demand COD and / or total organic carbon TOC etc. and by specific parameters, *i.e.* a pollutant or class of pollutants. Chemical coagulation is considered as the optimal potential method for treating wastewater from print shop (Metes et al. 2000). Fast coagulation results are a waiting for the advanced reduction of turbidity, the formation of a coagulating sludge as compact as possible, which later are complemented by other specific analyzes of the process. Coagulation is largely rivalling with more expensive treatments such as adsorption on adsorbent materials *i.e.* activated charcoal or oxidation by ozone (Fissinger & Bersillon 1977). Aluminium or iron salts such as chlorides or sulphates are used as coagulating agents. This type of coagulant determines the aggregation of the matter present in the wastewaters in the form of a fine suspension or in a colloidal state with the formation of large heavy flocks which deposit at the bottom of the vessel. Replacement of classical coagulation agents with coagulation agents from industrial waste which containing trivalent metal ions present a feasible option in terms of both sustainable waste management and of course, the much lower cost price. The purpose of the paper was to replace classical coagulating agents, *i.e.* iron chloride in the coagulation step of highly polluted water resulting from cardboard packaging units with a coagulating agent with high content of Fe and Al originated from industrial waste.

Materials and Methods

Wastewaters from a printing unit with characteristics listed in Table 1 have been studied. Wastewater is in the form of a fine dispersion of print agent of apparently black ink. The fine black suspension of the wastewater passed into the filtrate completely through filtering on the filter paper Sartorius filter papers FT 2-206. Waters have sweet smell. The pH of the water was between pH = 7.05 ± 0.34.The wastewater shows high pollution, *i.e.* chemical oxygen demand (COD) = 25,000 - 30,000 mg $O_2 \cdot L^{-1}$, Total organic carbon (TOC) = 3,600 - 4,000 mg $C \cdot L^{-1}$, dry matter = 9.55 - 10.45 $g \cdot L^{-1}$.

Table 1. Characteristics of waste water from a printing house

Crt. No.	Parameters	Value min-max
1	Apparently colour	black
2	Real colour	black
3	Smell	sweet
4	Aspect	fine dispersion of ink agent, who partial pass through Sartorius filter paper FT 2-206
5	pH	7.05±0.34
6	Turbidity [°NTU]	can not be determined*
7	COD [$mgO_2 \cdot L^{-1}$]	25,000-30,000
8	Dry matter [$g/\cdot L^{-1}l$]	9.550-10.450
9	TOC [$mg\ C \cdot L^{-1}$]	3,600-4,000

*Turbidity analyzes could not be performed in the initial waters

The coagulation agents used were ferric chloride p.a *Chimopar Bucharest* and a complex coagulant containing iron and aluminium salts obtained from industrial waste. The characteristics of the complex coagulant obtained from industrial waste used in the coagulation tests are presented in Table 2.

Table 2. Characterization of complex coagulant ***(FA)*** obtained from industrial waste

No.	Characteristics	UM	Determined values	Method
1	pH		2.18	SR EN ISO 10523:2012
2	Copper	$[mg \cdot L^{-1}]$	712.2	SR ISO 8288-01
3	Cadmium	$[mg \cdot L^{-1}]$	<0.02	SR ISO 8288-01
4	Total Chromium	$[mg \cdot L^{-1}]$	1.24	SR EN 1233-03
5	Nickel	$[mg \cdot L^{-1}]$	1.13	SR ISO 8288-01
6	Zinc	$[mg \cdot L^{-1}]$	1.16	SR ISO 8288-01
7	Lead	$[mg \cdot L^{-1}]$	0.24	SR ISO 8288-01
8	Manganese	$[mg \cdot L^{-1}]$	64.6	SR 8662/2-96
9	Aluminium	$[g \cdot L^{-1}]$	17.5	SR EN ISO 11885:09
10	Iron	$[g \cdot L^{-1}]$	28.0	SR 13315-96/C91:2008

It is noted that:

- Concentrations of Al^{+3} and Fe^{+3} are 17.5 $g \cdot L^{-1}$ respectively 28.0 $g \cdot L^{-1}$; these concentrations are large enough to allow the use of the inorganic phase as coagulation agent
- Strong acidic media (pH = 2.18) keeps metal ions in soluble form, usable directly in coagulation processes;
- Heavy metal content is relatively low, compared to iron and aluminium ions; under these conditions the contribution of heavy metals introduced into the wastewater with the complex coagulant FA, is insignificant.

To perform the optimal dose determination tests for the wastewater coagulant in the printing works, has been achieved diluting the complex coagulant FA, at 1:10. The coagulation solution contains ÷ 2.8 mg $Fe \cdot ml^{-1}$ and 1.7 mg $Al \cdot ml^{-1}$. The classic coagulation agent to which coagulation results were reported with the complex coagulant FA, was iron chloride. Iron chloride having 4.6 mg $Fe \cdot ml^{-1}$ was used in coagulation tests. Methods: coagulation was performed with a stirrer equipped with variable speeds (Phipps & Bird Company, USA). The optimal dose of coagulation agents for maximum pollutant removal were done by Jar Test. The coagulation pH of the water investigated pH = 7.5, revised with acid or base. In the supernatant separated from the treated/coagulated samples conventional parameters were analyzed according to the standardized norms: pH determined by pH- meter 290A ORION RESEARCH USA type, turbidity with Micro 100 Laboratory Turbid meter, Scientific Inc. USA; COD by hot K dichromate oxidation in strongly acidic medium; TOC by TOC Analyzer with Multi N/C 2100 Analytic Jena, Germany.

Results and Discussion

In Table 3 are presented the results obtained by applying the Jar Test method in determination the optimal dose for wastewater from printing house. The coagulation agent used was ferric chloride. Analysis of the coagulated water samples was performed after filtration of coagulated samples at the optimal dose.

Table 3. Determination the optimal dose of coagulation agent ferrous chloride for wastewater from printing house by Jar Test method. Coagulation agent $FeCl_3$ (4.6 mg Fe·ml^{-1}), coagulation pH = 7.5

No	Parameters	Treated samples			
		3	4	5	6
1	Dose [mg Fe·L^{-1}]	55.2	73.8	92.0	113.6
2	Colour	The filtered samples are black. Incomplete coagulation			Light yellow
3	Turbidity [NTU]		-	-	13.0
4	Reduction efficiency [%]		-	-	-
5	Dry matter [g·L^{-1}]	7.5	6.4	3.6	1.55
6	Reduction efficiency [%]	28.0	38.5	65.5	85.5
7	COD [mg O_2·L^{-1}]	18,560	17,650	10,200	7,900
8	Reduction efficiency [%]	25.8	29.4	59.2	68.4
9	TOC [mg C·L^{-1}]	2,400	1,670	1,235	930.5
10	Reduction efficiency [%]	33.0	53.6	65.2	74.1

The dose of ferric chloride coagulant to which the treated sample forms heavy flocks which are retained on the filter paper was 113.6 mg Fe·L^{-1}. At this dose, the amount of dry matter was reduced with 85.5%, to 1.55 g·L^{-1}. Organic load reduction efficiencies were for COD of 68.4% and for TOC of 74.1%. In the literature, has been reported effective reduction COD up to 92.1%, after coagulation with the optimal dose of iron polychloride (Wu et al. 2002). Selection of $FeCl_3$ as a coagulant for wastewater treatment from printers caused the reduction COD with 88.75% (Zhao et al. 2005). Table 4 shows the results obtained by applying the Jar Test method in determining the optimal dose for wastewater from printing works. The coagulation agent used was a complex coagulant FA, obtained from industrial waste. The rising addition of complex coagulant FA determined the gradual reduction of the amount of printing agent in the wastewater. Although the amount of suspension is reduced, the water remains strongly loaded with coloured organic matter, which prevents determination of turbidity. In the case of FA doses between 39.1 - 86.9 mg metal·L^{-1} the treated wastewater after coagulation-filtration still strongly coloured with colloidal particles. The COD and TOC organic load reduction efficiencies were higher than for wastewater treatment with the optimal dose of classic agent, ferric chloride. In addition, these increased efficiencies of the organic load reduction were obtained at optimal doses of complex agent, 30% lower than the classic agent used, ferric chloride. The residual Al amount of the treated sample was 1.75 mg Al/L. Increasing the amount of complex coagulant FA, determined the improvement of filtration capacity, due to the fact that the flocks formed during the coagulation were larger and easier to filter. When the dose of complex coagulants increased to 90 mg metal·L^{-1}, the amount of residual Al in the treated sample was increased by a similar amount with the excess of Al from the coagulation agent.

Table 4. Determination of the optimal dose of complex coagulation agent FA, obtained from industrial wastes for wastewater from printing house, by the Jar Test method, pH-coagulation=7,5.

No.	Parameters	Treated samples				
		1	**2**	**3**	**4***	**5***
1	Coagulation dose [mg Fe·L^{-1}]	11.2+	16.8+	33.4+	**47.6+**	56.0+
	[mg Al·L^{-1}]	6.8	10.2	21.0	**29.8**	34.0
	Total metal [mg metal·L^{-1}]	18.0	27.0	54.4	**77.4**	90.0
2	Colour	Black suspension filtered samples contains			**Low yellow**	Low yellow
3	Residual turbidity [NTU]	-	-	-	**20.9**	15.0
4	Reduction efficiency [%]	-	-	-	-	-
5	Dry matter [g·L^{-1}]	-	9.0	8.3	**1.68***	1.34
6	Reduction efficiency [%]	-	13.8	29.6	**83.9**	87.1
7	COD [mg O_2·L^{-1}]	-	23,490	21,149	**5,490**	4,992
8	Reduction efficiency [%]	-	6.0	15.4	**78.0**	80.0
9	TOC [mg C·L^{-1}]	-	2,360	2,190	**790**	830
10	Reduction efficiency TOC [%]	-	33.6	39.1	**76.9**	78.0
11	Al Residual content [mg Al·L^{-1}]				**1.75**	22.0

Coagulation agent used: 1ml of FA solution containing 2.8 mgFe·ml^{-1} and 1.7 mgAl·ml^{-1}.
Note: The coagulation process continues with more flocks formation during 5-6 hours. Increasing the coagulation dose to 77.4 mg metal/L caused the agglomeration of the printing agent particles from the treated water becoming removable by filtration. The obtained filtrate contains 1.68 g·L^{-1} of suspensions by 83.8% less than the initial wastewater. At this dose, the organic load reduction efficiencies were for COD of 78.0% and for TOC of 76.9%.

Conclusions

The complex coagulation agent behaved as an efficient coagulation agent compared to a classical coagulant such as ferric chloride. Thus, it can be used for coagulation of wastewater with high content of organic matter such as printing agents on paper, cardboard, etc in a state suspended, colloidal or dissolved. The COD and TOC organic load reduction efficiencies from samples treated with optimal coagulation agent doses were higher than for wastewater treatment with the optimal dose of classical agent, ferric chloride. In addition, the optimal dose of coagulation complex was with 30% lower than the optimal dose of classical agent used, ferric chloride. The residual Al amount of the treated sample was 1.75 mg Al/L. Not least, Fe-Al complex coagulation agent is a cheaper product than classical coagulants, being obtained from the process of recovery of industrial waste.

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INFLUENCE OF TiO_2 DOPANT TYPE UPON CYCLOPHOSPHAMIDE DEGRADATION EFFICIENCY

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Abstract

The influence of various dopant types like S, Fe, Co, Ni (5% wt.) in the photocatalytic degradation of cyclophosphamide under UV-VIS irradiation was investigated. The working conditions were as follows: irradiation time up to 270 minutes, photo catalyst dose 100 mg/L, initial pollutant concentration 19.15 mg/L. Pollutant degradation was found to follow a pseudo first order kinetic. CP degradation rate constants decreases in the following order $k_{Fe\text{-}TiO2} > k_{Ni\text{-}TiO2} > k_{Co\text{-}TiO2} > k_{S\text{-}TiO2} > k_{TiO2}$, which was also in accordance with chlorine mineralization rate constants.

Keywords: *advanced oxidation process, cyclophosphamide, metal and non-metal doped TiO_2, photo catalysis*

Introduction

Pharmaceutical compounds ussualy present a complex structure and can not be properly treated using conventional wastewater treatment processes (Zhang et al. 2013; Tiron et al. 2015). Cytostatics drugs residues were found in hospital wastewater discharges in concentrations up to µg/L (Mahnik et al. 2007; Kovalova et al. 2009; Mullot et al. 2009). Moreover just a part of administered cytostatic drugs are metabolized within human body (Zhang et al. 2013) and are presenting a potential danger upon human health and environment due to their cytotoxicity, genotoxicity, mutagenicity and teratogenicity (Constantin et al. 2016).

Cyclophosphamide (CP) is one of the most commonly cytostatic drugs to be found in sewerage systems. CP removal efficiency is largely dependent on wastewater treatment plant's operating parameters (Seira et al. 2016). Since conventional treatment processes are not assuring advanced degradation of CP there is a need for more performant treatment processes such as advanced oxidation processes (AOPs).

Among AOPs photocatalytic water treatment using TiO_2 is a well-known process used for wastewater treatment. TiO_2 assisted photocatalyse can mineralize a wide range of organic compounds (Nitoi et al. 2016) into harmless end products such as carbon dioxide, water, and inorganic ions.

TiO_2 doping with metals or non-metals can reduce the band gap of the doped catalyst, enabling light absorption in the visible region (Lazar et al. 2012) and therefore improving degradation efficiency. By doping TiO_2 more $\bullet OH$ and $\bullet O_2^-$ radicals are generated (Iliev et al. 2010). For example TiO_2 doped with Fe^{3+} presented an improved photocatalytic activity compared with un-doped TiO_2. Fe^{3+} can be easily inserted within TiO_2 structure due to the fact that Fe^{3+} and Ti^{4+} presents similar ionic radius (Farhangi et al. 2011; Crisan et al. 2016; Crisan et al. 2015).

The aim of the study was to investigate the influence of various dopant types: S, Fe, Co, Ni upon the photocatalytic degradation efficiency of cyclophospamide under UV-VIS irradiation.

Experimental

Photocatalytic experiments were performed using an UV Heraeus reactor with TQ150-Z1 immersed medium pressure mercury lamp. Aerobic conditions were assured through air bubbling Q = 50 L/h in order to avoid hole-electron recombination processes that are negatively influencing photocatalytic degradation efficiency.

The following reagents were used: cyclophosphamide (CP) (Sigma-Aldrich), TiO_2, 5%wt.S-TiO_2, 5%wt.Fe-TiO_2, 5%wt. Co-TiO_2, 5%wt.Ni-TiO_2 (synthesized by "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, via sol-gel method).

Determination of CP concentration was done by gas chromatography method using and Agilent 7890A gas chromatograph coupled with an Agilent 240 Ion Trap Mass Detector.

Chlorine mineralization was monitored using a Dionex ICS-3000 Dual Pump ion chromatograph.

Photocatalytic degradation were duplicated in order to assure reproducibility.

Results and Discussion

For an initial cyclophosphamide concentration $[CP]_0 = 19.15$ mg/L = 7.34×10^{-5} M irradiation time was varied within the domain 30-270 minutes. Photocatalyst dose was maintained at 100 mg/L.

The obtained degradation efficiencies are presented in Table 1.

Table 1. CP degradation efficiencies

Photocatalyst	TiO_2	S-TiO_2	Co-TiO_2	Ni-TiO_2	Fe-TiO_2
Time, min			η_{CP} ,%		
30	17.02	22.09	31.80	35.09	35.25
90	54.73	60.84	69.45	69.56	71.91
150	72.01	82.09	84.28	84.54	86.42
270	93.42	96.34	96.45	97.08	97.96

$[CP]_0 = 19.15$ mg/L = 7.34×10^{-5} M, [Photocatalyst] = 100 mg/L

Degradation efficiencies after 270 min of irradiation were higher than 93 % (for all catalyst types), residual CP concentration varying between 4.83×10^{-6} M (for un-doped TiO_2) and 1.49×10^{-6} M (for 5%wt.Fe-TiO_2).

Kinetic curves for all catalyst types were linearized by a pseudo-first order kinetic using the following equation.

$$[CP] = [CP]_0 e^{-kt} \tag{1}$$

$$-\ln(\frac{[CP]}{[CP]0} = k\ t \tag{2}$$

where k – pseudo-first order degradation rate constant, t – irradiation time, [CP] – cyclophosphamide concentration, $[CP]_0$ – initial cyclophosphamide concentration.

Rate constants k were calculated from the linear regression of equation 2. The linear regressions for all catalyst types are presented in Fig. 1.

Apart for using linearization method a non-linear least squares fit applied to equation 1 was used to calculate the constant rates and results for both linear and non-linear methods are presented within Table 2.

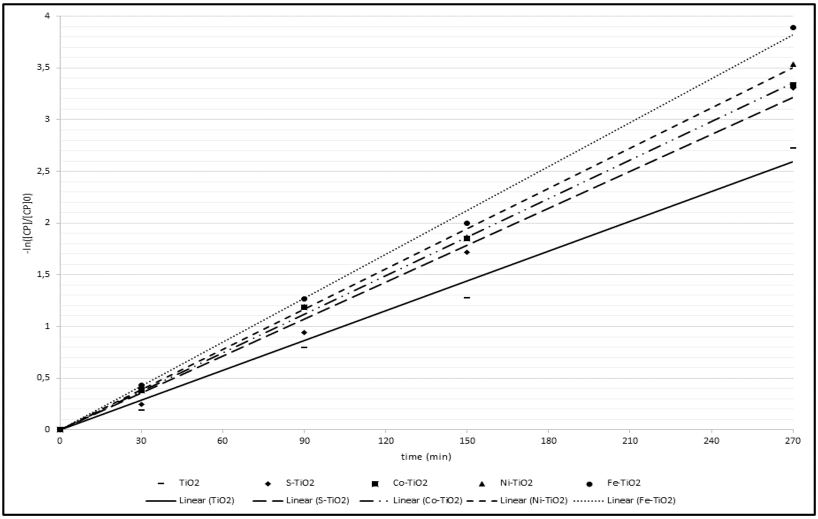

Figure 1. Linearization of CP degradation kinetic equations

Table 2. CP degradation rate constants
Linear *vs.* Nonlinear

Photocatalyst type	Linear		Nonlinear	
	R^2 (coefficient of determination)	k x 10^3 , min^{-1}	SS (sum of squares)	k x 10^3 , min^{-1}
TiO_2	0.9874	9.6	2.36 x 10^{-11}	8.54
S- TiO_2	0.9940	11.9	2.03 x 10^{-11}	10.52
Co- TiO_2	0.9993	12.4	1.25 x 10^{-11}	12.83
Ni- TiO_2	0.9988	13.0	4.42 x 10^{-12}	13.31
Fe- TiO_2	0.9977	14.2	1.54 x 10^{-12}	14.03

Pollutant degradation was found to obey pseudo first order kinetic. Degradation rate constants decreases in the following order $k_{Fe\text{-}TiO2} > k_{Ni\text{-}TiO2} > k_{Co\text{-}TiO2} > k_{S\text{-}TiO2} > k_{TiO2}$, which was also supported by chlorine mineralization efficiencies, presented in table 3, which were always lower that CP degradation efficiencies, due to formation of chlorinated intermediates.

Both linear and non-linear methods were also used in order to calculate organic chlorine mineralization rate constants. Linear equations are presented in Fig. 2 since a comparison between linear and nonlinear results is shown in Table 4.

Table 3. Chlorine mineralization efficiencies

Photocatalyst	TiO_2	S-TiO_2	Co-TiO_2	Ni-TiO_2	Fe-TiO_2
Time, min	η_{Cl} ,%				
30	16.70	21.88	27.64	28.99	31.10
90	34.17	38.58	49.53	55.86	57.78
150	44.92	55.48	65.65	67.57	74.29
270	71.60	84.65	88.49	92.72	94.64

$[CP]_0$ = 19.15 mg/L = 7.34 x 10^{-5} M, [Photocatalyst] = 100 mg/L

Table 4. Chlorine mineralization rate constants
Linear *vs.* Nonlinear

Photocatalyst type	Linear		Nonlinear	
	R^2 (coefficient of determination)	k x 10^3, min^{-1}	SS (sum of squares)	k x 10^3, min^{-1}
TiO_2	0.9889	4.5	0.098	4.46
S- TiO_2	0.9747	6.5	0.200	5.97
Co- TiO_2	0.9922	7.8	0.157	7.77
Ni- TiO_2	0.9787	9.2	0.194	8.80
Fe- TiO_2	0.9878	10.4	0.114	9.90

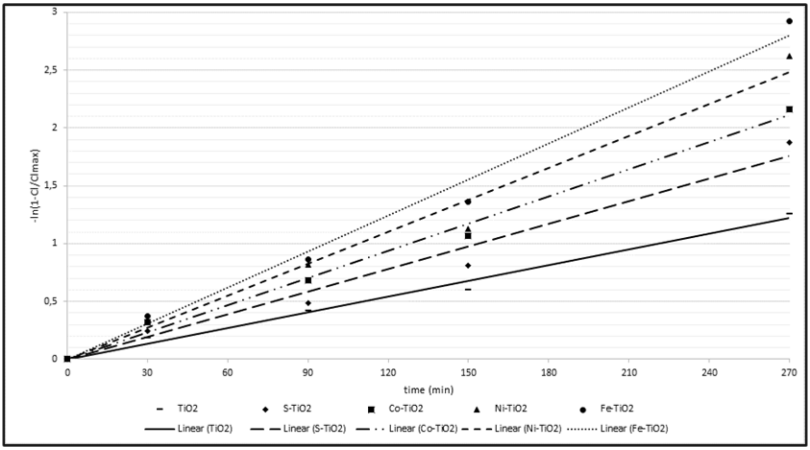

Figure 2. Linearization of Chlorine mineralization kinetic equations

Conclusions

CP degradation efficiencies were higher in the case of doped TiO_2 compared with un-doped TiO_2. The most efficient catalyst proved to be 5%wt.Fe-TiO_2 which assures a CP degradation efficiency higher than 97%, an organic chlorine mineralization efficiency higher than 94% and a remanent pollutant concentration of 1.49 x 10^{-6} M.
Constant rates for CP degradation and chlorine mineralization were calculated using both linear and non-linear models. Obtained values via linear method were compared with those calculated using a non-linear squares fit method and the results were

comparable, revealing the fact that CP degradation and chlorine mineralization processes are obeying a pseudo first order kinetic.

CP degradation rate constants followed the order $k_{Fe\text{-}TiO2} > k_{Ni\text{-}TiO2} > k_{Co\text{-}TiO2} > k_{S\text{-}TiO2} > k_{TiO2}$, which was also supported by organic chlorine mineralization rate constants.

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IN-SITU PHYTOREMEDIATION VARIANTS FOR TPH POLLUTED SOILS

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Abstract

A mixture of grassland species *Lolium perenne, Festuca arundinaceea, Medicago* sativa and Ttrifolium pratense were used in situ phytoremediation of oil polluted soil, with 70.45-120.52 g/kg d.m. Total Petroleum Hydrocarbons (TPH). They were studied variants of phytoremediation of oil polluted soils and fertilized with 50 t/ha stabilized sewage sludge in absence / presence of 50 t/ha fly ash, waste from coal burning power plants. Lolium sperenne herbs formed on the surfaces sown exclusive bouquets, in first weeks. After six weeks of vegetation appear and develop leguminous species Medicago sativa and Trifolium pratense. After five months, was a balanced distribution of species of legumes and grasses species on the surfaces sown. The efficiency reducing the TPH from oil polluted soil was 48.7% in variant fertilized with stabilized sewage sludge and fly ash. Efficiency was with 15.3% higher than the reduction efficiency of petroleum products in fertilized variants in fly ash absence. The process efficiency of oil polluted soil treated with stabilized sewage sludge and fly ash was similarly with phytoremediation variant with fertilizer and indigenous volcanic tuff realized.

Keywords: *fly ash, grassland species, in-situ phytoremediation, oil polluted soil, sewage sludge fertilizer*

Introduction

In addition to the phytoremediation in site, for soil polluted with oil products name total petroleum hydrocarbons (TPH) additional research is needed on specific method: selecting plant species tolerant and efficient evaluation of the merits of the polluted area, method and maintenance costs of implementing them, the prediction of risks occurring, likely results (Gerhardt et al. 2009). In polluted soil with compounds in oil are highly accumulations of derivatives of carbon. In relation to the high quantity of compounds with carbon content, the soil shows the amounts limiting nitrogen and phosphor. Bringing nutrients by plants based on C, N, P in relation to the optimal agronomic plant and provide the necessary micro-organisms in a complex process of development of the crop defaults. Biodegradation efficiency /reduction of petroleum products will grow in polluted soil (Basumatary et al. 2012). The addition of the adsorbent materials in polluted soil with TPH are able to correct soil characteristics polluted water loss in the petroleum polar compounds.

For example retain water in volcanic tuff and micro porous structure of this stock will release small amounts of water depending on the plants needs (Leggo et al. 2006). Fly ash acts by adsorbing properties and therefore reduce the early stages of development of plant stress caused by the amount high petroleum products in the polluted soil (Kishor et al. 2010). In addition, fly ash provides the required microelements from the soil (Basu et al. 2009; Ram & Masto 2014). They performed several studies of phytoremediation soil polluted with TPH. Studies phytoremediation are conducted in many countries, both on plants of meadows and shrub. It investigated the behaviour of several species of plants in the presence of different amounts of TPH in soil. Plants of meadows eg. species rye grass used in tests phytoremediation determine the effectiveness of reducing petroleum hydrocarbons in soil polluted with 6 g/kg up to 59% time in which to monitor the effectiveness of reducing soil pollution was for 80 days (Alarcón et al. 2008). Other species of perennial grasses such as tall fescue (Festuca arundinacea Schreb., or Lolium perenne) were also selected for phytoremediation of soils polluted with sheer oil because these species form an extensive network of roots and a robust development after installing culture. Grasses presents roots can penetrate the soil to a depth of up to 3m, and also, these plants show genetic diversity inherent which could give a competitive advantage to establish under adverse soil. Plants characteristic of natural grasslands based on grasses Festuca spp., Lolium spp., Cynodon dactylon have been used for the phytoremediation of areas with a higher pollution of 9 g/kg d.m. (Alarcón et al. 2008; White et al. 2006). In conclusion, TPH contaminated soil phytoremediation process can re-integrate the land destroyed into the natural circuits of the Earth (Aprill & Sims 1990; White et al. 2006).

Materials and Methods

The experimental study was conducted on soils contaminated with petroleum products conglomerates with high oil content had a diameter of between 3-10 cm, and range of TPH concentrations between 70.45-120.52 g/kg d.m. The conglomerate are black colour, with thick consistency, glossy and sticky smell of oil. Soil high conglomerate represents about 80-90% of studied soil and could not be crumbled. Soil inter conglomerate containing amounts between 3.57-11.50 g/kg d.m. The amount of petroleum products from contaminated soils used for phytoremediation experimental study is presented in Table 1. The experimental block is located in the experimental 46°16'.96.66"N, 21°43'46.1"E, elevation 150 m. Experimental block includes four lots/variants:

- soil polluted with oil products, lot P;
- soil polluted with oil products, fertilized with sewage sludge originated from the city wastewater treatment station, 50 t/ha treated with tuff indigenous, the amount of 5 t/ha, lot PNT;
- soil polluted with oil products fertilized with sewage sludge originated from the city wastewater treatment station, 50 t/ha and fly ash from burning brown coal in power plant (50 t/ha), lot PNC ;
- soil polluted with oil products, fertilized with sewage sludge originated from the city wastewater treatment station 50 t/ha, lot PN.

Surface of each experimental variants was a lot of 20 sqm. The experimental variants are separated from each other by spaces 1 m.

Table.1. Characterization of soils polluted with oil products (TPH) of experimental variation mixture of herbaceous plants cultivated in order of phytoremediation

No.	Lot	Soil deepness [cm]	pH	TPH in high soil conglomerates (min - max) [g/kg d.m.*]	TPH in soil inter conglomerates (min – max.) [g/kg d.m.]
1	PN	5-10	6,75	108,5-120,52	6,47-11,2
2	PNC	5-10	7,04	80,81-89,7	6,88-11,50
3	PNT	5-10	7,07	102,8-119,3g	5,88-6.11
4	P	5-10	7,18	70,45-71,3	3,57-5.32

*dry matter

Method for determining soil TPH

In an Erlenmeyer flask were mixed 3-5 g polluted soil with 5g anhydrous Na2SO4 and 25 ml tetrachloroethylene (Fluka). The content of Erlenmeyer flask was stirred 30 min at 100 rpm and then filtered through Whatman filter paper no. 4. Then flask and the filter paper were 3 times washed with 3 ml of solvent added to the filtrate in a porcelain capsule. The filtrate was evaporated at 75 °C until complete removal of the solvent. The residue of porcelain capsule was dissolved in 3 portions of solvent (15 ml, 10 ml and 5 ml) and passed (together with the undissolved parts) on the chromatographic column filled with aluminium oxide. The eluate was collected in a porcelain capsule. The solvent was evaporated from the capsule and weighed to constant mass. The identical residue was obtained from 28 mL of tetrachloroethylene (solvent), representing blank sample (without soil sample).

$$\mathrm{TPH}_{[\mathrm{mg/kg\ d.m.}]} = [(m_2-m_1) - (m_4-m_3)]/m_1 \times 1000] \qquad (1)$$

where m_1 - mass capsule 1 without residue, mg; m_2 - capsule 1 weight containing residue from polluted soil, mg; m_3 - mass capsule 2 without residue, mg; m_4 - capsule 2 weight containing residue from solvent, mg.

The volcanic rock comes from Marsid quarries and contains about 70% clinoptilolite 0,2-2 mm grained volcanic rock is used and strewn on the ground before spreading sewage sludge. Characteristics of sewage sludge ashes: humidity 99%, 35.4% organic matter, total nitrogen, 1.7%, 0.65% phosphorus, pH = 6.1. Fly ash and sewage sludge analysis were determined in ECOIND laboratory, as per national standardized. Metals content of fertilising materials / amendments is presented in Table 2.

Table 2. Metals content of fertilising materials / amendments

No.	Parameter	M.U.	Characteristics	
			sewage slugde	fly ash
1	Cd	mg/kg d.m.	3.43	2.43
2	Cr	mg/kg d.m.	134.7	92.4
3	Cu	mg/kg d.m.	333.9	74.3
4	Ni	mg/kg d.m.	27.4	51.7
5	Pb	mg/kg d.m.	157.8	67.4
6	Zn	mg/kg d.m.	304.6	169.0

The selection of plant species was made in view of resistance culture to extreme soil conditions with toxic elements, TPH and harsh climatic conditions, hot summers with prolonged drought. Plants tolerant which were selected was legumes and grasses meadows. The mixture of plant species selected included: *Lolium perenne, Festuca arundineceea*, *Trifolium pretense, Medicago sativa*. The seeding was done with an amount of 18-20 kg/ha**.**

Vegetation cover degree was determinated after Braun-Blanquet and Ellenberg and is presented in Table 3 (Wikum & Shanholtzer 1974).

Table 3. Abundence-Dominance Index after Braun-Blanquet and Ellenberg

No	**Level**	**Cover degree [%]**	**Abundence-Dominance mean, (*ADm*) [%]**
1	+ (scattered plants)	0.1-1	0.5
2	1 (diminshed)	1-10	5
3	2 (1/20 cover from area)	10-25	17.5
4	3 (¼-½ cover from area)	25-50	37.5
5	4 (½-3/4 cover from area)	50-75	62.5
6	5 (>3/4 cover from area)	75-100	87.5

Results and Discussions

Characterization presence grasses species in the experimental study of phytoremediation of soils polluted with petroleum products is presented in Table 4. Plants of the species *Lolium spp*. presented in Week 2 of vegetation a coverage area that lot of 40-50% for experimental versions of polluted soil, fertilized and treated with fly ash from coal combustion or fossil indigenous tuff. For these variants experimental area covered by plants of *Lolium spp*. was extended in the 6th week vegetation at 60-80%.

Table 4. The presence of the *Lolium spp* in the experimental lot

Lot	**Week 2 Total vegetation degree [%]**	**Week 6 Total vegetation degree [%]**	**Week 10-**		**Week 20 after harverst**	
			Total vegetation degree [%]	***Lolium spp.* cover of Total vegetation degree [%]**	**Total vegetation degree [%]**	***Lolium spp.* cover of Total vegetation degree [%]**
PN	20	40-50	70	80	75	40
PNC	40	60	80	90	90	50
PNT	50	80	95	100	100	50
P	-	5	60	40	70	40

The 6th week of the lots were invaded by weeds, which required their removal repeated. At week 10, demonstrated an overall areas planted vegetation cover 80-95% for experimental versions of polluted soil, fertilized and treated with native tuff or fly ash. Of the total area covered by plant species of grasses *Lolium spp.* has occupied 90% where it was used as an additive to fertilizer fly ash and 100% if it was used as an additive to fertilizer tuff indigenous. A satisfactory result was obtained in soil fertilized with sewage sludge when the area occupied plants was 70%. In this case the presence of *Lolium spp.* was 80% of the area covered by plants. In Table 4 are presented the results obtained after harvest. The 20th week showed a degree of vegetation cover 90-100% for experimental versions of polluted soil, fertilized and treated with fly ash or tuff indigenous. Of the total area covered with grass plant, species *Lolium spp*. occupies only 50%. A satisfactory result was obtained in soil fertilized when the plants area occupied was 75%. In this case the presence of *Lolium spp.* was 40% of the area covered by plants. Reducing the presence of *Lolium spp*., the total degree of vegetation cover resulting from expansion of other species of plants mixture was seeded lawns that lot. In the experimental variant unfertilized plants will recover delays due to late emergence. Of the total degree of vegetation cover 70% of this batch presence *Lolium spp.* up to 40%. In Table 5, is presented abundance–dominance index Braun-Blanquet for plant species to experimental variant PN after harverst.

Table 5. Abundance–dominance index Braun-Blanquet for plant species to PN after harvest (20th week)

No	Species of plants	The presence of plant species in total vegetation degree [%] / abundance –dominance index	Observations
Grasses			
1	*Lolium spp.*	40% / Level 3	large areas of the plant
2	*Festuca spp.*	5% / Level 1	individuals scattered
Legumes			
3	*Trifolium spp.*	5% / Level 1	some plants
4	*Medicago spp.*	20% / Level 2	plants as a group

It is noted from Table 5 that the experimental polluted variant and fertilized with sewage sludge and has developed best species of plants grasses *Lolium spp*. This plant has occupied 120 week after mowing, 40% of the area covered with plants and level 3 for Abundance–dominance index Braun-Blanquet. Ranked second in the standings is leguminous plant development (*Medicago sativa*) which occupied 20% of the area covered with plants and Level 2 for Abundance–dominance index Braun-Blanquet. *Festuca spp*. and *Trifolium spp*. occupied 5% of the area covered with plants and Level 1 for Abundance–dominance index Braun-Blanquet. In Table 6 is presented abundance–dominance index Braun-Blanquet for plant species to experimental variant PNC after harverst. Shown in Table 6 that the experimental variant polluted and fertilized with sewage sludge in fly ash presence was developed *Lolium spp*. and *Medicago sativa*. This plant has occupied after mowing, 50% of the area covered with plants and Level 4 for Abundance–dominance index Braun-Blanquet. Ranked second in the standings is leguminous plant development (*Medicago sativa*) which occupied 30% of the area covered with plants and Level 3 for Abundance–dominance index Braun-Blanquet. Addition of fly ash with sewage sludge fertilizer favoured the species *Medicago sativa and Lolium spp.*

These species occupied areas by 10% higher than in the case of variant fertilized in the absence of fly ash. *Festuca spp* and *Trifolium spp* occupied 5% of the area covered with plants and Level 1 for Abundance–dominance index Braun-Blanquet. In Table 7 is presented abundance–dominance index Braun-Blanquet for plant species to experimental variant PNT after harvest.

Table 6. Abundance–dominance index Braun-Blanquet for plant species to experimental variant PNC after harverst (20th week)

No	**Species of plants**	**The presence of plant species in total vegetation degree [%] / abundance –dominance index**	**Observations**
		Grasses	
1	*Lolium spp.*	50% / Level 4	large areas of the plant
2	*Festuca spp.*	5% / Level 1	individuals scattered
		Legumes	
3	*Trifolium spp.*	5 % / Level 1	some plants
4	*Medicago spp.*	30% / Level 3	bouquets branched

Table 7. Abundance–dominance index Braun-Blanquet for plant species to experimental variant PNT after harvest (20th week)

No	**Species of plants**	**The presence of plant species in total vegetation degree [%] / abundance –dominance index**	**Observations**
		Grasses	
1	*Lolium spp.*	50% / Level 4	large areas of the plant
2	*Festuca spp.*	Level + - 1-2 individuals	individuals scattered
		Legumes	
3	*Trifolium spp.*	10% / Level 2	some plant
4	*Medicago spp.*	30% / Level 3	bouquets branched

Shown in Table 7 that the experimental variant fertilized with sewage sludge polluted and treated with tuff native was developed best species of plants grasses *Lolium spp*. The presence of plant species in total vegetation cover grade and abundance – dominance index Braun-Blanquet it was similar to that obtained in the experimental variant of phytoremediation of polluted soils fertilized with sewage sludge and treated with fly ash. *Festuca spp.* only occurs sporadically, a few wires and legumes species of *Trifolium spp.* occupied 10% of the area covered with plants. The area covered with plants clover was 5% higher than in the experimental variant of phytoremediation of polluted soils fertilized with sewage sludge and fly ash treated with the surface covered with plants. 10% of the area covered by weed plants develop from the seeds made of sewage sludge (Level + respectively Level 2 for abundance –dominance index Braun-Blanquet). In Table 8 is presented abundance – dominance index Braun-Blanquet for plant species to experimental variant P after harvest. It is noted from Table 8 that the experimental variant polluted was developed best species of plants grasses *Lolium spp*. This plant has occupied 40% of the area covered with plants and Level 3 for abundance – dominance index Braun-Blanquet. The second place ranking is leguminous plant development which occupied 20% of the area covered with plants and Level 2 for index Braun-Blanquet. *Festuca spp.* appears only sporadically, *Trifolium spp.* increase as a few scattered groups.

In Table 9 is presented Total petroleum products (TPH) variation content in soils unfertilized / fertilized in the absence / presence amendments.

Table 8. Abundance–dominance index Braun-Blanquet for plant species to experimental variant P after harvest (20 th week)

No	Species of plants	The presence of plant species in total vegetation degree [%] / abundance –dominance index	Observations
Grasses			
1	*Lolium spp.*	40% / Level 3	large areas of the plant
2	*Festuca spp.*	-	-
Legumes			
3	*Trifolium spp.*	-1-2 plants Level +	few scattered groups.
4	*Medicago spp*	20 % / Level 2	bouquets branched

Table 9. Total petroleum products (TPH) content unfertilized / fertilized soil in the absence / presence amendments

No.	Lot	Total petroleum products **TPH [g/kg d.m.]**				
		Initial	**Week 6**	**Week 12**	**Veek 14**	**Veek 20**
1	PN	114,5	102,45	86,11	80.09	78,19
2	PNC	85,7	88,9	79,63	64,2	44,0
3	PNT	120,32	116,5	108,38	89,5	54,1

It notes that TPH products, reduce the variance of soil studied, planted with meadows. Noted that the polluted soil fertilized without amendments remain significant amounts of petroleum products: 78.19 g/kg d.m. The fertilized in the presence of polluted soil amendments remain after five months of growing quantity of oil in the range 44.0-54.1 g/kg d.m. TPH reduction efficiency was 48.7% in the experimental variant PNC and 54.8% in the experimental variant PNT. TPH reduction efficiency was 33.4% in the experimental variant polluted fertilized, but the non-amended.

Conclusions

Plants of the species *Lolium spp.* sprung up exclusively on the cultivated variants. The plants had during sprouting a degree of surface vegetation cover seeded 40-50% for experimental variants of polluted soil, fertilized and treated with amendments, fly ash resulting from burning coal on fossil power plant or native tuff. For these variants remains six week exclusively experimental area covered by plants of *Lolium spp*. After 10 week of vegetation, coverage sown variants reaches 80-95%. Plants of the species *Lolium perenne* have a twin. As a consequence the presence of the species reaches 90-100%. After harvesting, week 20, total vegetation coverage of the lot fertilized in the absence / presence amendments reaches 75-100%. After harvest the presence of *Lolium spp*. of the total coverage area was 40-50%. Leguminous plants have sprouted with delay of up to 6 weeks toward *Lolium spp.* The decrease in the area occupied by the *Lolium spp.* was due to the extension of the areas occupied by the leguminous plants. Effectiveness of reducing TPH products from studied soil variants, cultivated with grassland plants was 48.7% for the polluted, fertilized and fly ash treated, PNC, variant. The TPH reduction efficiency in the polluted, fertilized and volcanic tuff treated variant was 54.8%. The polluted soil fertilized in the presence amendments remain after 5 months of grass quantities of petroleum products in the range 44.0-54.1 g/kg d.m. TPH reduction efficiency was 33.4% in the polluted fertilized, but the non-amended variant. It should be noted, that in the polluted soil and fertilized in the absence of amendments, significant quantities of oil products remain in the soil, *i.e.* 1.5-1.8 times more than in polluted soil, fertilized in amendment presence and grass.

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KINETIC AND MECHANISM OF TNT DEGRADATION BY UV-VIS PHOTOCATALYSIS ON IRON DOPED TiO_2

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Abstract

2,4,6-Trinitrotoluene(TNT) is one of most common toxic pollutant identified in wastewater generated from ammunitions plants, due to its potential carcinogenic characteristics. Various treatment methods were investigated in order to remove such toxic pollutants and among them, photocatalysis was successfully applied. From various semiconductors, titanium was a widely studied photocatalyst, due to its chemical inertness, low cost, photo stability and nontoxic character. Since, TiO_2 is only photoactive under UV irradiation, modification of semiconductor by metal doping, aimed to reduce photocatalyst band gape and increase its quantum efficiency in visible domain represents an important issue. Fe-TiO_2 assisted photocatalytic degradation of TNT in aqueous media, under UV-VIS irradiation was studied. The effects of operating parameters such as catalyst loading and pollutant concentration were assessed. TNT degradation was found to follow a pseudo-first order kinetic. The main oxidative species responsible for pollutant degradation are the surface adsorbed hydroxyl radicals.

Keywords: *Fe doped TiO_2, kinetic, mechanism, photocatalysis, 2-4-6-Trinitrotoluene*

Introduction

2,4,6-Trinitrotoluene(TNT) is one of most common toxic pollutant identified in wastewater generated from ammunitions plants. Due to its potential carcinogenic characteristics, TNT presence in water bodies presents risk for human health and aquatic life (Won et al. 1976). These reasons, imposed including of TNT on the list of priority pollutants which are strictly regulated in EU countries.

Although, the major route of natural TNT degradation in aquatic environment is photolysis, with a half-time about 70 days (Nahem et al. 1997), partial aromatic ring cleavage and pure mineralization imposed implementation of powerful treatment methods in order to assure an adequate pollutant removal. In the last decade, advanced oxidation processes (AOPs) have been proved to be effective for destruction of refractory toxic pollutants (Zaharia & Suteu 2014). Several researchers studied the mineralization of nitro aromatic compounds using UV/Fenton's reagent (Li et al. 1998; Liou et al. 2003) or UV/H_2O_2 technique (Ho 1986; Hwang et al. 2004). Li et al. (1997) investigated the conversion of 2,4,6-TNT by Fenton's reagent, in which higher oxidation efficiency was obtained at pH 3.0. Some other publications have been issued on the decomposition of 2,6-DNT through ozonation, H_2O_2/O_3 or UV/O_3 methods (Beltran, et al., 1998) (Beltran, et al., 1998). Beside these photoinduced techniques, semiconductor photocatalysis has been proved to be effective in degradation of nitroaromatics (Vohra & Tanaka 2002). Among various semiconductors, titania was a widely studied photocatalyst, due to its chemical inertness, low cost, photostability and nontoxicity (Ribeiro et al., 2015; Petrov et al. 2007). However, TiO_2 is only photoactive under UV light irradiation due to its wide band gap energy (3.2eV: anatase). Therefore, the modification of semiconductor aimed to reducing the photocatalyst band gape and increase its quantum efficiency in visible domain represents an important issue. One feasible approach consists in doping oxide semiconductor with metal, which allows to extend the light absorption of photocatalyst in visible region (Feng et al. 2014). Also, it is experimentally found that the presence of iron in Fe–TiO_2 catalysts enhances the photocatalytic activity of TiO_2 by acting both as hole and electron traps (Zhu et al. 2004).

0.5%Fe-TiO_2 assisted photocatalytic degradation of TNT in aqueous media, under UV-VIS irradiation was studied. The effects of operating parameters such as catalyst loading, pollutant concentration and irradiation time were assessed. The kinetic and mechanism of pollutant degradation were also investigated.

Experimental

The photodegradation experiments were performed in a batch reactor equipped with cooling system and a medium pressure Hg lamp as UV-VIS light source ($\lambda = 320$-550 nm). Thin film catalyst supported on glass plate 4 pieces placed at equal distances from central positioned UV-VIS lamp were immersed into reactor filled with (nitrobenzene) NB aqueous solution with pH=7 and 2.51×10^{-4}M content . During photocatalysis experiment air was bubbled into solution at 50L/h flow. TiO_2 and TiO_2 doped with various Fe concentration (0.5-5%wt.) catalysts were tested in order to assess the influence of metal dopant presence and its concentration on NB degradation efficiency at various irradiation times (30 -240 min). In order to evaluate the effect of the main active species involved in Fe-TiO_2 assisted photocatalytic degradation of NB we suppressed the free $\bullet OH$ radicals mediated process by addition of 14.63×10^{-3} M iso-propanol (i-PrOH) scavenger. Lock of $\bullet OH_{ads}$radicals production on the catalyst surface was assured by addition of 14.63×10^{-3}M sodium iodide (NaI). The initial and irradiated samples were analysed for NT and inorganic nitrogen (N_{inorg}= N-NO_3^-+ N-NO_2^- + N-NH_4^+) concentrations by Gas Chromatography (GC), and Ion Chromatography respectively.

Results and Discussion

Effect of photocatalyst loading

A series of experiments were carried out on TNT solution with 2.72×10^{-4} M content at pH=7, by varying the 0.5%Fe-TiO_2 photocatalyst dose between 50-500 mg/L. For each photocatalyst dose, TNT initial degradation rates (r_0) were calculated at 30 min irradiation times.

The results presented in Fig. 1 show that r_0 values increases up to $0.64\times10^{-7}Ms^{-1}$ by increasing the catalyst dose from 50 to 200 mg/L. Increase of catalyst loading above 200 mg/L leads to degradation rate decrease. Thus, a value of $r_0 = 0.41 \times 10^{-7} Ms^{-1}$ was calculated at 500 mg/L dose. The enhancement of TNT initial degradation rate with catalyst loading was due to the increases in the surface area of the catalyst available for pollutant adsorption and degradation. Higher values than optimum catalyst dose (200 mg/L) increase the solution turbidity leading to decreases in the penetration depth of light into suspension and in the degradation rate (Robert et al.

2003; Daneshvar et al. 2004). In all subsequent experiments the optimum catalyst loading of 200 mg/L was applied.

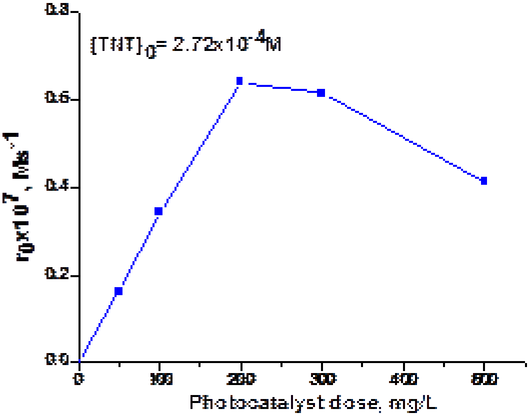

Figure 3. Evolution of TNT initial degradation rate (r_0) *vs.* photocatalyst dose

Effects of TNT initial concentration and irradiation time

Since TNT concentration in real aqueous systems varies, it was necessary to assess the influence of these parameters on pollutant conversion efficiency in order to set up the optimum working conditions which assure TNT advanced degradation. The experiments were carried out on four different initial TNT concentration, situated between (0.27-2.72) x 10^{-4} M, using established photocatalyst optimum dose, at pH=7 and various irradiation times (30-240 min). Experimental results are presented in the Table 1.

Under the same working conditions remanent pollutant concentration in irradiated samples increase with TNT initial concentration due to the competition between the organic degradation by-products and parent pollutant for the photo-generated species resulted by UV-VIS excitation of 0.5%Fe-TiO_2catalyst. This species, like •OH radicals and electrons are involved in oxidation and reduction reactions leading to organic pollutants conversion down to their mineralization. As result, at 60 min irradiation, ten times increasing of initial TNT concentration from 0.27 x 10^{-4}M to 2.72 x 10^{-4} M leads to decrease of TNT degradation efficiencies (η_{TNT}) from 91 to 67%. A similar behavior is observed in respect to organic nitrogen mineralization efficiencies (η_{Ninorg}) which decrease from 35 to 20%. The lower level of nitrogen mineralization compared with pollutant degradation is related to generation of nitrogen containing organic by-products during TNT degradation.

The negative effect of initial pollutant concentration increase on its degradation efficiency can be diminished by prolonging irradiation time, due to increasing of photonic energy absorbed by catalyst which assures higher concentrations of photo-generated •OH radicals and electrons, enhancing pollutant degradation efficiency. Thus, in the case of 0.27x10^{-4}M TNT initial concentration, prolonged irradiation time of 180 min assures the increase of pollutant degradation and organic nitrogen mineralization up to 99 and 71%, respectively. Comparable pollutant degradation efficiency was registered for 2.72 x 10^{-4} M TNT initial concentration, but only for 240 irradiation time, while organic nitrogen mineralization efficiency does not exceed 60%.

Table 5. Influence of initial TNT concentration and irradiation time on pollutant degradation and organic nitrogen mineralization by photocatalysis using 200 mg/L 0.5%Fe-TiO_2 catalyst

Irradiation time (min)	**$TNTx10^{-4}$ (M)**	**$N_{inorg}x10^{-4}$ (M)**	**η_{TNT} (%)**	**η_{Ninorg} (%)**
0	0.270	0.816*	0	0
30	0.107	0.149	60.37	18.39
60	0.025	0.282	90.74	34.81
120	0.003	0.463	98.89	57.16
180	0.0003	0.576	99.89	71.11
0	0.780	2.340*	0	0
30	0.368	0.750	52.82	13.85
60	0.168	1.532	78.46	25.00
120	0.032	3.200	95.89	42.87
180	0.008	4.536	98.97	59.19
240	0.002	6.048	99.76	69.10
0	1.500	4.500*	0	0
30	0.776	0.659	48.27	12.27
60	0.424	1.264	71.73	20.39
120	0.100	2.700	93.33	40.56
180	0.026	4.061	98.27	54.53
240	0.007	5.414	99.53	65.04
0	2.72	8.160*	0	0
30	1.566	0.553	42.43	12.80
60	0.901	1.105	66.87	19.70
120	0.298	2.210	89.04	37.69
180	0.089	3.415	96.72	40.55
240	0.019	4.960	99.3	59.33

**Organic nitrogen concentration corresponding to TNT initial concentration*

Kinetics and mechanism of TNT photocatalytic degradation

Using experimental data presented in Table 1, the kinetic curves in respect with pollutant degradation and organic nitrogen mineralization were draw. These curves were linearized by a kinetic equation of pseudo-first order. The Fig. 2 illustrates the kinetic equations for an initial TNT concentration of 2.72x10^{-4} M.

The rate constants for each pollutant initial concentration were calculated from the slops of linear plots. The k^I_{TNT} and k^I_{Ninorg} values decreased from 6.13 x 10^{-4} to 3.4 x 10^{-4} $s^{-1}$and from 1.16 x 10^{-4} to 0.59 x $10^{-4}s^{-1}$ respectively, for TNT initial concentration increasing between 0.27 x 10^{-4} and 2.72 x 10^{-4} M.

It is well known that understand the mechanism of the oxidizing species generated at the irradiated catalyst interface, is essential for understanding the mechanism of pollutant photocatalysis. Alcohols like iso-propanol (i-PrOH) are usually used as a diagnostic tool of •OH radicals mediated mechanism. To confirm the role of surface bound or free •OH radicals in the degradation mechanism, the photocatalytic experiments were carried out in the presence of NaI, a well-known surface •OH radical scavenger, as well as i-PrOH, a free •OH radical scavenger (Devi & Kavitha 2014). Besides, iodide ion is an excellent scavenger of hole which is easily captured by I^- and pathways due to oxidation by surface •OH radical are hindered (Yoon & Lee 2005).

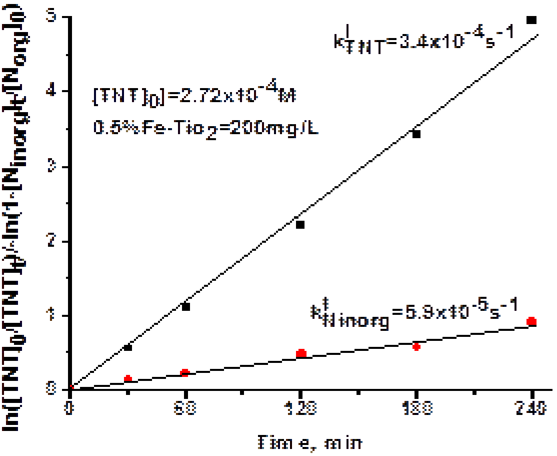

Figure 4. The pseudo-first order kinetics of TNT degradation and organic nitrogen mineralization

As is presented in Fig. 3 the rate of TNT degradation significantly decreased with NaI addition, indicating the crucial role of surface •OH radicals pathways. It should be emphasized that addition of NaI to the system allows TNT to react with $O_2^{\bullet-}$ radicals, resulted from reaction of electrons with dissolved O_2 (the experiments were performed under air bubbling), in the absence of surface •OH radicals which is a minor reaction pathway. However, it can be seen from Fig. 3 that adding of i-PrOH had smaller inhibitory effect on pollutant degradation rate than NaI, implying that free •OH radicals were not majorly involved in the TNT photodegradation process. The results showed that the surface $\bullet OH_{ads}$ radicals probably were responsible for the degradation of TNT rather than $\bullet OH_{free}$ radicals. Our findings are supported by the fact that presence of O_2 (electron scavenger) inhibited, reductive TNT degradation and pollutant direct photolysis occurs with much lower reaction rate than •·OH radicals mediated process.

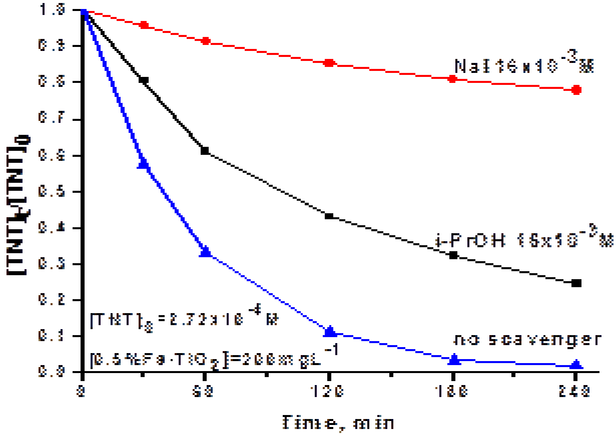

Figure 5. Effect of NaI and iso-propanol on efficiency of TNT photocatalytic degradation

Conclusions

TNT degradation and organic nitrogen mineralization was found to follow a pseudo-first order kinetics.

The main oxidative species responsible for pollutant degradation are the surface adsorbed hydroxyl radicals.

Application of UV-VIS photocatalysis, using 200 mg/L 0.5%Fe-TiO_2 catalyst, at pH=7 and 180-240 min irradiation time assures TNT advanced degradation (>99%) from initial concentrations situated between (0.27-2.72) x 10^{-4} M.

Acknowledgements

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LABORATORY STUDIES ON ACCIDENTAL POLLUTION AND SOIL REMEDIATION TECHNIQUES

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Abstract

In this paper there are presented laboratory studies on the influence of additives in diesel fuels on accidental pollution of the soil. The additive used in the experiments was cyclohexanone ketal glycerol. The presence of hydroxyl groups in the structure of ketals of glycerol decreases the solubility of hydrocarbons. To solve this disadvantage and for improving other features, in order to use as additives/ components for classic fuel, the hydroxyl group of glycerol ketal methyl ethyl ketone was block by transesterification with methyl esters of monocarboxylic acids.

The results obtained were compared to the content of nutrients (N, P, K) in the soil polluted with diesel fuel additives and diesel oil without additives.

It was performed the soils decontamination by applying the method of solvent extraction.

For ecological reconstruction there were used unpolluted soil samples, samples contaminated with diesel oil with and without additives and the resulting samples after the extraction with the solvents.

Keywords: *extraction, ketal, nutrients, soil*

Introduction

Diesel fuel is used in the diesel engines found in most buses, trains, freight trucks, boats, construction and farm vehicles, some cars and small trucks. Also, diesel fuel is used in diesel engine generators to generate electricity. The most common type of diesel fuel is a fractional distillate obtained from crude oil in the petroleum refineries, but in recent year's alternatives that are not derived from petroleum, such as biodiesel, biomass to liquid or gas to liquid diesel, are increasingly being developed and used.

Diesel oil derived from petroleum consists mainly of aliphatic hydrocarbons containing 8-28 carbon atoms with boiling points in the range of 130-370°C. Also, it contains sulfur, nitrogen and oxygen in low concentrations and metals such as lead, calcium, copper, nickel, sodium, and uranium. In addition, the diesel fuel contains additives which provide fuel detergency, corrosion control, and stability enhancement. They contribute to protect against wear by improving fuel lubricity, controlling harmful deposit build-up, improve fuel economy and reduce emissions (Ribeiro et al. 2007).

Both during production, transport, storage and use of the diesel fuel there are numerous soil pollution accidents, and not only it, even air and water pollution. Once in the ground, diesel oil can produce chronic or acute effects in various plant species. Excepting the direct and indirect toxicity, it causes interference in the hydric relations of the plants. This interference and the anaerobic and hydrophobic conditions are the most important effect of diesel oil contaminated soil on seed germination and plant growth (Racine 1994; Bona et al. 2011). For over two decade, many researchers have reported a lower rate of germination in soil contaminated by petroleum or its derivatives (Adam & Duncan 2002; Vavrek & Campbell 2002; Méndez-Natera et al. 2004; Achuba 2006; Smith et al. 2006; Sharifi et al. 2007; Besalatpour et al. 2008; Korade & Fulekar 2009; Njoku et al. 2009; Popa et al. 2010; Bona et al. 2011; Luhach & Chaudhry 2012; Cruz et al. 2013; Zarinkamar et al. 2013; Hawrot-Paw & Bąkowska 2014; Rusin et al. 2015; Shuang et al. 2015; Popa & Onutu 2016).

Oprescu (2013) has done research on the use of cyclohexanone ketal glycerol as additive for diesel fuels. It is reported that the hydroxyl groups in the structure of ketals of glycerol decreases the solubility of hydrocarbons. To solve this disadvantage and for improving other features, in order to use as additives / components for classic fuel, the hydroxyl group of glycerol ketal methyl ethyl ketone was block by transesterification with methyl esters of monocarboxylic acids.

The objective of this study was to research the effect of cyclohexanone ketal glycerol additive in diesel oil on the nutrients content (N, P, K) of an accidentally polluted soil in laboratory. The polluted soil was decontaminated by solvent extraction method. For ecological reconstruction there were used the following soil samples: unpolluted, polluted with diesel oil with additives and polluted with diesel oil without additives. The results obtained shows the differences between the nutrients content in the soil polluted with diesel oil, with and without additives.

Experimental

Table 1 shows the characteristics of cyclohexanoneglycerol ketal. In a typical experiment the glycerol ketal was synthesized into a 250 ml three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and Dean–Stark apparatus. In the first step the flask was charged with glycerol and SO_4^{2-}/SnO_2 catalyst and heated under reaction conditions for 10 minutes. After that, cyclohexanone and toluene were introduced.

Table 1. Characteristics of cyclohexanoneglycerol ketal

Parameters	Values
Kinematic viscosity at 40 °C (mm^2/s)	34.45
Density (g/cm^3)	0.8459
Pour point (°C)	−35.0
Flash point (°C)	117.2
Boiling point (°C)	165

The solvent was used to overcome the reaction equilibrium by forming a heterogeneous azeotropic system with water. The reaction mixture was heated to reflux. After the completion of reaction, the catalyst was filtered and the solvent and carbonyl compound in excess were removed by distillation

The GC/MS-MS analysis of cyclohexanone glycerol ketalindicates the obtaining of 2 isomers and a chromatographic purity over 99% (Figure 1).

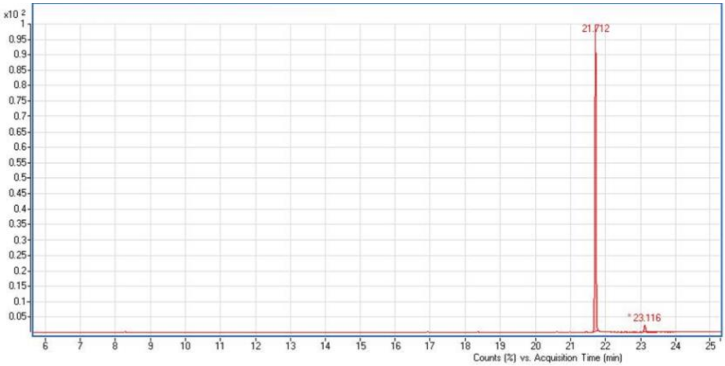


Figure 1. The GC/MS-MS analysis of cyclohexanone glycerol ketalindicates

The aim of the experimental determinations was the influence of the before-mentioned product, used for diesel fuel additives, for accidental pollution with liquid petroleum products.

Forest soil was analysed, for which the following samples were prepared:

- sample P_0 – witness sample, soil which is not polluted,
- sample P_1 – soil and diesel fuel (5,6%) – controlled pollution, undergone in the laboratory (this concentration was chosen because it is the closest to a real situation),
- sample P_2 – soil and equal quantities of diesel fuel and ketal.

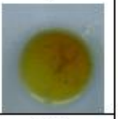
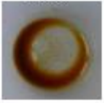
These samples have gone through succesive extraction with solvents - petroleum ether and benzene.

The installation that was used, Soxhlet apparatus, is shown in Fig. 2. The results obtained from the extraction process with solvents of P_0, P_1 and P_2 samples are presented in Table 2.

Figure 2. Soxhlet apparatus

The basic elements for a balanced soil, which have a decisive influence on the development of the plants – N, P, K (nitrogen, phosphorus, and potassium) are assimilated by the soil based on the pH. The nutrients are chemical elements which are necessary for the survival of plants, animals and people and it is normal for them to exist in water soil and underground. However, when the amount of nutrients is too high, it is the case of nutrient pollution which is dangerous both for our health and the crops. The nutrients (nitrates, nitrites, ammonium, and phosphates) might be in excess in water as well, either by an incorrect fertilisation with chemical fertilizers or compost, or by not respecting important rules regarding the construction of stables and wells or by mismanaging the trash which ends up infiltrating in the soil and groundwater. Nutrient pollution of the soil has negative consequences upon crops and the environment. The nitrogen which is absorbed by the soil is converted, through various chemical reactions, in amino-acids that can be assimilated and which ensures that the leaves and stem can grow, the radicular system can develop and the plant gains the absorbing function. The deficiency of nitrogen in the plants nutrition leads to the leaves turning yellow and slowing or stopping their growth. Phosphorous, assimilated by the plant in the form of phosphoric acid or phosphoric anhydride intervenes in the functioning of the immune system, increasing the resistance of the plant against to crop conditions, atmospheric conditions and attacks of the pests and administration of insecticides. Potassium is converted in potassium hydroxide and assimilated by the plant in this form. It increases the capacity of the plant to store nutritive substances in organs such as rhizomes and tubers.

Table 2. Results obtained from the extraction process

No.	Specified size	Clean soil sample P_0	Polluted soil sample P_1	Polluted soil sample P_2
1.	Quantity of sample, g	20,2 soil	20,2g soil 1,2 g Diesel fuel	20,2 g soil 1,2 g Diesel fuel 1,2 g ketal
2.	Quantity obtained with petroleum ether, g	0,2 	1,4 	1 
3.	Quantity obtained with benzene, g	0,05 	0,05 	0,45 
4.	Total quantity after extraction,g	**0,25**	**1,45**	**1,45**

The deficiency of potassium in the plants' nutrition diminishes their growth and development.

Using the laboratory kit for analysing soils from Hanna Instruments was determined the nutrient content. This soil sample has average nitrogen content, low phosphorus content and low potassium content (determination based on turbidity determination). The nutrient content for sample P_1 is shown in Fig. 3 and for sample P_2 is shown in Fig. 4.

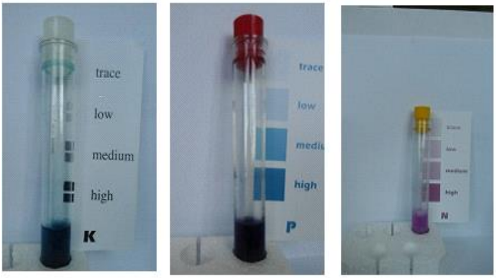


Figure 3. The nutrient content for sample P_1

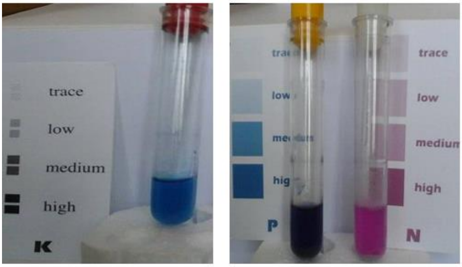


Figure 4. The nutrient content for sample P_2

Results and Discussion

Regarding the results from the ecological reconstruction it is observed (in the table 3) that the germinating potential is not completely destroyed for the analyzed samples.

Table 3. Results from the ecological reconstruction

	Clean soil sample P0	Polluted soil sample P1	Polluted soil sample P2
Ecological reconstruction			

Conclusions

For sample P_1 it is notices that there are extracted 1.45g (of which 0.25 are the organic material that was extracted and the rest of 1.20 is the entire quantity of diesel fuel that polluted the soil). In this case, there is a depollution rate of 100%.

For sample P_2, with the same quantity of material that was extracted, it is possible that this product, ketal, might not be extracted with these solvents which means that it will still exist in the structure of the soil. In a future paper we aim to analyse the products extracted in evaporating dish.

When it comes to the nutrient content, in the witness sample, there is a medium content of N and the content of P and K is reduced.

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MICROBIAL DISAGGREGATION WITH AND WITHOUT GAS BUBBLING UNDER CAVITATION CONDITIONS

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Abstract

Short-term cavitational treatment (22 kHz, 1.65 W/cm^3, 35 W) of the water showed an increase in the amounts of the cells of Bacillus cereus bacteria type that was explained by the process of cell disaggregation usage microscopical investigations. The duration of disaggregation process was 3-5 minutes with gas bubbling during sonication but 30 minutes without gas bubbling during sonication. It was shown an acceleration of disaggregation process under simultaneous action of gas and cavitation by 10 times (synergistic effect).

Keywords: *short-term treatment, cavitation, gas, bacteria, cyanobacteria, disaggregation*

Introduction

Common methods of water disinfection among many chemical methods are chlorination, ozonation, hydrogen peroxide treatment and others, but modern technologies allow disinfection of water without using chemicals. More and more importance is attracted to physical factors of influence on water system – magnetic, electric, ultraviolet, ultrasound (US). Among them the practical importance is acquired by sonochemical methods of water treatment. Practical application of cavitational influence on the microorganisms cells leads to an expansion of the opportunities and to improvement of water purification technology. But many experimental studies are devoted to removal of microorganisms from water under US action (Zhang et al. 2006; Wu et al. 2012). Information about water treatment during short-term exposure of contaminated water is limited. Hence, the aim of current research is investigate short-term duration of cavitational treatment of some microorganisms (spore-forming bacillary cells) in the water medium.

Previously, we investigated the processes of water disinfection from different types of microorganisms: *Diplococcus*, *Bacillus*, *Sarcina*, *Pseudomonas* and *Saccharomyces* yeasts (Koval et al. 2011; Koval et al. 2012; Koval & Starchevskyy 2012; Koval & Falyk 2016; Koval 2016), natural water and sewages disinfection (Koval et al. 2012). It was found that the values of effective constants of microorganisms destruction rate were determined by the nature of bubbled gas (O_2, CO_2, Ar, He) and were independent on the initial amounts of cells in the water system (Koval et al. 2012; Koval et al. 2014).

It was achieved the hıghest efficiency of sewage disinfection (97.9%) after Ar/US-action with exposure of 2 hours and an efficiency of 99.8% of model water disinfection from bacillary cells. The next step of our investigation is to study the short-term exposure on the cells that could be valuable for explanation of mechanical cells destruction after cavitational impact on individual cells.

Materials and Methods

The water objects of the research were model water medium prepared from natural water with *Bacillus cereus* (N_01) and model medium from air-free distilled water which were added pure microorganism monocultures of *Bacillus cereus* bacteria type (N_02).

The experiments were carried out under T = 298±1 K, P = 0.1 MPa, US frequency of 22 kHz, intensity of 1.65 W/cm^3, power of 35 W and the process time (t) was from 3 to 60 minutes.

The change of number of microorganism (NM) was investigated with and without gas bubbling under cavitation condition. The source of cavitation was UZDN-2T generator. Ultrasonic vibrations were transmitted by the magnetostriction radiator which was immersed into the model medium with the volume of 75 cm^3. As additional gases for the research were used argon, helium, oxygen and carbon dioxide. Gases were bubbled into the water during the whole process with the rate of ~ 1 cm^3/s.

Morphological and cultural features of microorganisms were investigated. Fixed cells preparations with safranin as a coloring agent were used to study the morphological features of the cells. The nature of colony growth on a nutrient medium in Petri dishes was study for cultural features. Meat and pepton agar were used as a nutrient medium for bacteria growth on Petri dishes at 37°C for 48 hours.

Results and Discussion

Bacillus cereus bacteria type as spor-forming cells were taken for investigation and as more resistant cells compared with vegetative cells. The initial NM (NM_0) of the model water N_01 was $8•10^2$ CFU/cm^3(NM_{01}) and $2•10^3$ CFU/cm^3(NM_{02}) and $8•10^2$ CFU/cm^3 (NM_0) of the model water N_02.

Cultural and morphological forms of *Bacillus* are illustrated on the Fig.1. On the base of general view of cellcolonies (Fig. 1-a) could estimate and describe colony characteristics, which are presented in Table 1. Optical microscopy images of the cells (Fig. 1-b) it is fixed cells preparation that allows to study morphological features. So, *Bacillus* are bacillary bacteria cells, belong to *Bacillaceae* family, they are spor-forming (form spore inside the cells, i.e. endospore within three days), spore diameter is smaller than cells diameter.

Here are presented dependences of NM changes of sonication time without gas bubbling (Figure 2) and with gas bubbling (Figure 3). It was shown that short-term exposure leads to the increasing of NM in both cases. But process duration was 30 minutes (Figure 2), unlike 3 minutes under simultaneous action of gas and cavitation (Figure 3). The results of cells increasing are represented in Table 2. The values of effective rate constants were calculated from kinetic equation of first order. Pitt and Ross have also reported about the increase of bacterial cell growth under cavitation but microorganisms were attached to a polyethylene surface (Pitt & Ross 2003).

Increasing of NM has been explained by the microscopical studies fixed cells preparations model water N_02 (Figure 4 a-c). It was found microorganisms which were connected into aggregates of different forms in an initial water samples before sonication (Figure 4-a). Cavitation broke the aggregates into smaller aggregates and into individual (separated) cells (Figure 4-b, 4-c). That is why, disaggregation processes took place during short-term exposure. The duration of disaggregation process was 30 minutes for model water N_01 (Figure 2) but 3-5 minutes for model water N_02 (Figure 3). Gas bubbling under cavitation conditions caused acceleration of disaggregation process by 10 times. So, synergistic effects were observed during short-term exposure under the simultaneous action of gas and cavitation. But these effects considerably depended on the nature of gas bubbling. The highest efficiency was obtained for argon.

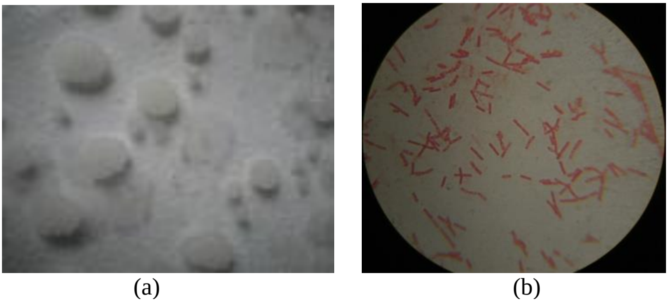

Figure 1. Microorganisms of *B.cereus*: (a) character of colonies growth on a nutrient medium in Petri dish; (b) optical microscopy images of microorganism cells (image magnification is 1500).

Thereby, during short-term treatment suffer damage aggregates that are cause of destroying connections between cells in an aggregate. But bacteria retained morphological features and fully viably after disaggregation and cell walls were not damaged. But, despite this, the cells lost reproductive ability and ability to the physiological generation of new cells even after short-term process, because cells on the stage of cell division weren't found during microscopically investigations.

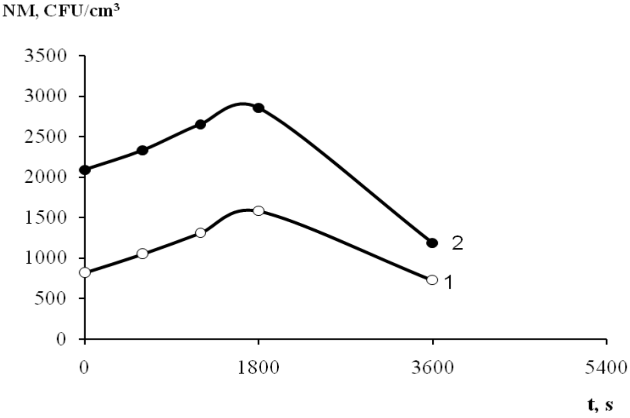

Figure 2. The change of NM values under US action in the model water N₀1. Conditions: N₀1 = 8•10^2 CFU/cm^3 (curve 1); N₀2 = 2•10^3 CFU/cm^3 (curve 2).

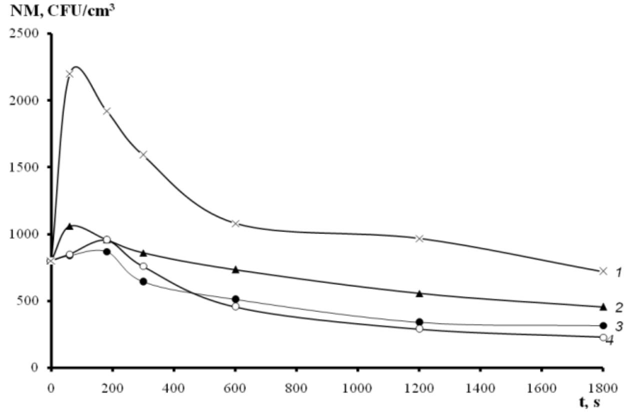

Figure 3. The change of NM values under the gas/US action in the model water N_02: Ar/US (4), O_2/US (3), He/US (2), CO_2/US (1). Conditions: $NM_0 = 8 \bullet 10^2$ CFU/cm^3.

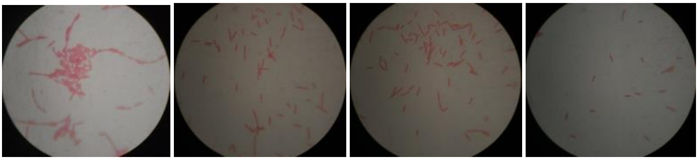
(a) (b) (c) (d)

Figure 4. Optical microscopy images of *B. cereus* before (a) and after (b-d) cavitation. Magnification of images is 1500.

Decreasing of NM was observed after full disaggregation process, because individual cells were more susceptible to the destruction. The NM reduction was connected with mechanical destruction processes of separated cells. Continued cavitation impact reduced an acutance of cell membranes external contours of cells that survived after treatment (Figure 4-d).

Hence, in the case of presence of disaggregation process under cavitation conditions the process of water disinfection requires a greater length of treatment time (more than 60 minutes for natural water without gas bubbling). Because NM after $t_{US} = 60$ minutes is equal $8 \bullet 10^2$ CFU/cm^3 and approximately equal to NM_0 (Figure 2, curve 1) and $1.1 \bullet 10^2$ CFU/cm^3 (Figure 2, curve 2). So, after this treatment time we can speak about disinfection process that demonstrates further cells reduction only. In general, disaggregation increases duration of the disinfection process that depends on the NM_0 in the water sample before treatment.

Conclusions

Results of experimental researches are presented below:

- Short-term cavitation leads to the cells disaggregation that discrubes the NM increasing.
- Gas bubbling under cavitation conditions accelerates disaggregation process by 10 times, unlike cavitation conditions without usage of gas (synergistic effect).

- Sonication enhances to break up microbial aggregates into single cells, which are more susceptible to the destruction under cavitational conditions.
- Sonicated *B. cereus* bacteria cells and *O. brevis* cyanobacteria, have lost their ability to the physiological generation of the cells.

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MINE WATER TREATMENT TESTS RESULTS FOR A CONTINUOUS FLOW REACTION SYSTEM

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Abstract

An experimental study has been carried out to assess sulphate precipitation via ettringite process from acid mine water (AMD) originating from closed non-ferrous Romanian mining areas. Such a treatment is required, because by conventional treatment of the AMD with calcium hydroxide, the conformity for sulphate will not be achieved, because the concentration correlated to gypsum solubility exceeds the limit value by roughly three times. Although sulphate is considered benign or with low toxicity, some countries have set limits for the wastewater discharged to natural receivers, from 500 to 1000 mg/L or 600 mg/L in Romania.

The process of sulphate precipitation as ettringite using solid aluminium sources is known to be slow. Tests for sulphate precipitation, using monocalcium aluminate cement as source of reactive aluminium for the ettringite formation were done using continuous flow mixed flow reactors in series (or continuous stirred reactors, CSTR). This reaction system allows the direct determination of the apparent reaction rate versus sulphate concentration which can be used further for various design tasks. The reaction rate for sulphate concentration below 600 mg/L may be less than 5 mg/L/min, depending on working conditions. The mixed flow reactors series has a net advantage over single CSTR, the best choice for a full scale treatment plant is a mixed flow reactors series also, as the results indicate that a system with a single mixed flow reactor is to be much larger.

Keywords: *CSTR, ettringite, mine water, sulphate*

Introduction

By treating the mine water with calcium hydroxide (the most common technological approach), the pH is adjusted to 8.5 ÷ 10.5 and the heavy metal ions will precipitate as oxo and hydroxy compounds, together with some gypsum if the initial sulphate concentration is higher than 1500 mg/L. This kind of treatment cannot remove sulphate beyond the concentration corresponding to gypsum solubility (Aube 2015*)*, besides the solution will remain supersaturated with calcium sulphate and improvements can be done by seeded gypsum crystallization and further by advanced sulphate removal, *e.g.* by membrane separation (Chesters et al. 2016) or ettringite precipitation (Ramsay et al. 2001; Kastle et al. 1990).

Sulphate concentration c(SO_4^{2-}) in mine water is typically high and the usage of water downstream can be affected (Meays 2013) that's so, despite the fact that sulphate is not an acute toxic compound, limits for discharge are stipulated, depending on country and sometimes depending on region, typically 250 to 1000 mg/L. As discussed above, these limits, lower than 1500 mg/L, cannot be met using conventional treatment methods. Sulphate precipitation as ettringite, calcium sulphoaluminate, $3CaO•3CaSO_4•Al_2O_3•32H_2O$) is an effective AMD treatment alternative and it is using aluminium containing reagents (Janneck et al. 2013).

An experimental study has been carried out to assess sulphate precipitation via ettringite process from AMDs originating from closed non-ferrous mining sites in the North Romanian mining area. Because the study was conducted at pilot level with continuous flow, multistage reaction system, it was able to provide useful data for the sulphate apparent precipitation kinetic. Evaluation of the overall kinetics of the reaction from flow-through tests is used by others also (Dietz et al. 2002).

Experimental

Mine water was treated in a three stage continuous flow process: metal oxidation and precipitation, ettringite precipitation and final pH adjustment, according to the flow sheet shown in Fig. 1. The performance requirements were in accordance with Romanian NTPA001, including the limit of 600 mg/L for sulphate ion, SO_4^{2-}.

Each of the reaction sub-systems for the first two stages comprised of a cascade continuous flow stirred reactors followed by vertical type settlers. The detailed design of the pilot plant was done by WISUTEC Umwelttechnik GmbH. Each reactor was equipped with mechanical mixer, direct drive, 3 blades propeller, Da = 0.225 m, n = 725 rpm and with individual pH control assembly (PID) with dosing pump for lime milk.

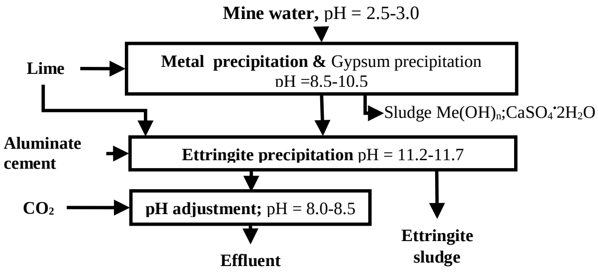

Figure 1. Pilot level basic flow-sheet for the AMD treatment

Ettringite precipitation module had three reactors R1 to R3 and a settler, according to Fig. 2. A fourth agitated vessel R4 in series (not shown in Fig. 2) acts as a feed tank for a daw-off pump which works by level control for R4, kept to a about 50% of total height. The estimated mixing parameters and the space-time values (corresponding to the working flow rate of 0.5 m^3/h or 1.0 m^3/h, as used, are shown in Table 1. Solid calcium aluminate cement (CA) was fed to the first reactor by a screw feeder with variable speed, adjusted manually to the required solids dosing rate. Lime milk was pumped to each reactor to keep the pH value between 11.2 to 11.4. *Calucem* monocalcium aluminate cement with Al content of 50% as Al_2O_3 was used (fineness, Blaine 3300-3800 cm^2/g, residue on sieve at 90 µm < 3%).

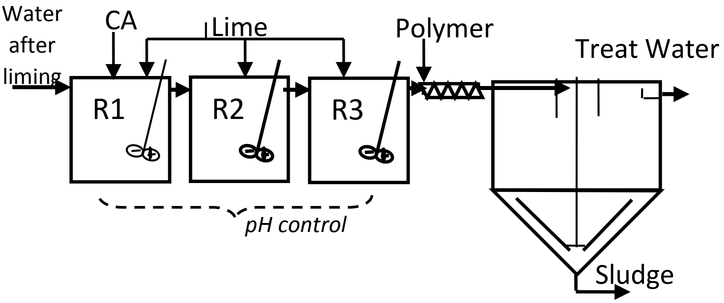

Figure 2. Basic flow-sheet of the ettringite precipitation sub-system
"CA" - calcium aluminate cement

Table 1. Ettringite reactors parameters

Parameter	Units	R1	R2	R3	R4	System
Space-time ($Q = 0.5\ m^3/h$)	h	1.0	0.8	0.8	*	2.6
($Q = 1.0\ m^3/h$)	h	0.5	0.4	0.4	0.2	1.5
Velocity gradient, G	s^{-1}	485	545	545	775	-
Dissipated power, P/V	W/m^3	710	885	885	1800	-

*Without sampling

For any change of parameters, the system was allowed to work for at least 10 times of total system space-time to reach the new steady-state and samples were drawn from ettringite reactors to assess the sulphate concentration. This reaction system allows the direct determination of the apparent reaction rate versus sulphate concentration which can be used further for various design tasks.

The treatment process was studied for several mine water sources originating in some Romanian mining perimeters, of which two are representing the *Case studies **1*** and ***2***, selective results being presented here. Each case study was structured with several *Runs*, having specific process parameters sets.

Results and Discussion

Modelling the pilot plant ettringite reaction system as ideal CSTRs in series (or mixed flow reactors), so each reactor steady-state is characterized by uniform concentration and also by constant in time concentration, there is a stepwise change in concentration from reactor to reactor. For any set of operating conditions, samples taken from each reactor allow to quantify the conversion for each space-time value, if sampling is done in steady-state. Thereby the assessment of the time required for the system to reach the steady state is important. For the ideal CSTR that has experienced a step decrease in feed concentration, the exit concentration dependence is (Davis et al. 2003):

$$C / C_0 = e^{(-t/\tau)} \qquad (1)$$

where $C_{A,0}$ is the inflow initial tracer concentration and C is the reactor concentration, $\tau = V/Q$ is the space-time, V is the reactor volume, Q is the volumetric flow rate and t is the time after the step change had occurred.

Computing for the R1 to R3 series the ratio C/C_0 as a function of the reduced time

$\theta = t / \tau_s$, where τ_s is the total system space-time, we have found that a value of $\theta > 3$ is required for the step perturbation to level out including for R3 (see Fig. 3). For our pilot level tests a minimum run time of 15 or 24 h (at least eightfold of total reaction system residence time) was considered enough to reach steady state.

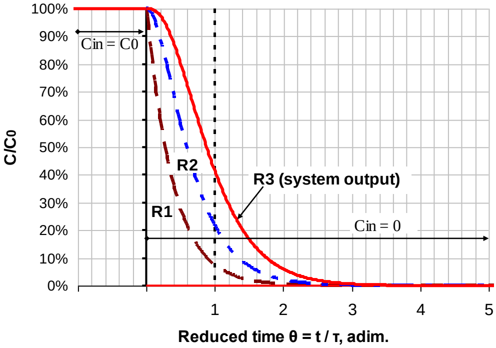

Figure 3. Stabilization of the CSTR series output calculated for a step perturbation (inlet concentration step decrease from $C_{in} = C_0 \neq 0$ to $C_{in} = 0$)

The sulphate concentration after metal precipitation settler (inflow for the ettringite precipitation stage) was 2800 mg/L to 2650 mg/L for the *Case Study **1*** mine water and 1940 mg/L to 1725 mg/L for the *Case study **2*** mine water.

The sulphate concentration profiles (sulphate concentration dependence of the space-time, along the reaction chain) in the ettringite precipitation reactors, for the two case studies and several runs are shown in Figures 4 and 5, respectively. Results for the *Case study **1*** for two runs are presented here, with different CA doses, 0.82 kg/kg SO_4^{2-} (*Run 1*) and 0.98 kg/ kg SO_4^{2-} (*Run 2*), the two runs being different from each other by some proprietary operational approaches also. Results for the for the *Case study **2***, for three runs with a CA dose of 0.95 kg /kg SO_4^{2-}, of which the 3rd *Run* was operated with a flow rate of 1 m^3/h with sampling for R1 to R4. The target sulphate concentration, 600 mg/L, can be effectively and safely reached only for a total system time of 2.6 h for the two case studies.

The reaction rate values can be calculated for each reactor considering the mass balance equation for an ideal stirred tank reactor CSTR operating at steady state which for the case of constant density is (Levenspiel 1999):

$$(C_{A,0} - C_A) = - \tau \bullet r_A (C_{A,f,}) \qquad (2)$$

where $C_{A,0}$ is the inflow concentration and $C_{A,f}$ is the reactor concentration for the component *A* (SO_4^{2-}, this case), $\tau = V/Q$ is the space-time and $r_A(C_{A,f})$ is the reaction rate, which is a function of $C_{A,f}$. For our particular reaction system, the reaction rate for sulphate was calculated for each reactor that is to say for each reactor sulphate concentration (Fig. 5 and 6).

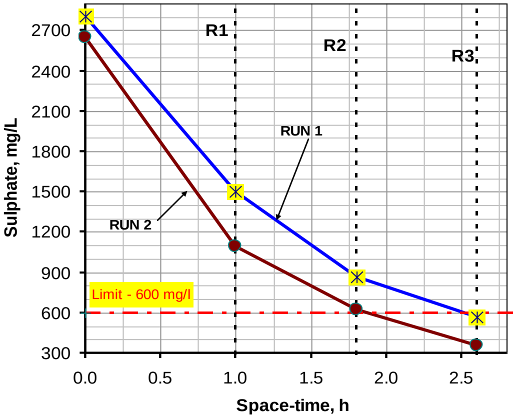

Figure 4. Sulphate concentration profile for the CSTR series - Case study 1

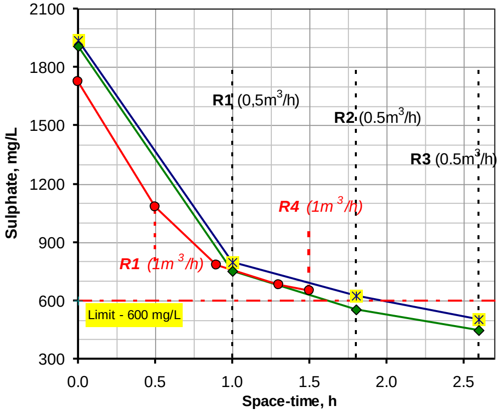

Figure 5. Sulphate concentration profile for the CSTR series - Case study 2

As the reaction rate is a result of a set of parameters, but also technicalities which are not detailed here, the values shown here are informative and of greater importance being the further discussion about the reaction system. With the assumption that the conversion for sulphate is to be obtained with the same performances as for the CSTR series, but using only one CSTR, the aluminate concentration for this reactor and also the sulphate reaction rate can be fairly approximated by those for the last reactor in the series Rx (x = 2 to 4), when the Rx effluent sulphate concentration is considered low enough. It can be computed that for the single reactor case, the space-time required, $\boldsymbol{\tau}_{\mathbf{1\ CSTR}}$, will be around 2 to 5 times higher than for the CSTR series and the same working parameters (Table 2 and 3).

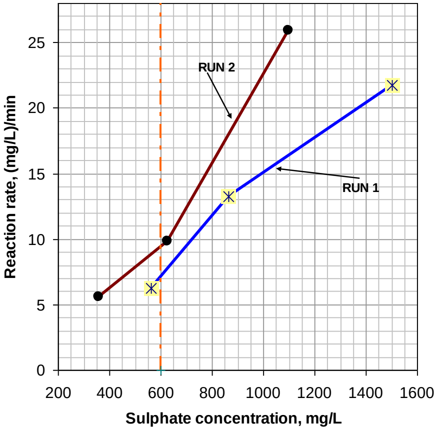

Figure 6. Sulphate precipitation rate - *Case study 1*

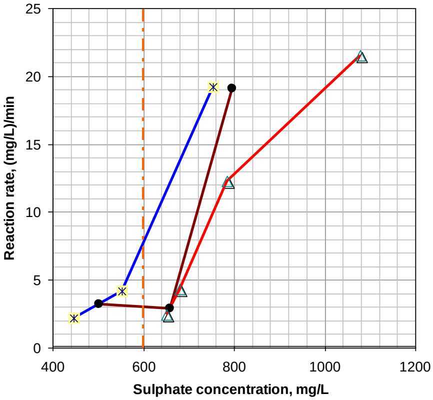

Figure 7. Sulphate precipitation rate - *Case study 2*

Important differences regarding sulphate precipitation yield and required reaction time between batch and continuous flow reaction system can be stressed on. Laboratory batch test results, showed that sulphate concentration values below 600 mg/L can be achieved for batch reaction time below 1.5 h for the both case studies, using reaction conditions close to that for the pilot plant, CA dose, temperature, etc. Despite the fact that, for some conditions, the reaction time requirements for the batch and continuous flow may look similar, this happens only for the CSTR series and it is obvious that the batch reaction time should not be used to assess the requirements for the continuous flow systems. If a proper kinetic law cannot be obtained from batch tests, the batch reaction time needed to obtain a certain conversion is only indicative.

Table 2. Space time required for a single reactor vs. CSTR series (Case study 1)

RUN -	**C_0** mg/L	**C_f** mg/L	**$\Delta c(SO_4^{2-})$** mg/L	**$r(C_f)$** mg/L/min	**$\tau_{1\,CSTR}$** h	**$\Sigma(\tau_{series})$** h
Comparison with the series R1 to R3						
1	2803	564	2239	6.3	5.9	2.6
2	2650	357	2293	5.6	6.9	2.6
Comparison with the series R1 to R2						
1	2803	864	1939	13.3	2.5	1.8
2	2650	625	2025	9.8	3.5	1.8

$\Sigma(\tau_{series})$ - Total space-time for CSTR series (experimental)
$\tau_{1\,CSTR}$ - The space-time required for a single CSTR (computed)
Temperature: 15.5 ± 0.7 ºC

Table 3. Space time required for a single reactor vs. CSTR series (Case study 2)

RUN -	**C_0** mg/L	**C_f** mg/L	**$\Delta c(SO_4^{2-})$** mg/L	**$r(C_f)$** mg/L/min	**$\tau_{1\,CSTR}$** h	**$\Sigma(\tau_{series})$** h
Comparison with the series R1 to R3 (run 1&2) or R1 to R4 (run 3)						
1	1906	446	1460	2.21	11.0	2.6
2	1940	503	1437	2.54	9.4	2.6
3	1725	651	1074	2.42	7.4	1.5
Comparison with the series R1 to R2 (run 1&2) or R1 to R3 (run 3)						
1	1906	552	1354	4.19	5.4	1.8
2	1940	625	1315	3.56	6.2	1.8
3	1725	680	1045	4.33	4.0	1.3

Temperature: 14.0± 0.6 ºC

Conclusions

Using for the continuous flow tests a series of mixed flow reactors gave important, useful results for the kinetic of the ettringite precipitation using solid aluminium source. This reaction system allows the direct determination of the apparent reaction rate versus sulphate concentration, which can be used further for various design tasks. When using calcium aluminate cement as the aluminium source, the reaction rate for sulphate concentration below 600 mg/L may be quite low, e.g 2.5 mg/L/min (no more than 6.3 mg/L/min) and represents the parameter to be used for basic design phase. The best choice for a full scale treatment plant is a mixed flow reactors series also, as the results indicate that a system with a single mixed flow reactor is to be much larger. Also the mixed flow reactors series has a net advantage over single CSTR for higher final sulphate concentration values, up to about 850 mg/L.

Acknowledgements
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NEW ADSORBENT MATERIALS ON THE BASE OF ASH AND LIME FOR LEAD REMOVAL

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Abstract

The development of new materials, with imposing properties - for environmental protection, represents a challenge for contemporary society. In this paper, we propose obtaining of new adsorbent materials from thermo plant ash and lime. The use of ash presents the advantage, because this waste is in great quantities, and it is a way for its capitalization. The new materials offer new scientific and technological perspectives due to the specific interesting physical properties of these materials. The utilization of adsorbents based on ash/lime, for waste water depletion, represents an alternative with ecological and economic implications. The authors present in this study the results of experimental researches on the adsorbents prepared in the laboratory using fly ash produced at CET Holboca Iasi and lime from Bicaz. The experimental conditions of obtaining new adsorbents were established and the characterization of synthesized materials was realized. Raw and synthesized materials were characterized by: SEM/EDAX (Quanta 3D - AL99/D8229), XRD (X'Pert PRO MRD X-ray diffractometer), BET (Quanta-chrome Instruments) and FT-IR analysis (DIGILAB FTS 2000). Experimental results demonstrated that the new materials can be successfully used for removal of lead from waste water. The removal rate was over 97%, after 60 minutes, and adsorption capacities were obtained of 21.25 mg/g. The resulted product is easy to separate and can be used as building material. On the other hand, the product is not polluted for the environment.

Keywords: *adsorbent, ash, lead, lime, synthesis*

Introduction

The contemporary development is strongly connected to energy production. Because the power plants based on coal fuel greatly affect the environment, the improvement of producing processes of energy by diminishing the ecological impact is welcome. In the last years the remove of the polluting agents, from the waters, is placed on the priority place. Heavy metal ions may cause health risks to humans, the ecosystems, and this has been a great motivation for increasing of researches for reducing of its content. From heavy metal, removal of lead is important, because of its toxicity and its attendance in the wastewater. Lead is a well-known, highly toxic metal considered as a priority pollutant (Mondal 2009). It is an industrial pollutant, which enters the ecosystem through soil, air and water (Golbad 2017; Harja 2013). Different industries, such as battery manufacturing, metal plating and finishing, tetraethyl lead manufacturing, ceramic, glass, etc., are the major sources of lead pollution (Arbabi 2015). According to the World Health Organization (WHO) and Environmental

Protection Agency (EPA), the maximum permissible limit (MPL) of lead is 0.05 mg/L in drinking water and in in wastewater (Abdel-Hakim 2003). In wastewaters, lead-ion concentrations may approach 180–450 mg/L, concentration very high in correlation with standards, consequently lead concentration from wastewaters must be reduced before discharging to effluent. The removal of lead ions from water may be used many processes like ion exchange, adsorption, biosorption, precipitation, coagulation/electro-coagulation, cementation, osmosis, electro-dialysis, etc. (Arbabi 2015; Golbad 2017; Remsi 2012; Wan Ngah 2010).

In order to remove lead ions, current methods, require the use of reagents for precipitation or coagulation. On the other hand ion exchangers are expensive. Treatment processes of Pb(II) removal from wastewater through adsorption on different low cost adsorbents were recently studied (Adebisi 2017; Arbabi, 2015; Nascimento 2009, Buema 2013; Harja 2013). Several natural or synthetic materials, such as natural/synthetic zeolites (Kotova 2017), fly ash (Harja 2016; Noli 2015), clays, carbonates, phosphate rocks, alkaline agents, carbon (Adebisi 2017), hydroxyapatite, etc. (Zarghami 2015) have been recently tested as to their ability to immobilize metals. Many researches are dedicated fly ashes and modified ashes as adsorbents for wastewater or air (Harja 2010). If the adsorption capacities of fly ash for lead ions were demonstrated (Buema 2013), we proposed synthesis and testing of new adsorbent materials obtained from ash and lime. The lime was used for precipitate soluble metals into their insoluble hydroxide forms, but in admixture with ash, under the imposed conditions for modification, can be obtaining of very efficient adsorbents. Analyzing the ash composition resulted from power plants, it was observed that it contains CaO and MgO, and by mixing with lime, in controlled conditions, it can synthesize adsorbents for environmental applications. By using the ash for obtaining the new materials, the pollution reduction is obtained in two ways:

- Reduction of lead content from wastewaters;
- Capitalization of the ash, it causes pollution of soil and air from thermo plant area.

The synthesis consists in preliminary hydrated of the lime, mixed with ash and mechanical agitation in imposing conditions. Solid/liquid ratio was varied between 1/2 … 1/5, temperature between 20-50°C, and the curing time between 1-4 hours.

The synthesized materials were characterized, and tested for adsorption of lead ions.

Materials and Methods

For adsorbent synthesis it was used lime from Bicaz and ash from power plant Holboca Iaşi. The lime and the ash were characterized from the chemical, mineralogical and technological properties. Morphology of particles was determined by SEM with Vega Tescan - Analytical Scanning Electron Microscope.

Chemical and mineralogical characterization were realized by:

- Microanalysis by SEM/EDX - with a QUANTA 3D series AL99/D8229.
- FT-IR analysis with spectrometer DIGILAB FTS 2000.
- Multi-Parameter Consort C831 (pH, mV, C, Conductivity), measures of pH 0-14.00, electrical conductance 0 - 200 mS.

Samples of 50 g were prepared, by introducing in the reaction vessel of lime, at working temperature, for hydration, after this was introduced ash, with imposed ratio. After hydration of lime, the slurry was agitated 1-4 hours, the synthesis conditions are presented in Table 1. The samples were filtered, dried and analyzed.

Table 1. Adsorbent samples and working conditions

Sample	Time (h)	Temperature (°C)	Lime/ash ratio
LA1	1	50	1/3
LA2	2	50	1/3
LA3	4	50	1/3
LA4	1	50	1/3
LA5	2	50	3/1
LA6	4	50	3/1

Adsorption experiments

For adsorption experiment was prepared a stock solution, with 0.1 mol Pb(II)/L by dissolving $Pb(NO_3)_2$ in distilled water. In this work, the ratio adsorbent/solution was 1:100. All chemicals used to prepare reagent solutions were of analytical grade. Before starting the experiment the solution was contacted with adsorbent, the pH of the solution was adjusted to the required value. The pH was adjusted by 0.1 M HCl and/or 0.1 M NaOH to cover a range from 2 to 12. After pH stabilization, in the adsorption column was introduced required stock solution. When the absorption was realized, the adsorbent particles were filtrated and the residual concentration of lead was determined. The atomic spectroscopy type Buck Scientific for heavy metals determined were used for lead content determined.

Results and Discussion

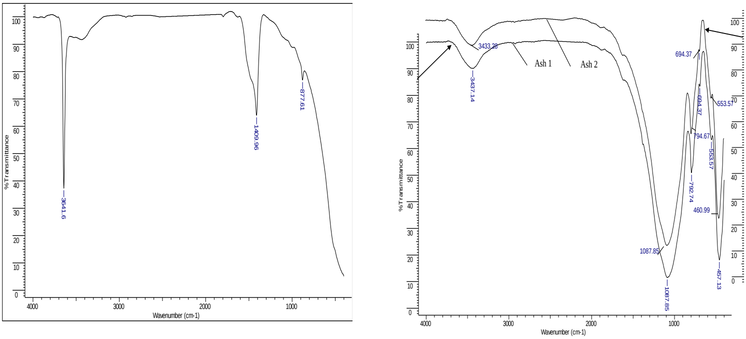
The principal component of lime is calcium oxide. Near this the lime contains a series of impurities from the raw material. The chemical composition of lime, in oxide components is presented in Table 2. The ash, used in this study, has the oxidic components presented in Table 2 (Harja, 2010, 2015, 2013; 2010; 2012a&b).

Table 2. Chemical composition of ash and lime used for preparing the adsorbent

Component	Ash	Lime
SiO_2	47.9	4.04
Al_2O_3	34.94	0.56
Fe_2O_3	4.82	0.34
CaO	2.86	87.4
MgO	1.42	3.65
K_2O	1.11	1.41
Na_2O	0.54	0.18
LOI	2.9	4.45

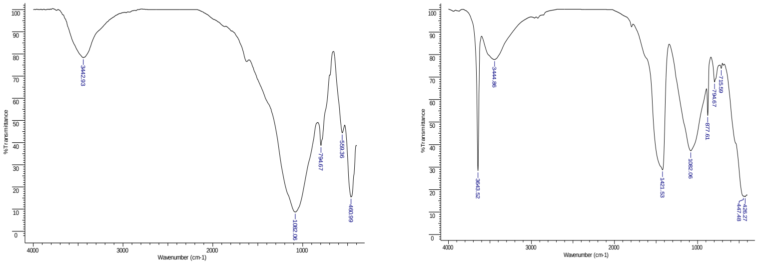
FTIR spectra are presented in Fig. 1, for lime and ash, resulted was in concordance with literature (Harja 2016).

From Fig. 1 it can observe that the principal component of lime is calcium oxide, but there are also some peaks which corresponds to the impurities from the coal, peak from 3641.6 cm^{-1} corresponds to water, that means the lime was hydrated. The ash samples have components such as: hematite, quartz, kaolin, illit, rutil, montmorilonit, carbon (Noli 2016a, 2016b; Buema 2013), which is found in argillaceous material, ballast coal respectively.



lime

Ash sample 1 and sample 2



LA6

LA4

Figure 1. FTIR spectra for raw and synthetized materials

The adsorbents were analyzed; FTIR spectra of LA2 and LA4 are presented. In the case of LA4 and LA6 it can observed peaks, corresponding to zeolitic/geopolimeric materials (Harja 2016; Harja 2009a; Noli 2015).

SEM analysis was done for all samples, for selected samples: LA2, LA4 and LA6 are presented in Fig. 2. By modification the new particles grow on the surface of oldest ash particles, obtaining a higher surface of adsorbent (Harja 2009b). SEM images to 10 and 5 µm respectively, allow the observed differences between the surface morphology of new materials function of modification conditions. The increase of temperature and curing time determined increasing of surface area.

By increasing the time of reaction, the adhesion of lime particles to the ash is better, for the same ratio lime-ash. Lime hydration has as effect the increasing of specific surface and a very good adhesion to ash particles.

Adsorption studies. For adsorption studies the, on the base of results obtaining from characterization, the LA6 adsorbent was selected. The adsorption capacity (q, mg/g) and the removal rate (R%) were calculated by means of the following relationships:

$$\text{Adsorption capacity (q, mg/g)} = (C^0 - C) \times V / m \qquad (1)$$

$$\text{Removal rate (R \%)} = [(C^0 - C) / C^0] \times 100 \qquad (2)$$

where C^0 and C, are initial and respectively, final concentrations of the lead ion in solution mg/L, V – volume, L, m – mass of adsorbent, g.

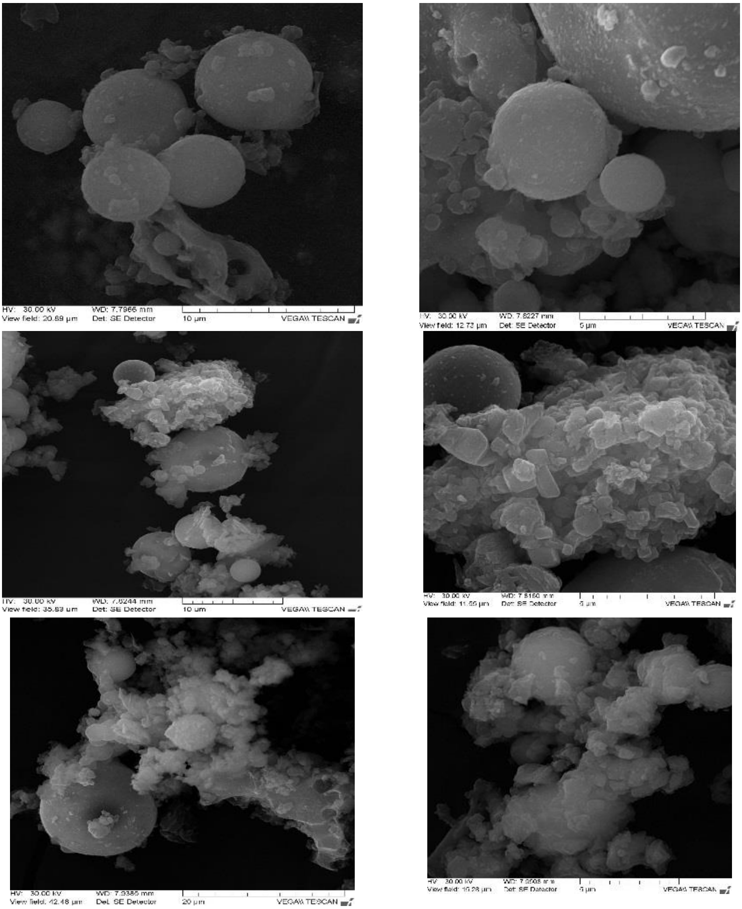


Figure 2. SEM analysis for samples LA2, LA4 and LA6

The pH of the solution plays a very important role in the removal of lead ions. The influence of the pH over adsorption capacities is presented in Fig. 3. The adsorption capacities of Pb^{2+} ions increased little from pH 4 to pH 6. After pH 7, we obtained a gradual increase in the Pb^{2+} ion removal up to pH 10, and then remaining almost constant up to pH 12. The obtained data show a very good adsorption capacity of Pb^{2+} ions, at a pH over 9, this was reason for use pH 9 in all other experiments. The adsorption capacity was 21 mg/g, and the removal rate was obtained over 97%.

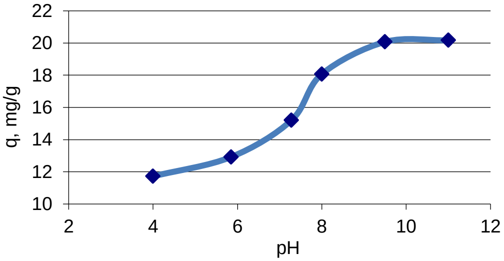


Figure 3. Influence of pH over adsorption capacity of Pb^{2+}

The effect of contact time on the lead removal (the initial pH 9, adsorbent dose 10 mg/L, initial concentration 65 mg/L, temperature 20℃) is depicted in Fig. 4.

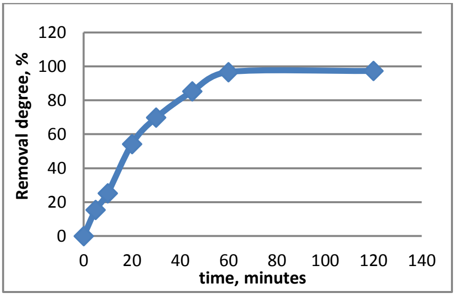


Figure 4. Influence of contact time over removal degree of Pb^{2+}

The amounts of the lead adsorbed on the LA 4 sample increased rapidly in the first 40 minutes changing them slightly over 60 minutes. The drastic increase of lead adsorption in the first 40 minutes may be due to the availability of numerous vacant sites, after this the adsorption sites become unavailable. The adsorption equilibrium time was prolonged from 40 min to 80 min on account of the slow pore diffusion of lead ions into the bulk of the adsorbent.

Conclusions

The objective of this study was to develop an effective adsorbent for the removal of lead ions from aqueous solution.

Adsorption of Pb(II) ions through new adsorbent is an economically feasible technique for removing metal ions. In the first stage of the study, the characterization of the adsorbent was done. The researches have continued with the study of pH and contact time influence over the removal process. The highest degree of lead ions removal was obtained at pH over 9. In the case of pH about 9, the degree of uptake was about 97%.

The kinetics study of lead ions removal onto new adsorbent materials indicates a removal degree over 60% after 20 min, which increases to 97% after 60 min.

It can be concluded that the new adsorbent can be used for removal of lead ions from wastewater with 21 mg/g adsorption capacity and removal rate over 97%.

Capitalizations of ash as adsorbent represent a superior way to the recovery of this waste and, on the other hand the water, air and soil pollution can be reduced.

Acknowledgements

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NEW SOLUTION IN REHABILITATION OF THE HYDRO-POWER SYSTEMS NOW IN RISK DUE TO THE INFILTRATION

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Abstract

In Romania, there are more than 200 dams realized during 1975-1990 from local materials, without any ulterior remediation or rehabilitations. Nowadays, many hydropower systems confront with infiltration through dams or lateral dikes, followed by unexpected erosions. In order to maintain the hydropower system active, the water level is drastically reduced, sometimes even with 10 m. Consequently, it means less water for the human necessities (water supply, irrigation), but mainly few resources to produce electric energy. The research paper starts by presenting the actual dams situation, structured on hydrographic basins. For the case study two hydropower lakes from Arges-Vedea hydrographic area that confront seepage through embankments were selected. In that area there are more than 100 lakes which confront with different functioning problems. The local geomorphologic structure and the water quality create an image of local functioning conditions. Further, there are briefly presented the mathematical and numerical models, elaborated as to establish the infiltration risk zones. The numerical model is tested and calibrated based on local conditions, showing the zone with erosion and infiltration risks. Finally, some conclusions, possibilities to extend the numerical model, the acknowledgements, and references are presented.

Keywords: *energy efficiency, environmental engineering, hydroelectric power generation, mathematical model, numerical simulation*

Introduction

First, it must be mentioned that there are 636 dams constructed from local materials nationwide, which have a number of shortcomings (revealed by the analyzes carried out in the last four years), as follows: 134 dams have damaged tiles and the grout; 69 dams shows infiltration into the dams body and the downstream areas; 143 have erosions through dams at access roads and pears;186 dams have the bottom of the emptying zone blocked, with major defects in the water discharge area, or are not equipped with surge arresters surfaces; 21 dams have flaws and are not functional; 35 dams have the basin's reservoirs filled with sediments at a rate of over 50%; 63 dams are abandoned without legal documentation or regulatory acts; 5 dams are proposed to be listed in the case of abandonment as required by law of the results (Radulescu & Nistreanu 2004).

The most serious of the problems mentioned are the infiltration into the dams body and the downstream areas, the erosions through dams at access roads, breaches in dams and lakes clogging (the lakes that are part of the case study have clogging of over than 50%). It should be mentioned that from the 640 dams, about 270, meaning almost 40%, have major problems. All these issues have diminished the payload, and

limited the possibilities to produce electricity. This happens at the same time with the worldwide efforts to develop new possibilities for intensive uses of renewable electricity generation, in the context of carbon dioxide emission reducing. A report on the dams' flaws is presented in Table 1.
The Arges-Vedea hydrographic basin is located in the south part of the country and has an area of 20.911 km^2 including the basins: Arges-12.590 km^2, Vedea-5.430 km^2, and Calmatui 1.413 km^2, out of the basin side of the Danube-2.025 km^2.

Table 1. Actual Situation of the Dams with problems in Romania

HB	ND	DT	I	SLP	PD	DD	CL	A	D
Someş – Tisa	33	21	5	3	3	0	1	0	0
Crisuri	31	6	4	9	22	0	0	0	0
Mures	10	6	0	1	1	1	1	0	0
Banat	1	0	0	0	0	0	1	0	0
Jiu - Dunăre	4	0	0	1	1	0	2	0	0
Olt	45	19	6	8	11	0	1	1	0
Arges – Vedea	119	24	18	43	29	0	0	1	4
Buzau-Ialomita	28	0	0	3	17	0	0	7	1
Siret	76	15	17	2	23	0	9	19	0
Prut - Barlad	285	43	19	71	79	20	18	35	0
Dobrogea – Seaside	4	0	0	2	0	0	2	0	0
TOTAL	636	134	69	143	186	21	35	63	5

HB - Hydrographic Basins, ND - Number of Dams, DT - Damaged Tiles, I - Infiltration, ESP - Erosions Slopes, Pears, PD - Problem Discharging, DD - damaged dams, CL - Clogged Lakes, A - abandoned, D - Decommissioning

The network has an average density of 0.36 km/km^2 ranging from 0.67 km/km^2 on the high mountains zone, 0.507 km/km^2 in the middle and up to 0.03 km/km^2 in the lower altitudes. Previous research results showed that the specific annual average leak in the mountains reaches 30-35 m/s/km^2. The value is due to the rainfall from the collecting basin, with an annual average of 1400 mm, and to the drain of the petrographic substrate with sharp slopes, and a good waterproofing of slopes. The lowest leakage is in the plain area, of 3 l/s/km^2, where rainfall values are much lower, with an annual average of 600 mm. The drain slopes are less pronounced and the petrographic substrate is permeable. The catchments area Arges-Vedea includes the following counties: Arges, Dambovita, Olt, Teleorman, Giurgiu, Calarasi, Ilfov and Bucharest territory.

Materials and Methods

In order to calibrate the numerical model, it is necessary to collect samples referring at hydrologic capacities, average values of rainfall, type of nature and dimensions of sediments, favorable area for infiltrations through dikes and dams (Bockman & Tom 2008). It is necessary to compare the obtained results with existent measurements database. Further, some measurements considered significant for further environmental analysis are mentioned.
In these conditions the main analyzed microclimate characteristics are:
- average annual temperature 8.5°C, medium temperature of January - 4.5 °C; average temperature of July 20°C;
- relative humidity 80 %;

- average rainfall during a year 500-600 mm (450 mm during summer);
- wind average velocity during the entire year 3.6 m/s, at the level of 10 m high.

Significant rainfalls variations appear in July-November; the quantities being even greater in the higher zones.

In Arges-Vedea hydrographic basin there are 24 hydropower lakes, from which 16 are in the Arges basin. The hydropower cascade lakes on Arges river, downstream the CHE Vidraru, are generally equipped with Kaplan turbines, with hydraulic falls between 10-20 m and electric power range between 8-16 MW, depending on the energy sector. There are hydropower plants (HPP) with dams at distance (Oiesti, and Cerbureni), with hydropower plants near the dams (Curtea de Arges, Zigoneni, Valcele, Budeasa, Bascov, Pitesti, and Mihailesti) or bypass-type hydropower plants (Albesti-Iasi, Noaptes, Baiculesti, Manicesti and Merisani).

The development scheme of the Dambovita river is generally for electricity production at Clabucet (P=64 MW), Rucar (P=23 MW), Dragoslavele (P=7.7 MW), Frasin P=0.6 MW), and Vacaresti (P=4.84 MW) and meets the needs for water suply of Bucharest and irrigation basins Dambovita and Colentina. The River Targului, where there are some HPP with significant problems, was developed to assure the water supply for Campulung city and electricity production in Leresti (19 MW), Voinesti (5.2 MW) and Schitu - Clears (1.55 MW).

Ialomita River is one of the oldest electric hydropower systems in Romania. There are three hydropower plants: Dobresti P=16 MW, Moroieni P=15 MW, and Scropoasa P=12 MW. Two lakes were selected for this analysis, confronted with massive infiltrations through dikes and dams, one on River Targului and one on Capra River. For this areas, 8 periods of significant increases in level and flow have been identified, most notably in April, July, and December. In these times, nationwide, of 32 stations danger levels were exceeded: in 10 - Danger of flooding, level was, in 14- flooding level and in 8 - damage level (Table 2). The most affected basins were in the southern half of Vedea, Cotmeana, Teleorman, Dambovnic, Neajlov, Urlui, and Calmatui. Regarding the maximum leakage at the two stations, they have exceeded the historical flows. The annual precipitation values recorded for the entire hydrographic basin were between 686.5 - 1304.5 l/m^2.

Table 2. Values registered for the flow rate in different stations

Nr.	Hydro Station	River	AMA (m^3/s)	AD (m^3/s)	%
1.	Ciobani	Cotmeana	0.866	7.32	845
2.	Buzesti	Vedea	0.969	11.0	1135
3.	Valeni	Vedea	3.16	28.5	902
4.	Tatarasti	Teleorman	1.06	11.6	1094
5.	Mill Groapa	Neajlov	1.07	15.3	1430
6.	Slobozia	Dambovnic	1.17	12	1026
7.	Balilesti	Bratia	2.73	6.73	247
8.	Rausor	Rausor	0.733	1.63	222
9.	Priboieni	Carcinov	0.589	1.92	326
10.	Gura Foii	Potop	0.578	3.64	630

AMA - Average Multi-Annual flow rate, AD - Average December

The infiltration through dikes and dams represents in many cases a major problem. Solving the stability problem for dikes and embankments is the main purpose of the present analysis. Schematically, the problem of seepage through dams can be presented, as in Fig. 1-a, and in reality it can be seen in Fig. 1-b the appeared infiltrations.

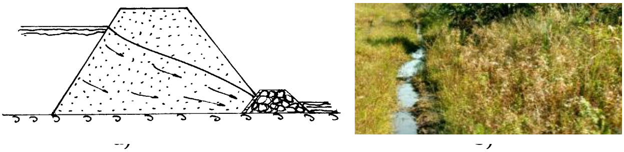
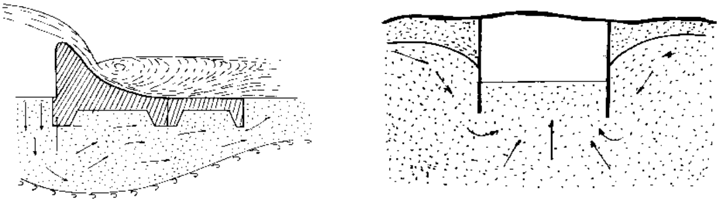


Figure 1. Schematic and real infiltrations through dikes and dams

In Fig. 2-a, the dam is realized from local materials, with a drainage prism at the bottom of the downstream face. Size selection for such a dam can be based only on a study of the seepage through the dam. In Fig. 2-b a dam realized of concrete is represented, founded on a non-cohesive land.



a) b)

Figure 2. Different solutions of dam executions

Here (in the second case), due to the water infiltration under the concrete constructions, it is particularly important to estimate the pressure exerted on the construction by the groundwater. It is necessary to determine by mathematical models the water velocity which goes out, the underground downstream after the concrete slab. A problem is represented by the evaluation of infiltration speed; dω is an elementary cross-section of the elementary seepage, and dQ the infiltration flow through this elementary area. In this case, the infiltration rate is (Seteanu & Radulescu 1998):

$$U = \frac{dQ}{d\omega} \tag{1}$$

The infiltration rate is different from the actual velocity at which the water flows through the earth pores. If ω is the total area of the filter, ω' is the surface of all the pores, then the actual average speed through the soil pores, V' will be:

$$V' = \frac{Q}{\omega'} \tag{2}$$

Noting with $p = \frac{\omega'}{\omega}$ the porosity coefficient, the velocity becomes, $V = p \cdot V'$.

The flow rate is:

$$Q = k \cdot \omega \frac{h_w}{J} \tag{3}$$

where: k-is the infiltration coefficient, ω-the cross-section area, h_w-the hydraulic losses between sections 1 and 2, situated at distance l, H_1 and H_2 the static loads in specified sections, and the hydraulic slope $J = h_w/l$ (Vagma & Torn 2006).

$$h_w = H_1 - H_2 \tag{4}$$

With these notations, the infiltration velocity may be written (Aqeel, Al-A 2013):

$$U = -k \cdot \frac{dH}{ds} \tag{5}$$

One of the following methods may be used to evaluate the infiltration coefficient:
- Relations with computing, which includes physical soil constants
- Experimental laboratory measurements on soil samples
- 'in situ' measurements by sample pumping or injection

Hazen relation has been used in the numerical model:

$$k = A \cdot c \cdot \tau \cdot d_e^2 \tag{6}$$

where (Seteanu & Radulescu 2005):
- A - coefficient depending on the measurement system, A=1 if k is in m/day,
- c - coefficient depending on the sands clay content, so for the clean sands c = 1000-700, and for sands with clays c = 700-500; d_e(mm)
- the effective diameter defined by the diameter of the granule to which the soil samples are lower, only 10% (by weight) of the granules of the earth.
- τ is a correction factor depending on the temperature (t^0 in degrees Celsius)

$$\tau = 0{,}70 + 0{,}03 \cdot t^o$$

The Hazen relation may be applied to sand with d_e= 0.1-3 mm and soil non-homogeneity coefficient, that the ratio $d_0/de \leq 5$ (d_0 being the diameter of the pitch to which 60% of the granules have a smaller diameter).

Results and Discussion

The seepage through both the embankments (the right bank and the left one) have been modeled. For each case three water levels have been chosen in the lake. For modeling, the cross-sections quotas mentioned in Table 3 deemed special problems of the current exploitation were chosen. The downstream dike is discontinuous, consisting of fine sand, medium or rare gravel, sandy clay, loam sands, lens mud, and vegetal elements. The bedrock is alternate marl clay, marl, tuff, and fine sands, (Radulescu & Zetenyi 2009).

Table 3. Analyzed cross-sections

Dike left bank						Dike right bank			
Developing area	Manifestation					Developing area	Manifestation		
Profile	BU	BB	RU	TU	G	Profile	BU	BB	G
300.5- 300.6				X		410.0- 413.0	X	X	X
303.1-303.4			X	XX	X	416.7-417.0	X	X	X
303.8- 303.9			X	XX	X	429.0- 430.0	X	X	
303.0- 304.0				X		434.0- 435.5	X		
303.6- 304.5			X		X	437.5- 437.9	X	X	X
307.1- 307.3	X	X			X	438.5- 439.5	X	X	X
307.5- 307.9	X				X	439.0- 446.3	X	X	
308.0- 308.2	X					445.0- 445.9	X	X	X
356.0- 356.2	X	X				458.0- 460.0	X	X	
						462.0- 465.0	X	X	

BB - puddles on lateral side, BU - wet–lateral side, TU - wet batter, RU - wet ramp, G - ice on lateral side, X - appearance of the mentioned phenomena, XX - very intense mentioned phenomena (Seteanu & Radulescu 2004)

For these sections the flows in 24 cross sections for different levels in the lake were modeled. For each variant three sub-variants were tested:

Variant A1, B, and C1 - state of the shield would be built into the bedrock, and the upstream lateral side has a compact sealing mask, without cracks. It represents the ideal case. In this case, there are no leaks. Experience has shown that any screen is that is not embedded in the bedrock or the mask is not compact (there are cracks in the sealing portion, is broken, etc.).

Variant A2, B2, and C2 - with the shield case is embedded in the bedrock and the lateral side upstream has small cracks in the waterproofing mask.

Variant A3, B3, and C3 – the shield is not embedded in the bedrock, and the lateral upstream sides have cracks on relatively large portions, often the sealing being destroyed. This is the reported case, and the two sides (left and right) were molded separately, with the specific permeability, designated A-3A, A-3B, B-3A, B-3B, C-3A, C-3B. For the studied domain the mesh was performed for each cross-section, depending on the specific material permeability in the structure, Figure 3 - 5. Each field is represented by a different color. Depending on the material characteristic, the water level in the lake and the cross-sections, the depression curve is determined. The program performs automatic finite element meshing, based on which the calculation is performed. The streamlines are plotted, and the infiltration velocity is obtained. Further some results are presented for each of the cases mentioned above.

The seepage quantity through the dam and lateral dikes can be observed in the Variant 3, indifferent of the case. The velocity has a wide distribution, which quickly leads to erosion and destruction of the concrete slabs.

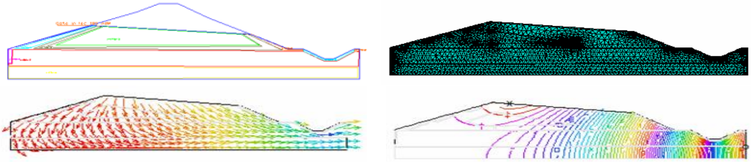


Figure 3. Results for Variant 1

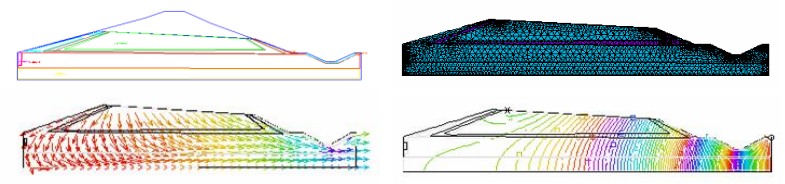


Figure 4. Results for Variant 2

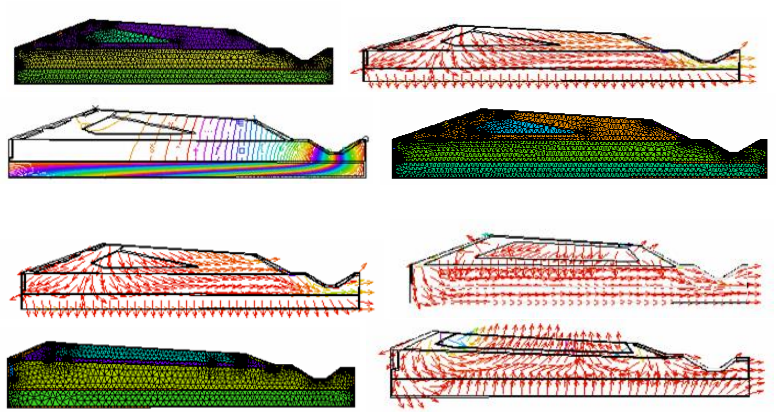


Figure 5. Results for Variant 3-Case 1, Case 2, Case 3

Conclusions

The nationwide situation of the hydroelectric plants confronted with various problems in operation was presented. For the testing area, hydrographic Arges-Vedea basin some data collected "in situ" was presented. It is necessary to calibrate the numerical model that was developed based on the presented mathematical model. The numerical model highlights areas of infiltration followed by a rising erosion risk.

By changing the cross-section structure and dam permeability, a complete risks modeling can be achieved of the any dam now in operation. This way, an image of the risk areas that need to be monitored continuously can be realized, as well as of the sections for which urgent maintenance and repairs should be done (Turbatu et al. 2004).

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REMOVAL OF Cr(VI) AND Cd(II) FROM AQUEOUS SOLUTIONS USING NATURAL SORBENTS: VOLCANIC TUFF AND WALNUT SHELLS

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Abstract

Some natural adsorbents were evaluated for the advanced removal of pollutants from aqueous systems. The sorption capacity of walnut shells and volcanic zeolite tuff (from Mirsid-Cluj Romania) to remove the chrome and cadmium at different experimental conditions was studied. The concentration of metal ions in aqueous systems was evaluated with an inductively coupled plasma mass spectrometer (ICP-MS) and an atomic absorption spectrometer. The effect of time, initial concentration of the metals and solution pH on the adsorption at room temperature was studied. pH of the solutions was found to influence the adsorption. Higher Cr(VI) adsorption was observed at lower pH and at low concentration of metal ions. The maximum efficiency of volcanic tuff in acidic media was 97.12% for chrome and 57.04% for cadmium, respectively, for 0.1 mg/L initial concentration. Moreover, in the same experimental conditions, the maximum efficiency of walnut shells was 61.24% and 44.51% for chrome and cadmium. The two low-cost natural sorbents were efficient for the remove of pollutants from aqueous systems.

Keywords: *adsorption, heavy metals, volcanic tuff, walnut shells*

Introduction

Conventional sorbents used in water treatment are activated carbons, polymers, oxides, zeolites, etc. (Worch 2012). Engineered sorbents can be very expensive and in recent decades, the interest in using alternative low-cost sorbents can be observed. Some of the reported low-cost sorbents with high absorbency for metals include chitin/chitosan (Lazaridis et al. 2007), natural zeolite (Wanga & Pengb 2010), lignin (Srivastava et al. 1997), seaweed/algae/alginate (Anastopoulos & Kyzas 2015), and others with less efficiency like dead biomass (Niu et al. 1993), clay (Azejjel 2009), fly ash (Banerjee 1997), yeast (Stanila 2016) etc. These natural sorbents are more suitable for wastewater treatment and less for use in drinking water treatment due to quality requirements for adsorbents in this case. Although many studies have been conducted on low cost adsorbents, it is necessary to continue this work in order to better understand adsorption processes involved and to demonstrate the technology.

The mean research goal is to identify and develop inexpensive and effective adsorbents from plentiful sources of raw material. The aim of this paper is to study the potential of some natural (organic / inorganic) adsorbents as low-cost adsorbents for the removal of heavy metals from aqueous systems. The adsorption capacity of walnut shells and volcanic tuff is studied under different experimental conditions. Metals of interest were Cr and Cd. They were chosen based on their potential pollution

impact on the environment. The effect of contact time between sorbent and metal ions, pH of the sorption medium and initial concentration of ions on the adsorption parameters at room temperature were investigated.
In the past years, volcanic tuff of different origins has been explored as adsorbent for removal of various heavy metals and organic substances (Inglezakis 2003; Wanga & Peng 2010; Taffarel & Rubio 2010). Also walnut shells were studied and presented in different articles (Pehlivan & Altun 2008; Kazemipour 2008; Petuhov 2015) as alternative adsorbent for pollutants removal.

Experimental

Walnut shells (WS) from an area close to Botosani in northern Romania were used as raw material. The volcanic tuff (VT) comes from Mirsid near Cluj. Synthetic aqueous solutions containing Cr(VI) or Cd(II) were prepared by diluting the 1g/L stock monoelement solution (CPAChem) metal salt by ultrapure water. Nitrogen acid of analytical grade was used to set the right pH of the aqueous systems. The concentration of metals was measured using an atomic absorption spectrophotometer (Perkin Elmer PinAAcle 900T) and an inductively coupled plasma mass spectrometer (Bruker Aurora M90).
The walnut shells, were first washed extensively with deionized water, then crushed rough with a hammer. Pieces of nut shells were grinded in two steps using Rotor Beater Mill SR 300 – RETSCH and Vibratory Disc Mill RS 200 – RETSCH. The resulting fine powder was sieved through a 100 micron sieve and dehydrated at 105 °C for 24 hours. The volcanic tuff was also ground using the same protocol as in the case of walnut shells in order to obtain a fine powder of micrometers and dehydrated at 105ºC for 2 hours.
Batch adsorption tests were carried out at room temperature by adding 2 g of adsorbent to 100 ml flasks containing synthetic aqueous solutions of desired metal salt, at room temperature. The mixture was stirred with a magnetic stirrer at 150 rpm. With the aid of a syringe and a filter, samples were collected at given intervals of time and analyzed.
The concentrations of heavy metals in aqueous solutions before and after adsorption were measured and the adsorption efficiency was calculated as follows:

$$Q = (C_i-C_e)*V/m \tag{1}$$

where Q (mg/g) is the adsorption capacity of the adsorbent, C_i and C_e (mg/L) are the initial and final concentrations of metal ion in solutions, respectively. V (L) is the volume of the adsorption medium and m (g) is the mass of the adsorbent. The adsorption efficiency can also be expressed in percent:

$$\eta= (C_i-C_e)*100/C_i \tag{2}$$

where η (%) is the adsorption efficiency of the adsorbent.

Results and Discussion

Volcanic tuff is compose of zeolites who can be considered as derivatives of silicates where Si is partially substituted by Al. The framework structure containing pores occupied by water, alkali and alkaline earth cations (Wanga & Peng 2010). The zeolite framework carries negative charges, which are compensated by metal cations. The Mirsid volcanic tuff contains mainly clinoptilolite (about 70%), and as extra minerals eulandite. The chemical and mineralogical composition of the tuff is presented in reference (Rusu & Rusu 2009).

The walnut shells are composed of cellulose, hemicellulose and lignin. Cellulose is a common material in plant cell walls and lignin is relatively hydrophobic and aromatic in nature.WS sorbent carry the some polar functional groups such as alcoholic, carbonylic, carboxylic and phenolic groups which are believed to be the active sites for metal ions attachment.

The behaviours of volcanic tuff and walnut shells in aqueous acidic media were analysed in aqueous medium in order to predict the ionic charge released by the adsorbent. To carry out this analysis some solutions were prepared, one with 2 g of volcanic tuff and the other with 2 g of walnut shells in 100 ml deionised water in which nitric acid was added in order to bring pH value in 5 to 2 range. After 120 min of stirring the final solutions were analysed. The results shows that the adsorbent are stable at pH 4-5. When pH decreases to 2, some metallic ions from volcanic tuff (Al, Fe, Mn, Cu) migrate in the aqueous system and the aluminosilicate crystalline network silicates is affected.

Adsorption activity of volcanic tuff

The adsorption capacity of volcanic tuff was tested on synthetic solutions containing chromium and cadmium under different experimental conditions. In Fig. 1 is presented the evolution of the amount of chromium adsorbed in time, starting from a initial concentration of 10 mg/L and 2 g of adsorbent. The influence of pH on the adsorption were studied. The results showed that the percentage of Cr(VI) ion adsorption by VT increased with increasing adsorption time. In terms of kinetics, adsorption of Cr(VI) by volcanic tuff occurs in two stages: one fast during the first 5 minutes, then the rate of adsorption is slowing down until the equilibrium is reached.

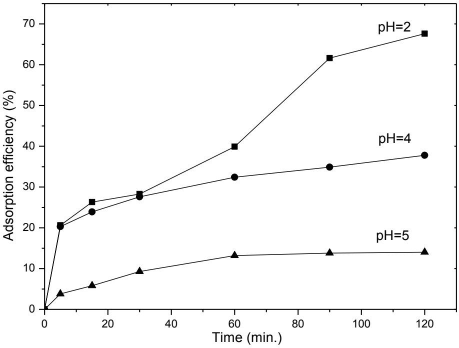

Figure 1. Effect of contact time on the adsorption of Cr(VI) by VT. Initial concentration of Cr (VI): 10 mg/L

The aqueous systems appear to stabilize after 60 min for the solutions at pH 4 and 5. At pH 2 the adsorption process seems to continue after 120 minutes.

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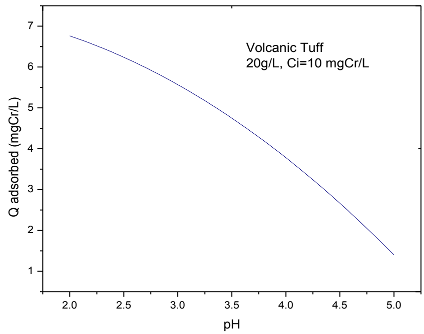

Figure 2. Effect of pH on the adsorption of Cr(VI) using the VT. Initial concentration of Cr (VI): 10 mg/L

The effect of Cr(VI) concentration on the sorption by the VT sorbent was investigated by using two ions concentrations : 0.1 mg/L and 10 mg/L, at a pH of 4 for 120 minutes equilibrium time (Figure 3).

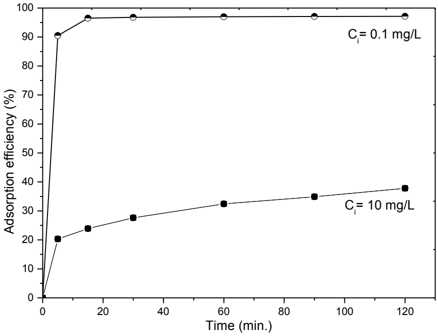

Figure 3. Effect of initial concentration on the adsorption of Cr(VI) using the VT. pH=4

As it can be seen from the shape of the kinetic curves, the first stage of the adsorption corresponding to 10 mg Cr/L initial concentration is much faster and the maximum adsorption capacity is reached after 10 minutes. In addition, it is observed that the lower the initial concentration, the greater the efficacy. This may be due to the fact that the most easily accessible adsorption sites on zeolite volcanic tuff are quickly occupied by the smaller amount of Cr ions. Also, the fractional sorption became independent of initial concentration for the low concentration of Cr(VI) in adsorption media. In other words, the ratio between the number of Cr(VI) ions and the number of adsorption sites is much larger in case of higher concentrations. The amount of Cr(VI) ions adsorbed per unit mass of the VT increased with the initial Cr(VI) concentration as expected. The adsorption capacity was 3.40 mg/g for 10 mg Cr/L initial concentration.

The evolution in time of **cadmium** amount adsorbed by volcanic tuff is presented in Fig. 4, starting from a initial concentrations of 0.10 mg/Land 1 mg/L Cd(II) using and 2 g of volcanic tuff at pH=2.

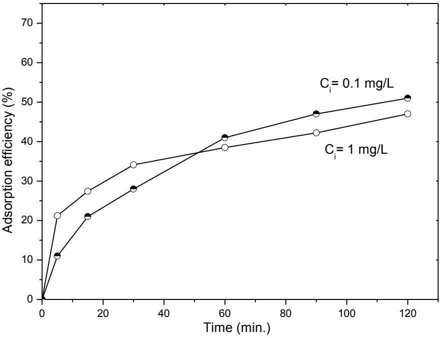

Figure 4. Effect of initial concentration on the adsorption of Cd(II) using the VT at pH=2

The cadmium adsorption efficiency is lower than in chromium case. As it can be seen, the rate of cadmium adsorption is slower. In what concerning the initial concentration factor, the values for cadmium adsorption efficacy is relatively close, around 50%. The difference consists in the initial rate of adsorption, in the case of 1 mg/L the first stage is faster. A maximum adsorption capacity of 0.23 mg/g was measured.

Adsorption activity of walnut shells

The adsorption capacity of walnut shells was tested on synthetic solutions of chromium and cadmium with different concentrations at pH = 2. The effect of **Cr(VI)** concentration on the adsorption by the WS was investigated using starting concentrations of 0.1 mg/L and 10 mg/L. The results of adsorption efficiency are plotted in Fig. 5. Two stages of adsorption can be distinguished, one fast the first 15 minutes, and a slower stage until 120 minutes. As it can be seen from the slope of the curves, the equilibrium is still not reached at the end of the batch experiment. The adsorption of Cr(VI) on walnut shells occurred on the lignin molecules containing hydroxyl and phenol functional surface groups.

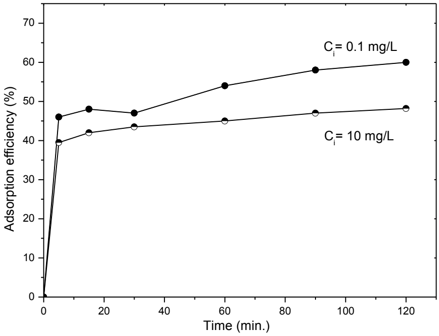

Figure 5. Effect of initial concentration on the adsorption of Cr(VI) using the WS at pH = 2

The adsorption of chromium on walnut shells is also fast. Comparing the curves for 10 mg Cr(VI)/L, using VT (Figure 1) and WS (Figure 5) at pH=2, the adsorption is more efficient in the volcanic tuff case, the difference in behavior is due to the different type of adsorption mechanism. In Fig. 5 the adsorption efficiency value corresponding to 30 minutes is probably due to a sampling error. A maximum adsorption capacity of 2.34 mg/g was measured.

The evolution of **cadmium** adsorption on walnut shells at pH=2, starting with two solutions with 0.1 mg/L and 1 mg/L, is plotted in Fig. 6. The efficiency values in both cases are comparable. Adsorption is initially faster for the 1 mg/L solution, but in the long term, adsorption at lower concentrations is slightly more efficient.

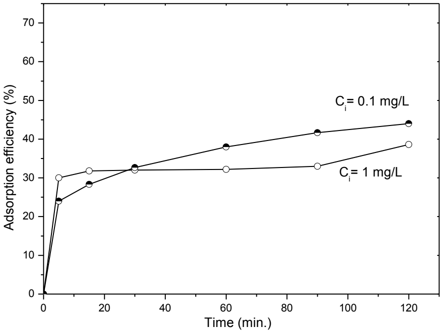

Figure 6. Effect of initial concentration on the adsorption of Cd(II) using the WS at pH=2

As can be seen from Fig. 5 and Fig. 6, chromium adsorption on walnut shell is more efficient than cadmium in 0.1-1 mg/L range of concentration, at pH=2, using 2 g of adsorbent, 100 mL of adsorption medium, temperature: 23°C and agitation speed: 150 rpm. The maximum adsorption capacity was 0.19 mg/g.

Conclusions

The toxic Cr(VI) and Cd(II) ion sorption on the inexpensive and natural sorbents as walnut shells and volcanic tuff have been investigated as alternative to conventional adsorbent for wastewater treatment. Volcanic tuff consisting mainly of clinoptilolite are in general a good natural adsorbents. The adsorption behavior of these sorbents depends on the nature of the metals studied. The adsorption of Cr(VI) onto VT is strongly pH dependent, the uptake of the chromium decreases with the increase in pH from 2 to 5. Volcanic tuff demonstrated to have very good performance at low concentration of Cr(VI) in acidic media. The cadmium adsorption on this adsorbent is lower than in chromium ions case. This is certainly due to the nature of the specific charge of cadmium and chrome ions.

Having a lower efficiency than volcanic tuff, the walnut shells showed to be an effective natural adsorbent for the removal of cadmium and especially chromium ions from aqueous systems. Walnut shells in 10 mg/L chromium solution (pH=2) reached 48.2% the efficiency, compared with 67% in case of volcanic tuff, but the adsorption is faster in case of walnut shells use. The cadmium adsorption onto WS is slightly smaller (10%) than in adsorption onto volcanic tuff at pH = 2 using 0.1 mg/L or 1 mg/L starting concentrations. Adsorption of chromium and cadmium ions was generally more effective at low concentrations.

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PARALLEL AND CONSECUTIVE REACTIONS IN FUEL GAS COMBUSTION

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Abstract

The kinetics of the oxidation process of the organic substances known as fuel gas (the alkanes class in general) deals with reactions whose mechanisms are analyzed in many theories and models. Irrespective of the nature and excess of the carburant, all partial combustion intermediates are revealed: alcohols, aldehydes, organic acids (that together with other derivatives from catalytic reforming reactions are characterized by the global parameter VOCs), carbon monoxide and carbon dioxide and finely divided carbon under the form of soot. The volume of oxidation intermediates increases when the carburant excess decreases monotonously to values below the stoichiometric ratio, so that when the limit is reached the carbon dioxide and water vapor volumes can be minimal. This paper puts forward a kinetic combustion model based on the parallel and consecutive reactions producing part of the chemical compounds that form the concentration of VOC, carbon monoxide and finely divided particles of the gas produced by fuel gas combustion.

Keywords: *combustion, equations, nanoparticles, reactions, VOC.*

Introduction

The smoke produced by any quick oxidation reaction in the presence of the oxygen in the air is a composite mixture of finely divided solid particles, liquid particles difficult to volatilize at a given temperature and gas, mainly carbon dioxide and nitrogen oxides (Cornellier 2005). The reactions that take place during the combustion of fuel gas such as methane or calor gas (a combination of equal propane and normal butane concentrations) are consecutive combustion reactions rendered by the following equations:

$2\ A - CH_3 + O_2 \rightarrow 2\ A - CH_2\text{-}OH$ Alcohol X (1)
$2\ A - CH_2\text{-}OH + O_2 \rightarrow 2\ A - CH{=}O + 2\ H_2O$ Aldehyde Y (2)
$2\ A - CH{=}O + O_2 \rightarrow 2\ A - COOH$ Acid Z (3)
$4\ A - COOH + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$ Carbon dioxide B (4)

taking into consideration only the oxidation reaction at the end of the chain.

In reality, however, the equivalent reaction, quick and complete in case of oxygen excess, can be written as follows:

$$C_nH_{2n+2} + (3n+1/2)\ O_2 \rightarrow n\ CO_2 + 2(n+1/2)\ H_2O \qquad (5)$$

Nitrogen oxidation occurs simultaneously with carbon oxidation to CO_2. The higher the flame temperature, the more intense the oxidation (Strambeanu 2003):

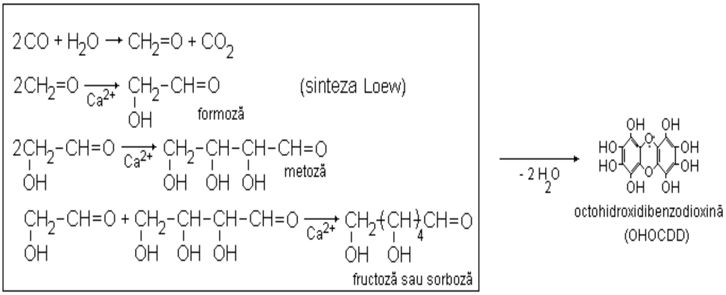
$N_2 + X\,O_2 \rightarrow 2NO_x$ Nitrogen oxides (6)

Irrespective of the oxygen excess, at the same time with the oxidation process, the thermal decomposition of the fuel gas occurs as other parallel processes that produce carbon monoxide or finely divided carbon under the form of nanoparticles (smoke black or soot) (Strambeanu et al 2007, NATO 1988):

$C_nH_{2n+2} + (2n+1)\,O_2 \rightarrow n\,CO + (n+1)\,H_2O$ Carbon monoxide (7)

$C_nH_{2n+2} + (n+1)\,O_2 \rightarrow n\,C + 2(n+1)\,H_2O$ Carbon nanoparticules (8)

In addition, especially if carbon monoxide is present even in strictly limited concentrations, slow cooling involves other inevitable concurrent processes of reforming, through *de novo* or Loew synthesis, stable cyclic compounds of the carbohydrates and dioxin classes, in liquid and solid state respectively, that complete the loading in particulate matter the flue gas flow.



(9-13)

Therefore, as far as the chemical composition is concerned, the gas released in the atmosphere during fuel gas combustion can be analyzed by interpreting three global parameters: VOC (TOC) (volatile or total organic carbon), particulate matter and carbon monoxide concentration. At the same time, the three parameters also characterize the quality of the combustion, since in oxygen-deficit combustion processes they increase significantly, proving that combustion is incomplete and as a result part of the fuel is lost in secondary and concurrent reactions (Lungu & Neculae 2014).

The reaction rates for the consecutive chemical processes of a complete combustion process (1–5) are given by the following system of first-order differential equations written under a matrix form (Abdi & Hojjati 2011):

$$\frac{d}{dt}\begin{bmatrix} C_A \\ C_X \\ C_Y \\ C_Z \\ C_B \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 \\ k_1 & -k_2 & 0 & 0 & 0 \\ 0 & k_2 & -k_3 & 0 & 0 \\ 0 & 0 & k_3 & -k_4 & 0 \\ 0 & 0 & 0 & k_4 & 0 \end{bmatrix}\begin{bmatrix} C_A \\ C_X \\ C_Y \\ C_Z \\ C_B \end{bmatrix} \tag{14}$$

or a scalar form:

$$\begin{cases} \dfrac{dC_A}{dt} & = & -k_1 C_A \\ \dfrac{dC_X}{dt} & = & k_1 C_A - k_2 C_X \\ \dfrac{dC_Y}{dt} & = & k_2 C_X - k_3 C_Y \\ \dfrac{dC_Z}{dt} & = & k_3 C_Y - k_4 C_Z \\ \dfrac{dC_B}{dt} & = & k_4 C_Z \end{cases} \tag{15}$$

A and B are the initial concentrations of alkanes and carbon dioxide produced in the gas flow. The last equation of the system is not a differential equation *per se*, and the initial conditions are the following:

$C_A(0) = C^0_A$, $C_X(0) = C_Y(0) = C_Z(0)$ and $C_B(0) = 0$ (16)

Consequently, the solutions to these equations, namely the concentrations of the intermediates of the consecutive reactions can be written as follows:

$$C_A(t) = C_A^0 e^{-k_1 t} \tag{17}$$

$$C_X(t) = k_1 C_A^0 \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right]$$

$$C_Y(t) = k_2 k_1 C_A^0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right], \tag{18}$$

$$\begin{aligned} C_Z(t) \quad &= k_3 k_2 k_1 C_A^0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)(k_4 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)(k_4 - k_2)} + \right. \\ &\left. + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)(k_4 - k_3)} + \frac{e^{-k_4 t}}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} \right] \end{aligned} \tag{19}$$

$$C_B(t) = k_4\int_0^t C_Z(\xi)\,d\xi = C_A^0\left[1-\frac{k_4k_3k_2e^{-k_1t}}{(k_2-k_1)(k_3-k_1)(k_4-k_1)}-\frac{k_4k_3k_1e^{-k_2t}}{(k_1-k_2)(k_3-k_2)(k_4-k_2)}-\frac{k_4k_2k_1e^{-k_3t}}{(k_1-k_3)(k_2-k_3)(k_4-k_3)}-\frac{k_3k_2k_1e^{-k_4t}}{(k_1-k_4)(k_2-k_4)(k_3-k_4)}\right] \quad (20)$$

The kinetic model put forward in this paper is a linear, ideal one, solved with the Laplace transform method. It can be optimized, but it will no longer be linear. For this reason, an exact solution is impossible. However, the equations of the model can be solved with adequate numerical methods.

Experimental

The variation of the VOC concentration in flue gas includes all the volatile compounds of organic nature existing in the flue gas flow: alcohols, aldehydes (ketones), organic acids and the compounds resulted through the *de novo* syntheses in which carbon monoxide or the other volatile organic compounds take part.

In incomplete combustion systems (with oxygen deficit), the carbon monoxide concentration can become significant. Therefore, especially at temperatures between 200 and 600°C carbon monoxide can produce compounds with cyclical organic structures, some of which can harm the environment and the population's health. In a similar manner, in fuel gas combustion, the particulate matter concentration contains exclusively finely divided carbon produced by the carbon-producing reaction (8).

Figure 1 shows VOC variation with temperature at the start-up of a special waste industrial incineration plant fueled only with methane. As seen in this figure, the higher the temperature, the lower the VOC concentration in flue gas, due to the gradual reach of the operating temperature (600°C), at which VOC declines towards zero.

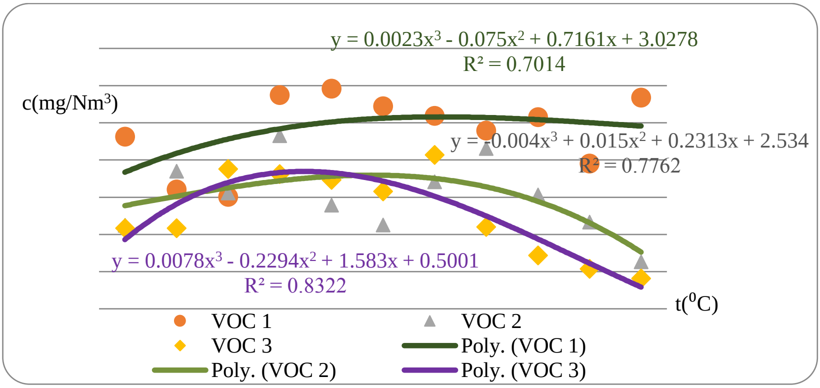


Figure 1. VOC variation with temperature at the start-up of a special waste industrial incineration plant fueled exclusively with methane

The representations of VOC = f(t) values within the 100-600°C range, during three successive start-ups after maintenance works that required cooling the combustion and post-combustion chambers of the incinerator in 2017, indicate that the variation of this parameter corresponds to a correlation coefficient acceptable to the modelling of a global characteristic parameter of an industrial process with a third-degree polynomial function having the following form:

$$y = ax^3 + bx^2 + cx + d \qquad R^2 = 0.7014 – 0.8322 \qquad (21)$$

As confirmed by the brief theoretical considerations above, VOC has maximum concentrations between 250 and 350°C. This shows that the mixture of partially oxidized methane fractions and fractions reformed through *de novo* and Loew synthesis or other parallel complex reactions reaches maximum values. At the same time, carbon monoxide has minimum values corresponding to the maximum VOC values, which characterizes its conversion to organic compounds (figure 2).

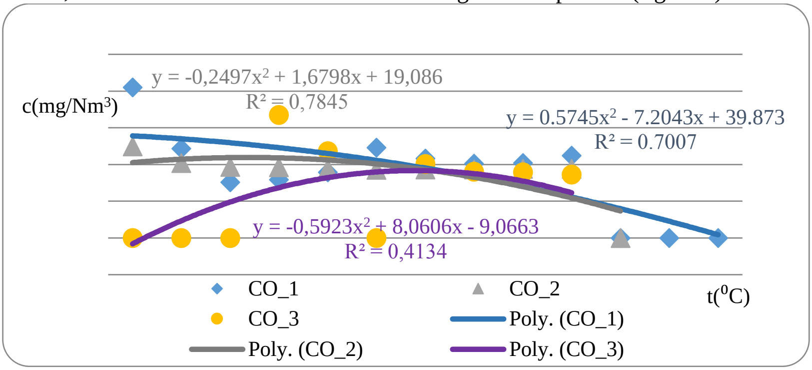


Figure 2. Variation of carbon monoxide concentrations in a special waste industrial incineration plant fueled exclusively with methane, during three successive cold start-ups after maintenance – data registered in 2017

The particulate matter concentrations reach maximum values within the same temperature range of 250–400°C. They can be formed both directly from methane through the carbon-producing reaction (8) and *de novo* forming, following a reaction parallel to the oxidation phases, according to equation (22):

$$2\ CO \rightarrow CO_2 + C \qquad (22)$$

It should be noted that both for carbon monoxide and particulate matter the concentration the variations represent second-degree polynomial curves with correlation coefficients varying between 0.0522 and 0.9364, acceptable to industrial applications.

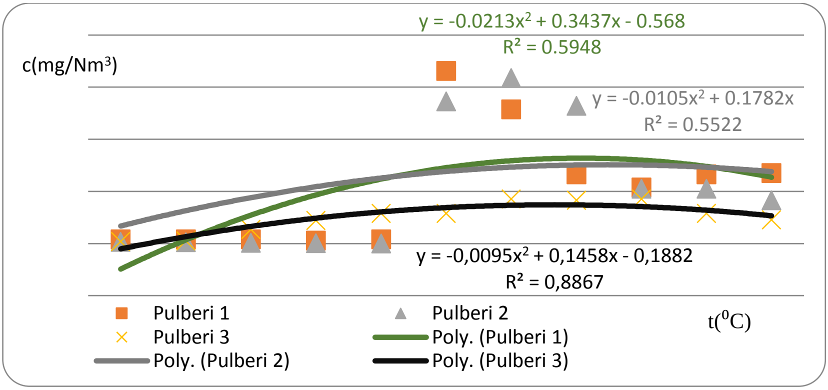


Figure 3. Variation of particulate matter concentration in a special waste industrial incineration plant fueled exclusively with methane, during three successive cold start-ups after maintenance – data registered in 2017

Conclusions

Fuel gas combustion involves consecutive and parallel reactions producing carbon oxidation intermediates whose oxygen concentration in the molecule increases successively and monotonously from 0 (the alkane phase) to values higher than 73% (the CO_2 phase). The successive oxidation reactions have first-order kinetics, but the succession of the registered reactions makes it impossible to solve the system of equations other than with numerical methods.

The parallel reactions occurring in gas hydrocarbons combustion produce reaction intermediates whose number increases with the decrease of the oxygen excess in the oxidation (combustion) phase. Nevertheless, it should be noted that however high the oxygen excess may be, fuel combustion is never total, as shown by the registered values of VOC, carbon monoxide and finely divided carbon (soot).

The experimental studies will continue with specific measurements of the VOC constitutive elements to reveal the parallel and consecutive mechanisms of the oxidation process of gas hydrocarbons combustion.

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STUDY ON NANOPARTICLES FLOW REDUCTION TESTS TO HWI PLANTS USING NUMERICAL SIMULATIONS

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Abstract

This study deals with the experimental evaluation of some relevant ash samples collected from the flue gas filters of a hazardous waste incinerator plant. The experimental analysis focuses on size, distribution and dielectric properties of the samples. The reported results reveal the presence of nanoparticles in the samples and the possibility to use dielectrophoresis for their handling. The study exploits also numerical simulations in order to investigate the behavior of nanoparticles with size range from 50 to 150 nm, which is fructified as a micro channel - working unit used as a particulate trap. Based on the experimental data and a proposed mathematical model, the concentration profile of nanoparticles suspension inside a micro fluidic separation device is calculated and the performance of the device is analyzed in terms of three new specific quantities of separation process, called *Recovery*, *Purity* and *Separation Efficiency*.

Keywords: *air pollution, dielectrophoresis, filtration rate, flue gas filtration, hazardous waste, incineration, microfluidic device, nanoparticle separation, $PM_{2.5}$, PM_1*

Introduction

Timisoara (45°46' N, 21°26' E) is a city located on the south-eastern edge of the Pannonia plain, and lies at an altitude of 85 m, being one of the largest Romanian cities, with a population of over 300 thousands inhabitants and more than 170 thousands automobiles. The air quality in urban areas is determined by the intensity of emissions (Sbrizzai et al. 2005; Rickerby & Morrison 2007). The principal sources of pollution are from transportation (emission from traffic), industrial and households. The main pollutants tend to be airborne particles, sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone and volatile organic compounds (VOCs).

Health effects of air pollutants, i.e. nanoparticles, is an old issue in cities and urban areas around the world, but became evident during severe air pollution episodes in the first part of the 21- th century. Once the association between the existence of fine particles suspended in atmosphere and their negative impact on the human health has been proved clearly, the problem of the control of the toxic emissions has become of great scientific interest. Recent health effects studies have shown an association between existing levels of fine particles (size, concentration) and health effects such as increased respiratory illness, cardiopulmonary morbidity, and premature mortality (Minutolo et al. 2010; Rickerby & Morrison 2007).

From a public health standpoint, the size of a particle is as important as its composition, recent research showing that although raw materials may not be dangerous, they can become toxic under the form of nanoparticles. Although the nanoparticles have smaller masses than microparticles, their number is at least four orders of magnitude higher than the number of all other particles found in the flue gas. Incinerator-related activities result in the emission of a host of air pollutants that adversely affect public health and the environment, including nitrogen oxides (NO_x), hydrocarbons (HC), particulate (PM), carbon monoxide (CO), which causes lung irritation and aggravates diseases such as asthma, chronic bronchitis, and emphysema (Chang & Huang 2001). In this context, the problem of obtaining information about the composition and dispersion of different resulted combustion residues is a first and fundamental step. The transport process of the components is investigated numerically with the *CloseView* software. The input program data are the concentration and the chemical properties of the components detected experimentally in the combustion chimney. Our study takes into account the effects that the height of the combustion chimney, the velocity and the direction of the wind has on the dispersion process. The concentration profiles are calculated for a geometry specific to the city map of Timisoara. This analysis provides relevant information on the distribution of the pollutants and the most exposed zones of the city. In this paper we take a close view of pollutant dispersion in the environment, how the wind and atmospheric condition affects the dispersion for point like emission sources. As a result of highlighting for this micro pollutants by the mentioned method and considering that emissions sources are generally equipped with filters able to retain only micro particles, usual methods (retention and separation) have not been successful for the separation of nanoparticles (Lungu et al. 2010). The most promising technique for nanoparticle trapping and controlled spatial separation is a method based on dielectrophoresis (DEP), phenomenon in which a spatially non-uniform AC electric field induces a dipole moment in a dielectric particle. Hence, the particle undergoes a DEP motion under the resulting translational force. This force does not require electrically charged particles; the strength of the force depends on the medium and particle's electrical properties, particle's shape and size, and on the applied electric field amplitude and frequency (Pethig 2010; Neculae et al. 2012; Green et al. 2002).

Materials and Methods

Hazardous waste incineration is one of the widely used waste disposal technologies which both reduces waste volume and NOx amount and recovers energy as a last alternative of judicious use. This technology complies with specific regulations that establish a threshold for direct VOC emissions or other forms of spreading volatile, powder and other waste gases type at the stack of incineration plants.

Filtration of submicron particles suspended in flue gas is an important technological challenge, as in urban environment the burning processes including incinerators of waste or diesel emissions are responsible for the emission of a significant amount of nanoparticles (Sbrizzai et al. 2005). The presence in the environment of nanoparticle with size ranging from 50 nm to 200 nm has a profound impact on human health (Rickerby & Morrison 2007). Once inhaled, due to their tendency to remain trapped in the inner respiratory ways, infiltrate into the blood and cannot be eliminated, because the macrophage cells cannot identify them. Inhaled nanoparticles may generate free radicals, affect the DNA and alter the genes, being responsible for mutagens and carcinogenic effects or causing a variety of lung-disease typologies. From a public health standpoint, the size of a particle is as important as its composition, recent research showing that although raw materials may not be dangerous, they can become toxic under the form of nanoparticles (Rickerby & Morrison 2007; Minutolo et al. 2010). Although the nanoparticles have smaller masses than microparticles, their number is at least four orders of magnitude higher than the number of all other particles found in the flue gas. As a direct and immediate consequence, the filtration of nanoparticles is an important technological challenge, as they are produced in large quantities from material synthesis and combustion emission. Sources of polluting emissions are generally equipped with various filters that capture the micron particles, but permit nanoparticles to escape in atmosphere (Chang & Huang 2001; Lungu et al. 2010). In many scientific and technical areas, a considerable interest is shown to the separation of nanoparticles in accordance with their physical or chemical characteristics. The methods utilizing electric fields are emerging as most promising techniques for nanoparticle manipulation, namely those based on dielectrophoresis (DEP): a phenomenon in which, under spatially non-uniform AC or DC electric fields, dielectric particles move because of the interaction of the dipole induced in the particle and the applied field gradient. DEP methods can be used in many forms to manipulate and more generally, control the position, orientation and velocity of submicron scale particles. DEP force does not require electrically charged particles; the strength of the force depends on the medium, particle's electrical properties, particle's shape and size, and on the applied electric field frequency (Pethig 2010; Neculae et al. 2012). Since the relative dielectric polarization of the nanoparticles depends on the driving frequency of the applied electric field, an alternating (AC) electric field is usually applied to generate DEP forces of different magnitudes and directions. In classical dielectrophoresis, the positive DEP force attracts particles into the regions of strong electric fields, while negative DEP force repels them from those regions (Green et al. 2002; Çetin & Li 2011). More recently, using advanced microelectrode fabrication techniques, the technology has moved into the submicrometer world so that nanoparticles can now be characterized and separated. The manipulation of nanoparticles in microsystems by using DEP forces has many existing and potential applications, presenting the advantages of voltage-based control and dominance over other forces: in the range above a few millimeters, the electrical forces are rather ineffective, but in the micrometer (and submicrometer) scale the electrical forces dominate. Microfluidics involves the manipulation of nanoparticles within a microscale chip. Within microfluidic systems, the manipulation of nanoparticles is of fundamental importance, including patterning, focusing, sorting, trapping, handling and separation (Zhang et al. 2010).

For the modern hazardous waste incineration plants, the current standards provide strict limits both for $PM_{2.5}$ and indirect nanoparticle emissions released as heavy metals that are more or less volatile at high temperatures (Strambeanu & Demetrovici 2009; CD 438/2006).

The identification of the primary composition of stack emissions has led to the conclusion that some improved particulate retention systems were effective in removing about 99.99% of particles, with similar efficiency in reducing particles of smaller diameter (Buonanno et al. 2011). However, it has been found that the boiling points of incinerated elements have special significance: higher boiling point elements like were frequently identified in larger particles, while lower boiling point elements like arsenic and cadmium were more common in ultrafine particles whose toxicity level they increased (AEA 2012).

Table 1. Emission limits recommended for incinerators of hazardous waste and sludge in treatment stations (CD 438/2006)

	Code	Name			
NFR Source Category	5.C.1.b.i, 5.C.1.b.ii, 5.C.1.b.iv	Industrial waste incineration including hazardous waste and sewage sludge			
Fuel	NA				
Not applicable	HCH				
Not estimated	NH_3, Cr, Cu, Zn, Se, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, PCBs				
Pollutant	**Value**	**Unit**	**95% confidence interval**		**Reference**
			Lower	**Upper**	
NO_x	0.87	kg/Mg waste	0.087	8.7	European Commission (2006)
CO	0.07	kg/Mg waste	0.007	0.7	European Commission (2006)
NMVOC	7.4	kg/Mg waste	0.74	74	Passant (1993)
SO_2	0.047	kg/Mg waste	0.0047	0.47	European Commission (2006)
TSP	0.01	kg/Mg waste	0.001	2.3	European Commission (2006)
PM_{10}	0.007	kg/Mg waste	0.0007	0.15	US EPA (1996) applied on TSP
$PM_{2.5}$	0.004	kg/Mg waste	0.0004	0.1	US EPA (1996) applied on TSP
BC	3.5	% of $PM_{2.5}$	1.8	7	Olmez et al. (1988)
Pb	1.3	g/Mg waste	0.48	1.9	Theloke et al. (2008)
Cd	0.1	g/Mg waste	0.048	0.15	Theloke et al. (2008)
Hg	0.056	g/Mg waste	0.04	0.08	European Commission (2006)
As	0.016	g/Mg waste	0.01	0.019	Theloke et al. (2008)
Ni	0.14	g/Mg waste	0.048	0.19	Theloke et al. (2008)
PCDD/F	350	µg I-TEQ/Mg waste	0.5	35000	UNEP (2005)
Total 4 PAHs	0.02	g/Mg waste	0.007	0.06	Wild (1995)
HCB	0.002	g/Mg waste	0.0002	0.02	Berdowski et al. (1997)

While incineration of any kind of waste has a small contribution to anthropogenic nanoparticle emissions (CD 438/2006; AEA 2012; Buonanno et al. 2011), there are studies that attempt to establish a direct correspondence between thermal waste elimination and the statistical parameters of population health (Buonanno et al. 2011; BS 2005).

For instance, particle size distribution by specific particle weight may cause serious errors, especially in hazardous waste incinerators equipped with catalytic systems for reducing nitrogen oxides, which may actually double the $PM_{2.5}$ emissions (BS 2005). Most stack emissions contain ultrafine particles of the most dangerous type and fabric filters with Teflon membrane are ineffective against such particles, especially those under 200-300 nm which are considered extremely harmful to health.

Most current modelling methods do not take into consideration the particles that are reformed from atmospheric gas emissions far from the incinerator stack, although a number of studies have shown how in 95% of cases ultrafine heavy metal particles combine with polynuclear aromatic hydrocarbons (PAH) to produce PM_3 or smaller conglomerates. PAHs are toxic, mutagenic, teratogenic and cancer-causing. Such combinations increase the lung cancer risk by almost eight times (BS 2005).

Timisoara (45°46' N, 21°26' E) is a city on the South-Western border of the Pannonian Plain. Situated at an altitude of 85 m, it is one of Romania's largest cities, with over 300,000 inhabitants and more than 170,000 cars. Starting with 2001, a hazardous waste incineration plant built in compliance with the EC construction and operation standards has been in operation in the city's southern industrial area.

The study investigates the behavior of nanoparticles with size ranging from 50 to 150 nm in a DEP-based microsystem, which consists in a microchannel-working unit of a particulate trap. After a brief presentation of the theoretical model, we proceed to the experimental determination of the key characteristics of the particles suspended in flue gas: the size distribution of the submicron particles collected from the flue gas filters of a hazardous waste incinerator plant and their dielectric properties are evaluated. Based on the experimental data and the proposed model, the concentration profile of nanoparticle suspension inside the microfluidic separation device is calculated and the performance of the device is analyzed in terms of new specific quantity of separation process, called *Filtration rate*. The final goal of the study is to identify a suitable way to predict accurately the nanoparticle entrapment and find the optimal values of the control parameters for separation process, to be useful in designing of microfluidic devices for separating nanoparticles from combustion gases.

Theoretical consideration

The theoretical approach of particulate diffusion in the atmosphere is based on Fick's second law:

$$\frac{dc}{dt} = D\frac{d^2 c}{dr^2} + G(c) \tag{1}$$

This equation is the mathematical expression of concentration *c* in time *t* in a space-time coordinate point (*r*, *t*). The *G(c)* function defines the nanoparticle content in the sedimentable particle flow released at the stack. The diffusion coefficient *(D)* is proportional with the temperature *(T)* and indirectly proportional with the amount of diffusing particles, as well as their form. The diffusion coefficient has a large range in gases: $D \sim 10^{-5}$ m^2/s. For colloidal spherical particles, it is calculated with the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi}(p1 + p2)\square \tag{2}$$

where: *k* – Boltzmann's constant; *h* – dynamic viscosity coefficient; $p_{1,2}$ – average radii of sedimentable / non-sedimentable particles.

The integration of equation (1) can lead to precise analytical solutions, but it requires certain initial conditions that can frequently differ from those required for finding solutions for similar differential equations without physical-chemical signification.

In such cases, the numerical integration methods usually lead to experimentally reproducible models with satisfactory results. The transport of settled particles experimentally defined below was numerically shaped through the original *CloseView* program (Strambeanu et al. 2016). The time averaged DEP force acting on a spherical particle situated in an AC electric field can be written as (Morgan & Green 2003):

$$\langle \mathbf{F}_{DEP} \rangle = 2\pi a^3 \varepsilon_m K_R(\omega)\nabla\left(\left|\nabla V_R\right|^2 + \left|\nabla V_I\right|^2\right), \tag{3}$$

where we denoted by a the particle radius, ω the angular field frequency, and V_R, respectively V_I the real and imaginary part of the electric potential phasor, $\tilde{V} = \ddot{V}_R + \jmath V_I$, with $j = \sqrt{-1}$. For a homogeneous medium, the electric potential satisfy the Laplace equation: $\Delta^2 \tilde{V} = 0$. $K_R(\omega)$ is the real part of the complex quantity

$$\tilde{K}(\omega) = \left(\tilde{\varepsilon}_p - \tilde{\varepsilon}_m\right) / \left(\tilde{\varepsilon}_p + 2\tilde{\varepsilon}_m\right), \tag{4}$$

named as Clausius–Mossotti (CM) factor, which is a measure of the effective polarizability of the particle. $\tilde{\varepsilon}_p$ and $\tilde{\varepsilon}_m$ are the complex dielectric permittivities of particle and medium. The complex permittivity is defined as $\tilde{\varepsilon} = \varepsilon - j\left(\sigma/\omega\right)$, where σ is the electrical conductivity.

The CM factor depends on the dielectric properties of the particle and medium and on the frequency of the applied field; at low frequencies the sign is determined by the electrical conductivities of the particle and the medium and at higher frequencies by the permittivities. The variation in this factor results in a frequency-dependent dielectrophoretic force that is unique for a particular type of particle. Therefore, DEP is an effective tool for separating particles, based solely on their dielectric properties and size. When the sign of K_R is positive, the particle is attracted to the locations of electric field intensity maxima and repelled from the minima, phenomenon known as positive dielectrophoresis (pDEP). The opposite occurs when K_R is negative, situation referred to as negative dielectrophoresis (nDEP).

A typical DEP-based separation device has parallel interdigitated bar electrodes placed on the bottom surface is illustrated in Fig. 1.

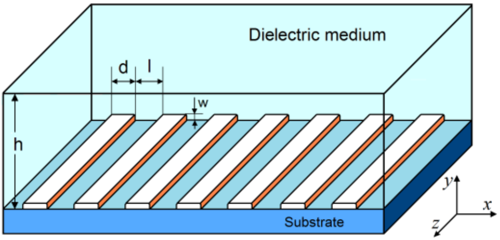


Figure 1. Schematic representation of experimental device used for DEP separation

In most of the reported models, due to the symmetry of the geometry and considering the electrodes much longer than their width, the problem is treated in two dimensions and the electrodes' height is neglected. In our study, in order to have a more realistic description of the experimental device, a 3D geometry and a detailed description of the electrodes shape are used. Anyway, taking into account the periodic distribution of the electrodes, the numerical calculations of the DEP force and the concentration field can be performed considering as computational domain only a so called "basic unit cell", which fully describes the entire system, except the vicinity of the walls. The geometry of the computational domain, together with the associated boundary conditions necessary to solve the Laplace equation for electric potentials V_R and V_I are presented in Fig. 2.

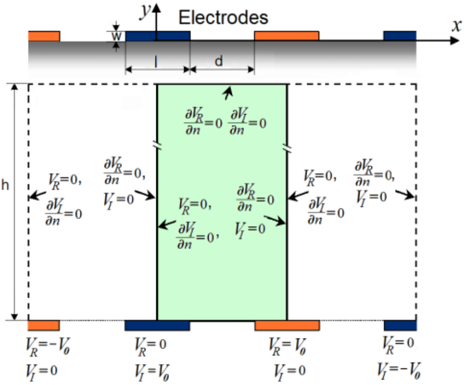


Figure 2. The geometry of the computational domain and the associated boundary conditions for the electric potentials. The solid lines indicate the basic unit cell

The macroscopic behavior of a suspension of spherical particles of radius *a* in a fluid of viscosity η is modeled by considering the mechanical equilibrium between an external force **F** (DEP force in this case) and the Stokes drag force. For small particles (i.e. nanoparticles), the dynamics of the system is governed by the following system of equations (Neculae et al. 2012):

$$\mathbf{v}=\mathbf{u}+\frac{2a^2}{9\eta}\mathbf{F}\,, \tag{5a}$$

$$\frac{\partial C}{\partial t}+\nabla\cdot\mathbf{j}=0\,,\ \text{where}\ \mathbf{j}=C\mathbf{v}-D\nabla C \tag{5b}$$

Here **u** and **v** are the fluid and particle velocities, *t* is the time, **j** is the particle flux, *D* is the diffusion coefficient of the particles, and *C* is the particle volumic concentration. The fluid flow field inside the separation device, **u,** is calculated by solving the classical Navier-Stokes equation in the compressible case, together with the corresponding boundary conditions. For the obtained DEP-force and fluid flow field, the particle concentration is evaluated by numerically integrating equations (5a) and (5b). This calculated particle concentration field gives information at a local scale, showing how the particles are attracted on the margins of electrodes and the influence of the main parameters of the problem on this process. For the analysis of the filtration process we define the novel quantity named *Filtration rate* (*F*), which describes the process in terms of nanoparticles entrapment at the electrodes, related to the concentration distribution:

$$F=\frac{C_{input}-C_{output}}{C_{input}}=1-C_{output}/C_{input}\quad[\%] \tag{6}$$

where C_{input} and C_{output} are the mean concentrations of suspended nanoparticles at the input and the output surfaces of the device, respectively, as schematically sketched in Fig. 3.

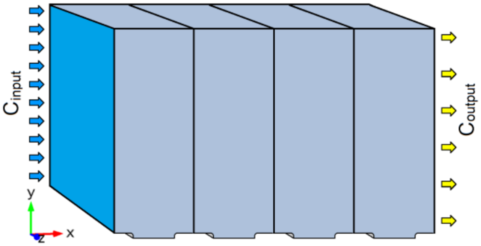


Figure 3. Schematic representation of the separation device revealing the parameters used for defining the *Filtration rate*

This proposed quantity gives the global information on the filtration process, and can be used in order to evaluate the efficiency of the filtration process.
At the end of this theoretical section is important to conclude that the electrokinetic forces depend in a complex manner on system dimensions, frequency, field, etc. In separation systems, the buoyancy force can be sometimes significant but often the magnitude of this force is much lower than the other forces acting on nanoparticles.

Results and Discussion

Emissions measurements

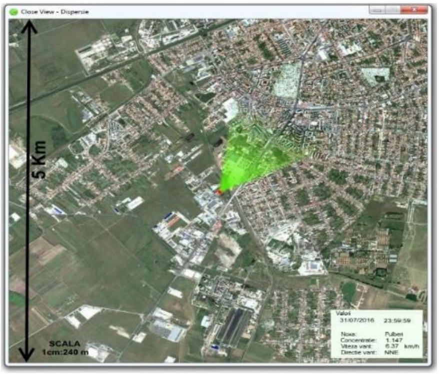
Incineration activities generate atmospheric pollutant emissions with a harmful effect on health and the environment, including NOx, hydrocarbons (HC), particulates, carbon monoxide (CO) that cause lung damage and aggravate diseases like asthma, chronic bronchitis, emphysema etc. (Zhiqiang et al. 2000; Popescu et al. 2011). Consequently, obtaining information about the composition and dispersion of various combustion components is the first essential step to take against polluting emissions.
The system of continuous monitoring of the particulates at stack is shown in Table 2. The system measures the emissions every two minutes. The analyser sends the data to the central command-control unit that compares it to the admissible values and adjusts the flow chart.
The particle transport was modelled numerically with the original *CloseView* software. The study quantified the effects that the height of the stack identified as point source and the wind speed and direction have on the continuous particle dispersion process. The concentrations were calculated for the geometry specific to the city map of Timisoara, for the last five years (2011-2016). The graphic representation of the particulate dispersion statistics for the last five years reveals the areas of the city that are mostly exposed to nanoparticle emissions at the incinerator stack (Figure 4). These are represented by the SE–NW sectors, reproducible with 3-5° deviations every year.

Table 2. Data about the measuring and control equipment

Parameter	Method	Equipment
Particulate	Triboelectric	DURAG D-RX250 System
Flow rate	Prandtl congestion tube	DURAG D-RX250 System
Humidity	Capacimetry	Calibrated condenser
Temperature	Thermo-electrical	Thermocouples, thermal resistors

Some references indicate that the waste incineration plants generate relevant amounts of fine and ultrafine particulates, as the current standard value for particulate emissions (10 mg/Nm^3) provides a filter retention rate of only 5-30% for $PM_{2.5}$ and 0% for PM_1 (BS 2005).

As a result, a fraction ranging within the above-mentioned limit values consists of non-sedimentable nanoparticles that can affect a city area far larger than that revealed by the statistical calculations of long-term particulate emissions which determine the particulate number and size, but not the particulate flow rate at the stack or the imissions (AEA 2012; BS 2005).



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Viteza vant: 6.37 km/h
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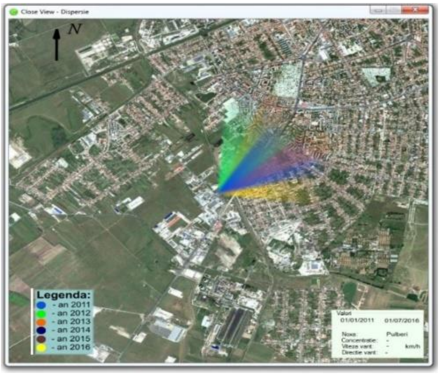
Figure 4. Prevailing particulate dispersion at the stack of the incineration plant (2011-2015)

Such considerations have underlined the necessity to investigate the technical possibilities of limiting nanoparticle emissions. These are to be applied at the emission point source represented by the flue gas evacuation system of the hazardous waste incinerator, in relation to the specific context of the area where the incinerator is located.

Flue gas filtration

In order to obtain relevant input data for the simulations, we investigated three probes, named as A, B and C, consisting in samples of ash resulted from the combustion of different wastes, collected monthly from filters of Pro Air Clean Timisoara hazardous waste incinerator, within a period of three months. These probes were analyzed from dimensional and dielectric point of view. For dimensional characterization, we prepared for each of the three probes a mixture of 5 mg ash in 100 ml distilled water at room temperature, and put it to rest for 20 minutes, in order to decant the microparticles. Then we collected the remained slurry liquid and analyzed the particle size/concentration distribution using a Nano Sight LM 10 nanoparticle visualization system, based on nanoparticle-tracking analysis method. Fig. 4a-4c illustrate the particle size/concentration distribution for the three probes. The distribution diagram indicates that it contains four significant groups of nanoparticles, having sizes of 55 nm, 100 nm, 155 nm, and 275 nm, respectively.

These diagrams show that the gas resulting from the combustion of waste contains nanoparticles, nanoparticles having radii ranging from 50 to 200 nm, considered potentially harmful for human health. For each of the three probes one observe higher concentrations for particles with radii of about 50 nm, 100 nm, and 150 nm, values that will be considered relevant in our future analysis. The efficiency of the filtration process can be evaluated by calculating the *Filtration rate* (6) for different values of problem's parameters. The computation is performed using an iterative procedure: the output concentration in one unit cell is considered the input concentration for the next unit cell, in order to describe the cumulative effect of the filtration inside the dielectrophoretic device. This type of analysis allows an estimation of the necessary number of cells (or electrodes) in order to obtain a certain desired filtration rate, when the other parameters of the problem are fixed. The results presented in Fig. 5-a show that in the case of particle having size of 100nm, a desired filtration rate of 90% can be obtain by using about 30 electrodes when applying a voltage of 24 V, about 60 electrodes for 18 V, and nearly 200 electrodes for an applied voltage of 12 V.



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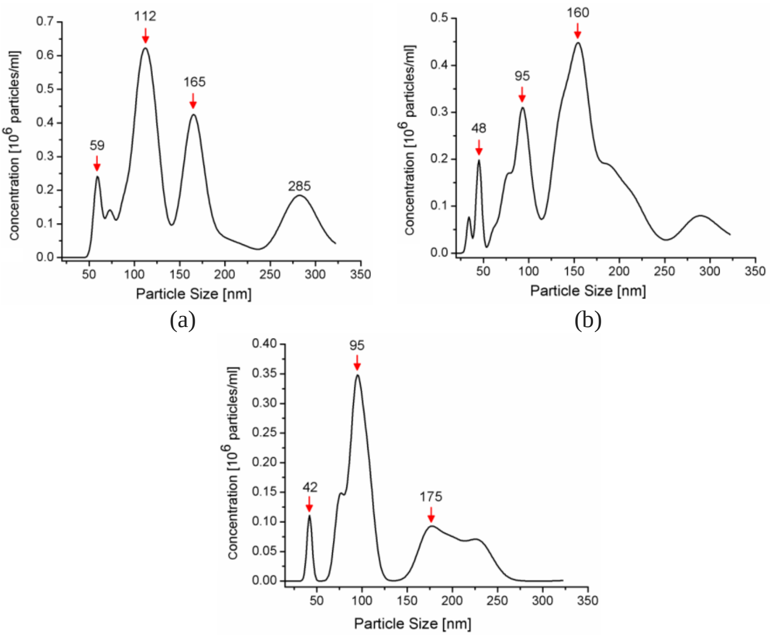
01/01/2011 01/07/2016
Noxe: Pulberi
Concentratie: -
Viteze vant: - km/h
Directie vant: -

Figure 5. Change in average annual angular dispersion depending on atmospheric conditions (2011-2015)

When we analyze the effect of particle radiion the filtration capacity, the results presented in Fig. 8-b predict that, for example, when the applied voltage is 18 V, particles of 150 nm are completely captured after 10 electrodes, for particles of 100 nm we need about 150 electrodes for the complete capture, while for the particles of 50 nm are captured less than 60% even if one use devices with 250 electrodes.

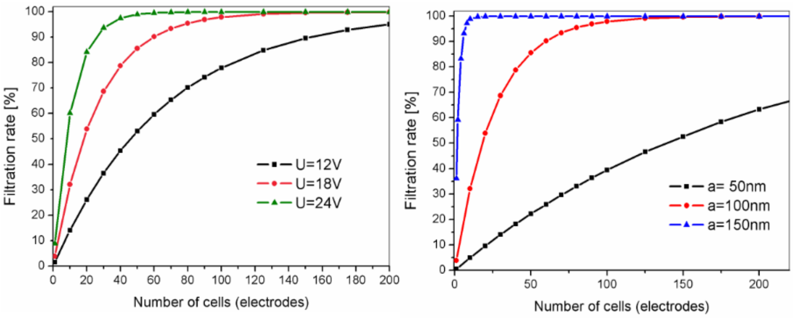
The next step of our research activity will focus on the validation of the theoretical model. Some preliminary but promising experimental results were already obtained.



(a) (b)

(c)

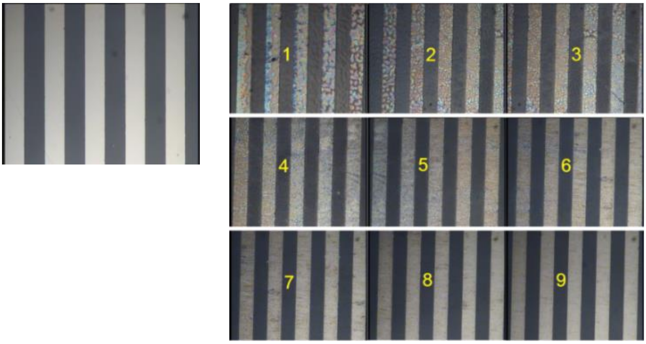
Figure 6. Particle size/concentration distribution diagram for probes a, b and c, after 20 minutes of decantation



(a) (b)

Figure 7. Calculated filtration rate versus number of cells for a) particles with a = 100 nm at three different applied voltages and b) particles with three different radii at an fixed applied voltage of V_0 = 18 V ($d = l$ = 100 µm, w = 2 µm)

The tests performed with a DEP-based separation device having $l = d$ = 100 µm and H = 1000 µm reveal that in the absence of the applied voltage the particles are not at all attracted to the electrodes (Figure 6-a), while once applied an AC voltage of 12 V the dielectrophoretic effect appears (Figure 6-b). More than that, the concentration of captured particles clearly diminishes while we depart from the input region, which is in concordance with our simulations.



(a) (b)

Figure 8. DEP-based separation device with $l=d=100$ μm; a) before fumigation, b) after fumigation, successive snapshots, U=12V, AC, 50Hz, time of fumigation t=30s

After this qualitative validation, a quantitative evaluation of the concentration of nanoparticles captured at the electrodes, at different distances from the input of the device, is necessary in order to give a solid validation of the model.

Conclusions

We introduced a theoretical model and applied it to a physically realistic problem, and then we predict a novel mechanism of particle entrapment, which is not only fundamentally different from the one conventionally known but also, is proven to be efficient at small scales. The particle concentration distributions for a typical interdigitated electrodes array are calculated using the proposed theoretical model. The efficiency of the manipulation process is discussed in terms of *Filtration rate*, for different values of particle radius and applied voltage. The optimal parameters of the separation process can be determined through a detailed numerical study performed in the frame of the proposed mathematical model and used for designing more efficient separation devices.

Acknowledgments

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TECHNOLOGICAL MODEL TO COLLECT AND PARTIALLY DRY THE ACTIVE SLUDGE FROM NATURAL LAKES USING SOLAR PANELS

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Abstract

In Natural Reservation is very important to maintain the environmental, the equilibrium for the protected species, flora, and fauna. The paper presents a technological model perfect adapted to these conditions as not disturb the local equilibrium. In the first part are mentioned the topic importance and the new problems appeared into last decades, related to the environmental problems in Natural Reservation Lake Techirghiol. This new solution placed on a mobile pontoon uses renewable resources as to collect and partially dry the collected sludge from the lake. Some experimental measurements were done in 2015, as to determine the quality of water, the main parameters, and the conditions responsible for disturbing the eco-system. The technological model intends to solve the local problem, to collect, compact and partially dry the active sludge. The extracted sludge can be in short time integrally consumed for agricultural purpose, as ecologic and nutritive fertilizer for the adjacent area, known as the Plover, with low potential for agriculture. The sludge, well known in the past for its human therapeutic utilization, more, then one hundred ago, nowadays-due ecological and biological changes lost his efficiency. The reconstruction of the local ecologic balance and for the sludge to recover its therapeutic properties, using renewable resources, without disturbing the environment are the main objectives of this research. Some conclusions, the acknowledgements, and references are also presented.

Keywords: *environmental engineering, environmental monitoring, prototype, renewable energy sources, water conservation*

Introduction

Techirghiol lake, a Natural Reservation, is the biggest lake with salt water in Romania, provided by the Decision 1266/2000. Techirghiol Lake is RAMSAR site since 2006, with the number 1610, included in Nature 2000 on the base of the EU Birds Directive, having the RoSPA0061 code. Here, more than 150 bird species are permanent present in transit or in wintering, because the water never freezes, even in cold winters. There are also fish and specific salt water vegetation.

In the last decades, earthquakes with small magnitude occurred in the Black Sea, in the south part of Romania, near the Bulgarian border. This is exactly the place where the lake is situated. Some tectonic plates have been shifted and allowed freshwater to infiltrate the edge of the continental part. As consequence, the local salinity of the water decreased. The local shores restoration works that were carried out in 1980-1983 let also supplementary clean water to enter into the lake, this being another source changing the water salinity. Shortly perturbations of the environmental conditions were observed. Some species aquatic vegetation specific to fresh water, rapidly grew and invertebrates have appeared and developed. That was the reason that made monitoring of the water parameters in different points of the lake necessary. The lake's water surface has an altitude between 0-80m, being near the vicinity of the Black Sea.

During the bird passage, in the lake are presently more than 20,000 birds, of different species. Many of them are protected by law and are into a permanent surveillance.

Other solutions known until now can't be applied in this case. Chemical solutions can't be used, due to the fact that that would change the chemical composition of the water, affecting the entire ecosystem. The biological solutions with the freshwater fish cannot be applied. They already began to emerge, develop, and grow without any intervention. The conventional, mechanical, harvester solutions use gasoline or diesel fuel with an unpleasant smell and produce noise, which disturbs the birds. Moreover, they would immediately destroy the bird nests and the rearing areas.

At present, due to eutrophication, many lakes have a diminished capacity. Massive sludge deposition was registered, favorable for the aquatic vegetation development. In short time the development being the following: massive amounts of invertebrates, interference scallops, and predator fish, followed by a decline of the specific fishes.

The proposed solution is ecological without disturbing the local environment. Its primary objective is to rebuild the local, natural, biological balance. In order to solve the problem an experimental model was realized, an autonomous pilot station placed on a mobile pontoon, powered in co-generation with PV panels, to collect, compact and partially dry the sludge.

The sludge, due to its structure full of nutrients and nitrates is perfectly ecologic to be used as a biologic fertilizer to restore the soils affected by demineralization. By repeated applications, the lands are restored and playback for agriculture; the yields were higher on the tested land.

The solution has a double benefit: restoring the ecologic equilibrium and assuring a proper and efficient consumption of the extracted sludge, as organic fertilizer on affected soils. By partially drying the sludge, the time until the economic use becomes possible is shortened and also insects' development is restricted, and the putrefaction of parasitic is reduced. Renewable energy resources are used in order to collect, compact and partially dry the sludge.

Materials and Methods

Mangalia Lake is the largest salted water lake in Romania, with a water body of 1226.97 hectares. It is located in the immediate vicinity of the coastline, approximately 15 km south of Constanta city. Its name means Lake of mullets (Mullus barbatus).

Sludge and lake waters are used for their health benefits since the 19th century. In 1924, at the Universal Exposition from Paris, the Techirghiol mud received the gold medal. The quality appears as result of the bacterial decomposition of the aquatic organisms after their natural cycle, especially by Artemia salina shellfish and the marine algae that live in the lakes' water. The sapropelic mud of Techirghiol is used warm for different kind of procedures as cataplasm, massage, skin elasticity, hydration for cell strengthening, skin healing in cases of psoriasis and eczema, improvement of pain from anterior accidents, rheumatism, and muscular immobility.

The mud from Lake Techirghiol is shiny, unctuous as black oil and has a characteristic odor (Shumway 1990).

Water salinity variation directly affects marine algae life, followed by the disappearance of the specific aquatic organisms. That's why the sludge's properties are affected, as well as the water chemical composition.

The lake's Techirghiol salinity measured in 1936 was 99.6 g/l, in 1996-81.485 g/l, 2004– 65.1 g/l, and in 2010 was below 60 g/l, which proves the cumulative effects of the natural fluctuations, but also, the environmental problems. Due to the almost permanent wind, which constantly mixes the lake's waters, the lake rarely freezes (especially in the middle area). This water characteristic, remaining unfrozen even if the air temperature gets to -2^{0}C or -3^{0}C during winter, makes this place so attractive to numerous wintering waders (Figure 1).

Figure 1. Images with the Techirghiol Lake

During 2014-2016 measurements of the water quality were made. Currently, the lake water chemistry is influenced by the great extension of human activities. The results are presented below, with some secondary environmental indicators in Lakes Techirghiol, Costinesti I and Costinesti II. Techirghiol Lake suffered the most important changes of level and in salinity. The water sweetening can be, in this case, harmful. In these circumstances, the therapeutic mud is recovering with difficulty.

Table 1. The main measured water parameters

Lake	Chemistry	TDS	EC	pH	U	Dissolved oxygen		
	g/l	mg/l	mS/cm		mV	mg/l	%	mbar
Techirghiol	59.7 Hyper-alkaline	92	91	8.4 alkaline	77.7	0.63	8.1	16.4
Costinesti I	10.7 Mezzohalin	205	17.96	9.99 alkaline	170.9	7.45	96.2	193.4
Costinesti II	0.3 Fresh	1050	1046	9.1	118.2	3.16	37.3	76.6

TDS - the total dissolved salted, EC - Electric conductivity, U - Tension

The calcareous deposits under the loess allow an important throughput quantity of groundwater. Unfortunately, the lake is poorly maintained and there are highly eutrophic waters. It comprises a system of more or less of three lakes, the upstream main water body being isolated. The upstream lake clogging is strong and entirely covered with floating plants, reeds, and bulrush at edges. Near Techirgiol Lake, two other lakes are found: Lake Costinesti I and upstream, the Lake Costineşti II. Here the salinity also varies, with a considerable difference in time: in 1963 was 1927 g/l; 1969 to 17.1 g/l and in 2004 to 10.7 g/l. The fresh water contribution is due to the underground waters flows, which greatly varies depending on the season (Radulescu 2004).

Currently, Techirghiol Lake waters are divided into three separate entities. That is a consequence of the dams constructed in 1983 and 1989 and due to the infiltrations that appeared after more than 82 small earthquakes, registered in the last 30 years. There is a salt water area (52-55 grams of salt per litter) located near the sea, a brackish area (6 -8 g/l), intermediate and freshwater area (1 to 2.3 g/l), located at the "end of the lake". This part has nowadays areas filled with marsh vegetation characteristic for freshwater (Radulescu & Nistreanu 2004).

According to the standard registration, Techirghiol is important for the wintering of many bird species. Part of them: 7,000 red-breasted geese, one of the rarest species of geese in the world, 40 copies of whooper swan (*Cygnus cygnus*), 34 large egrets (*Egretta alba*), winter hawk (*Falco columbarius*), Falcon (*Falco peregrinus*), polar (*Gavia arctica*), 1,800 (Mergus albellus), 800 White-headed ducks (*Oxyura leucocephala*), and small cormorants 800 (*Phalacrocorax pygmeus*). Among the species that nest here, worth to be mentioned are also: 30 pairs of stilt (Himantopus himantopus) and 12 pairs of Little Bittern (*Ixobrychus minutus*). During the passage, the site is used inter alia for 20 pairs of Kentish Plover (*Charadrius alexandrinus*), 1,300 white storks (*Ciconia ciconia*), 600 black head seagulls (*Larus melanocephalus*), 5,200 small gull (*Larus minutus*), 100-120 pelican (*Pelecanus onocrotalus*), 100 thugs (*Philomachus pugnax*), 20 copies of the small tern (*Sterna albifrons*). In the migration periods, the site waters are used for more than 20,000 waders. For all the birds, the marine algae, marine shellfish, and marine species of fish, small frogs, or snakes represent the main food.

Dense algae growth (over 25% of the surface area) and other water plants can seriously interfere with normal aquatic life and definitely affect the life of birds, producing discrepancies for the normal environment (Caraco 2005).

During the nighttime, the oxygen depletion has supplementary biological effects; the green plants produce oxygen in sunlight, but they consume oxygen during the night. They further reduce the water of the dissolved oxygen.

Modification of water chemistry can deplete the oxygen supply, resulting in fish death by suffocation. Prolonged exposure to low oxygen concentrations can weaken the fish, making them susceptible to diseases and toxicants.

The key factors contributing to the biological process forming the therapeutic mud in Techirghiol are (Smith et al. 1999):

- *Artemia salina*, which is a crustacean philopodia, with a role in the peloidogenesis. It is the main filter and has three generations in Techirghiol lake: from April to May, June and August-September depending on weather conditions.
- Cladophora is a crystalline, reticular, filamentous alga known as "bad weed" consumed as a delicacy. It plays an important role in increasing phosphorus levels. The organic oxidized substances coming from lake inhabitants marks an increase from the surface to depth, i.e. from area trofolitica to area trofogena. Dissolved oxygen varies in different regions of the lake, but in all cases there is a decrease with the depth. On the surface, in the trofogena, oxygen consumption is high and less oxygen is consumed in the trofolitica.
- The sludge is, however, the factor that brought the lake fame.

It is part of a therapeutic underwater sediments organogenesis being characterized as a shore mud. Such sludge is the product of the chemical and biochemical processes that are extremely complex and lengthy, altering the minerals and organic substances from the lake (Sharpley et al. 1998).

Results and Discussion

The further solution is a prototype tested for the first time in Techirghiol Lake. It represents an autonomous innovative solution (under license), perfect ecological, and partially energetic independent. Realized on a mobile pontoon, it may be commanded from distance, and powered by co-generation, with two photovoltaic (PV) panels. They assure the pontoon movement. Sludge drying is realized in a fiberglass tank, located under the PV. The dried sludge represents a natural fertilizer that can be used for de-mineralized lands, to restore their biochemical potential.

The solution has a double benefit: restoring ecologic equilibrium of the implementation areas and to assure an efficient consumption of the extracted sludge. By additional drying, the time until economic use is shortened and insects development is restricted. Only the sludge obtained as results of the lake's eutrophication is collected, generated by the putrefaction of the aquatic, newly developed vegetation, by fresh water supplying. Taking only the sludge without any therapeutic effects, the prototype assures that the active sludge maintains its parameters and needed concentrations.

The experimental solution is efficient, using renewable resources and participates at environment and agricultural lands restoration. It can be moved in different areas, the natural reservation being completely unaffected. In Figure 2 the installation and structure are schematically presented. The setup consists of three functional blocks of the collecting system, coupled to Photo-voltaic-PV panels, the system for compacting, and the system for partial drying.

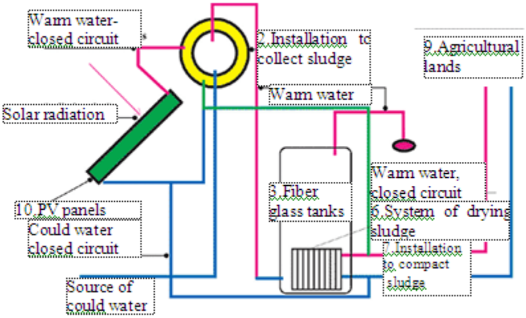

Figure 2. The prototype structure

Separately, the lakeshore commanded movement system was designed and executed, as well as the automation system to stop the pontoon when the fiber glass tank is filled with sludge, the automation system to coordinate one cycle, and finally the alimentation system from the PV panels. Between all blocks a permanently adapted to the meteorological conditions system of interconnection is realized.

The main steps in a functioning cycle are described as it follows. The prototype, placed on a mobile pontoon can advance by propulsion, commanded from the lakeshore (1). During the advance, the pump aspires sludge and sediments. The sludge is conducted directly into a compacting system (7). At a time interval, the compacting system starts and releases the sludge into a fiberglass tank (3) to be partially dried. When the tank is filled, the automation system interrupts the alimentation (2) and the pontoon stops (5). The collected and compacted sludge starts to be dried (6), due to a system of pipes, which assures warm water circulation. After being partially dried, sediments are evacuated and used as fertilizer. The fiberglass tank is placed on the pontoon, under the PV panels (10). The prototype is automatic and autonomic. After evacuation, the pontoon movement is commanded and the cycle repeats. The main prototype components:

1. PV with a storage system (Figure 3-a)

The main advantage of this system is its small weight. The system components are an Off-Grid of 1 kW with energy storage in batteries. The package contains two 500 W panels, an inverter 24V/UPS system 1000 with Controller 60 A 12-24V EP Solar, plus accessories. The modules are reliable photovoltaic panels, with great efficiency and high yield. Even with a reduced incidence of light, the module achieves a good performance and yield. Before and after lamination, each module undergoes an electroluminescence test.

(a) (b)

Figure 3. Prototype components

Performance guarantee: Up to 10 years: 90% of nominal output; Efficiency to 25 years: 80% of nominal power; the product warranty is 11 years for the photovoltaic panel. The Off-Grid inverter is a professional device, designed for harsh conditions. The inverter consumes firstly the battery power, until it reaches the minimum voltage consumption. Only then, it inverter automatically switches to the power supply. The inverter's power saving function has automatic detection of the battery options. This method saves battery capacity and consumption in standby mode. The inverter is in standby power mode, and its consumption is < 2W. Overcharging batteries is prevented because the controller will stop the charging when the full capacity is reached. The solar controller is compatible with all brands of solar modules. The controller 12V-24V 60A is suitable for gel and acid batteries. The integrated microprocessor controls the charging switching thresholds of the precise and stable temperature. The controller keeps the battery fully charged.

2. The sludge collecting system of the (Figure 3-b)

The collector is represented by a Screw Pump, with electric alimentation, an aspiration pipe of 55 mm diameter, and a flowrate of Q=25 l/min, the voltage can be of 110V or

220V. The pump can be used for pumping dirty water with sediments or sludge, Power P=0.75 kW, Hmax=40 m, being made of stainless steel. It is specially designed to aspire sediments or sludge from reservoirs, lakes, or channels bottom.

3. The Fiberglass tank (Figure 4-a)

On the deck, the sludge is deposited in a fiberglass tank, with a capacity of around 5 m^3, placed under the PV-s, realized with holes on both sides, of 2540x1960x980 mm as to assure a good deposition of the collected sludge.

4. Sludge compacting system (Figure 4-b, 4-c)

It refers to a small compression of sludge directly after it's extraction from the lake, before depositing it into the fiberglass tank. It is formed by a screw system (augers), moving through a conic portion, assuring sludge compacting.

When the tank is full, filled with partially compacted sludge the pontoon stops. At pre-selected time interval, in conformity with the atmospheric parameters and the local conditions, the compacted sludge is dried due to warm water circulation through a system of small pipelines.

A silent and environmentally friendly engine, adapted to the specific area of the Natural reservation drives the hydraulic system of the collector. The propellers for the pontoon movement prove to be durable to ensure the maximum maneuverability of the prototype, back and forth, even in shallow water.

The solar modules are directly connected to the heating element with an electrical efficiency of 99%. There is no need to use here for an inverter. The system just consists of a heating element and a control system. This saves initial costs and maintenance.

After being partially dried, the sludge is evacuated and deposited into a special sector until it will be transported to lands as fertilizer.

Besides the mentioned parts of the prototype, there are some other components which have been realized or bought. As examples the interconnections, the pontoon's distance command, fill-up sensor for the fiber glass tank, automation of the pontoon's start and stop of the, and sensors for detecting the corresponding the sludge water contents, in accordance with the atmospheric parameters (temperature, humidity).


(a) (b) (c)

Figure 4. Components of the prototype

Conclusions

The paper presents an innovative solution to collect and use the inactive sludge from the deposits from a Natural Reservation, Lake Techirghiol. The excess aquatic plants putrefaction that appeared, the developed vegetation, lead to this sludge amounts. It affects the active sludge, existing for hundreds of years, and famous for its effectiveness in treating many diseases. The sludge with health benefits is a result of bacterial decomposition of the aquatic organisms, which have completed their existence, especially of Artemia salina crustaceans and the algae living in salted water. The prototype represents a technical challenge concerning design, execution, automation, and control, in accordance with environmental conditions imposed for Natural Reservations. It represents a solution that uses renewable sources, being perfectly ecologically, without disturbing the local conditions. The solution eliminates the nutrient base that helps excess vegetation development and ensures the effective sludge use lands, as a fertilizer. The region where the lake is located is well known with less fertile soils. This sludge assures an ecologic and biologic supplement to increase the soil productivity. The elaborated database will allow further studies and research. The study aims to improve the environmental conditions, in accordance with the appropriate European standards referring to protected areas. By its functionality, the salted water quality was improved and restored the local environment. The prototype has an actual character and contains some new developed mathematical and numerical models in the realization of the technical referential. The numerical model refers to the interconnection of the formative modules. The reconstruction of the local ecological balance without using conventional fuels as not disturb the ecologic equilibrium of the reservation represents the main objective of this research (O.U.G.57). During migration, in the mentioned lake area, more than 20.000 birds of different species are present, many of them being legally protected. This solution is in accord to the Romanian reply for EU Council Directives, UE-EUCO 75/13 CO EUR 7 signed in Brussels at 22/05/2013, referring to the promotion of new solutions based on renewable technology use in the ecologic environment.

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THE SONODEGRADATION OF ORGANIC COMPOUNDS FROM INDUSTRIAL WASTEWATER

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Abstract

Removal of the organochlorine compounds from industrial wastewater by sonochemical processes was performed in order to evaluate process' efficiency. Sonochemical degradation of the following organochlorine compounds: 1,2 dichloropropane, 1,1,2-trichloroethane, 2 ethylhexanol and β, β'-dichlorodiisopropyl ether was carried out. The experiments was realized with two types of equipment: ultrasound bath UCD-150 and sonotrode UP 200 Ht.

Experimental results showed high efficient removal for all compounds: 1,1,2-trichloroethane and β, β'-dichlorodiisopropyl ether 78.0%, 1,2 Dichloropropane 66.0%, 2 ethylhexanol 35.0 % in bath ultrasound treatment after 60 minutes. Degradation of β, β'-dichlorodiisopropyl ether, 1,1,2-trichloroethane, 1,2 dichloropropane and 2 ethylhexanol performed much better for sonotrode with 14 mm diameter (89.0%, 77.5%, 73.0%, respectively 73.0%) than for sonotrode with 40 mm diameter (64.0%, 64.0%, 53.0% and 48.0%). This difference between the two probes regarding removal efficiency can be explained by different amplitudes of equipment.

Keywords: *organochlorine compounds, ultrasonic irradiation, sonochemical processes, wastewater*

Introduction

The chlorinated volatile organic compounds (Cl-VOCs) including polychloromethanes (PCMs), polychloroethanes (PCAs) and polychloroethylenes (PCEs), are a group of ubiquitous contaminants that have been widely detected in environment media in recent years. These compounds possess high volatility and strong recalcitrance to degradation, for instance, the atmosphere lifetime of carbon tetrachloride and 1, 1, 1 - trichloroethane could reach as high as 100 and 6 years, respectively, allowing them to be transported over long distances in various environment media (Nenciu & Vareanu 2014; Cohl 2015; Iordache 2017).

The ultrasound use in the water and wastewater treatment have acquired considerable attention, mostly due the extreme condition effects during the cavitation collapse. Cavitation collapse generates sites with locally very high temperatures and/or pressures for short periods of time, which are responsible for unusual sonochemical effects. It is now well established that this process is capable of providing very high temperatures (4500 – 5000^{o}K) and very high pressures (aprox. 1000 atm) in extremely short times (in the range of microseconds), thus rendering cavitation a quasi-adiabatic phenomenon (Blume 2000; Leonelli & Mason 2010; Cravotto 2015; Iordache 2017).

Since the beginning of the investigation on sonochemistry processes a lot of works have been published on ultrasound wastewater treatment. The mechanism proposed for the sonochemical degradation of organic pollutants is usually based on the formation of short life radicals generated in violent cavitation events (Suslick 1990; Visscher 2003; Iordache, M. 2009).

$$H_2O \rightarrow HO\bullet + H\bullet \tag{1}$$

The "hot spot" model was adopted to explain the sonochemical effects and results. In light of this theory the reactions caused by ultrasound irradiation of waters are heterogeneous and processes occurred due to the reactive species and heat generated during the cavitation collapse. That can by imagined as a "micro-reactor" which encompasses three areas: the cavity interior, the cavity ultrasonic gas-liquid interface and the liquid from the vicinity of the interface. The next processes are considered for destruction or decomposition of the pollutants: oxidation by hydroxyl radicals, pyrolytic decomposition and combustion and finally supercritical water oxidation conditions (Serpone 1994; Iordache 2016).

Materials and Methods

Sonochemical method

The experiments were conducted in wastewater and irradiation processes were performed using an ultrasonic baths UCD-150 type, 35 kHz, 325 W (Raypa Spain) and a sonotrode UP 200 Ht type, 26 kH, 200W (Hielscher, Germany).

A volume of 2500 mL of wastewater was transferred to the ultrasound bath. The wastewater have been irradiated for 10, 20, 30, 40, 50 and 60 minutes in the ultrasound bath.

The second set of experiments have been realized using sonotrodes with two diameters, 14 mm and 40 mm. A volume of 400 mL of wastewater was transferred into a Berzelius beakers where then was introduced the sonotrode. The wastewater have undergone to ultrasonic treatment for 2, 4, 6, 8, 10 and 12 minutes.

Analytical methods

1,2 Dichloropropane, 1,1,2 Trichloroethane, 2-Ethylhexan-1-ol, β,β'diclordiizopropilic ether concentrations were determined by gas-chromatography (GC) using flame ionization detection. The GC analyses were designed and performed according to SR EN ISO 10301:2003. The pH was measured using the electrochemical method, according to SR EN ISO 10523:2012. Determination of the chemical oxygen demand (COD-Cr) was performed according to SR ISO 6060:1996 and the chloride, according to the SR ISO 9297:2001, volumetric method.

Results and Discussion

The sonodegration experiments were carried out on industrial water (P1 and P2) containing 1, 2 Dichloropropane, 1, 1, 2 Trichloroethane, 2 Ethylhexanol, and β,β' diclordiizopropilic ether. From the analysis results shown in Table 1 it has been found that industrial wastewater is highly alkaline with a pH between 11.47 and 11.88. For the analyzed wastewater samples, the inorganic charge expressed in chlorides took values in the range of 18081.0 mg/l and 18258.3 mg/l while the organic load expressed in COD-Cr was in the range of 1094.4 mg O_2/l and 1920.0 mg O_2/l. Waste water samples were analysed by gas chromatography to determine the organochlorine compounds, and have found values between 0.444 and 0.48 mg/l for ββ'diclordiizopropilic ether, values between 0.15 and 0.64 mg/l for 1,1,2 Tricloroethane, values between 13.88 and 17.61 mg/l for 1,2 Dichloropropane, and values between 0.81 and 1.38 mg/l for 2 ethylhexanol.

Table 1. Physical and chemical characterization of industrial wastewater

Crt. No.	Polluted	U.M.	P1	P2
1	pH	Unit. pH	11.88	11.47
2	COD-Cr	mgO_2/l	1094.4	1920.0
4	Cl^-	mg/l	18081.0	18258.3
5	1,1,2 TCE	mg/l	0.64	0.15
6	1,2 DCP	mg/l	13.88	17.61
7	2 EH	mg/l	1.38	0.932
8	β β' eter	mg/l	0.444	0.48

Irradiation experiments using ultrasonic bath

Since the pH was located in the highly alkaline zone: pH 11.47 and 11.88, the pH adjustment to neutral pH with H_2SO_4 was used and the irradiation was performed using an ultrasonic baths UCD-150 type, 35 kHz. Experimental results for 1, 2 Dichloropropane (Table 2) show its degradation from the initial value of 17.61 mg/l to 6.07 mg/l in 60 minutes, which means a degradation efficiency of 66.0%. For 1,1,2 trichloroethane the initial value was 0.15 mg/l and after 60 minutes it reached 0.033 mg/l, with a removal efficiency of 78.0%, a similar removal with ββ' ether, in while removal efficiency for 2 Ethylhexanol was 35%.

Irradiation experiments using ultrasonic processor

In Tables 3 and 4 are presented the experimental results obtained during sonochemical decomposition of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using sonotrode with a diameter of 14 mm and 40 mm.
The ultrasound treatment of 1,2 Dichloropropane using sonotrodes reached satisfactory efficiency after 12 minutes. The best results were obtained using thesonotrode with small diameter (14 mm) compared to bigger diameter (40 mm). The final concentration of 1,2 Dichloropropane reached 3.8 mg/l for first experiment (14 mm) and 7.77 mg / L for second (40 mm), the efficiency is 73.0% respectively 53.0%. The experimental results for 1,1,2 Trichloroethane, showed a similar trend like for 1, 2 Dichloropropane. The efficiency removal of the 1,1,2 Trichloroethane with small diameter sonotrode (14 mm) was 77.5% while 40 mm sonotrode was 64.0 %, the difference is more evident now. The efficiency degradation of 2-ethylhexan-1-ol from waste water using sonotrode irradiation are showed in Tables 3 and 4, also. In this situation the sonotrode with the smallest diameter (14 mm) presented the best results compared to bigger one (40 mm), for which the degradation efficiency was 73.0% and 48.0%. For the ultrasound treatment of β,β'diclordiizopropilic ether, best results were obtained using thesonotrode with small diameter (14 mm) compared to bigger diameter (40 mm). The final concentration of β,β'diclordiizopropilic ether reached 0.444 mg/l for first experiment (14 mm) and 0.46 mg / L for second one (40 mm), the efficiency was 89.0% respectively 64.0%.

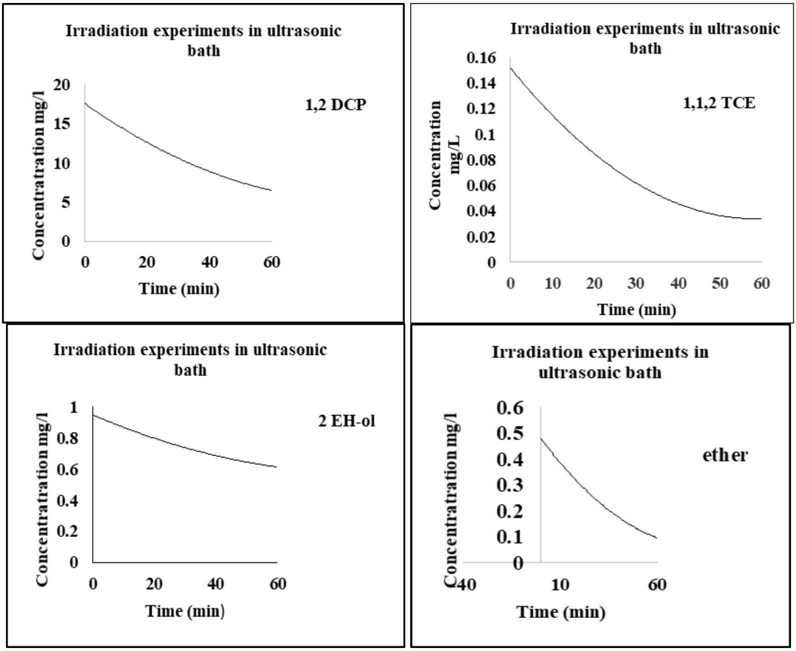

Figure 1. The evolution of concentration on sonochemical decomposition of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether

Table 2. Results obtained after irradiation 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using ultrasonic bath

Time	**pH (U. pH)**	**COD-Cr mgO$_2$/l**	**Cl^- mg/l**	**1,2 DCP mg/l**	**1,1,2 TCE mg/l**	**2 EH mg/l**	**Eter ββ' mg/l**
0	6.87	1920.0	18258.3	17.61	0.15	0.932	0.48
10	6.86	1824.0	18258.3	15.13	0.12	0.91	0.39
20	6.61	1728.0	18258.3	12.27	0.082	0.77	0.282
30	6.53	1632.0	18081.0	10.44	0.056	0.732	0.266
40	6.47	1536.0	18081.0	8.7	0.052	0.69	0.167
50	6.38	1536.0	18081.0	8.46	0.036	0.65	0.115
60	**6.31**	**1440.0**	**18081.0**	**6.0**	**0.033**	**0.61**	**0.104**

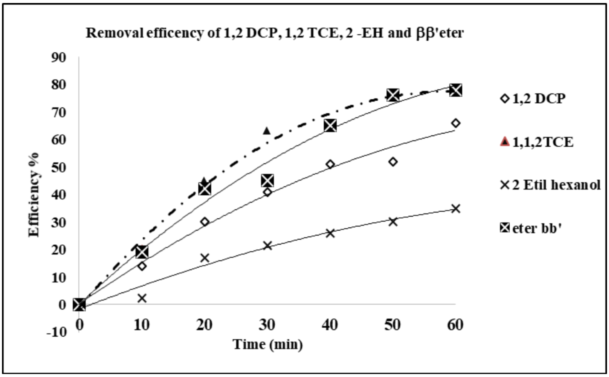

Figure 2. The evolution sonochemical decomposition efficiency of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether

Table 3. Results obtained after irradiation 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using sonotrode having a diameter of 14 mm

Time	pH (U.pH)	COD-Cr mgO_2/l	Cl^- mg/l	1,2 DCP mg/l	1,1,2 TCE mg/l	2 EtH mg/l	Eter ββ' mg/l
0	6.95	1094.4	18081.0	13.88	0.64	1.38	0.444
2	6.93	1048.8	18081.0	12.63	0.484	1.114	0.329
4	6.77	1003.2	17726.5	9.58	0.344	0.93	0.222
6	6.70	912.0	17372.0	8.35	0.267	0.746	0.148
8	6.64	866.4	17372.0	6.58	0.192	0.62	0.112
10	6.53	820.8	17372.0	5.35	0.154	0.41	0.066
12	**6.44**	**775.2**	**17372.0**	**3.8**	**0.144**	**0.37**	**0.049**

Table 4. Results obtained after irradiation 1,2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using sonotrode having a diameter of 40 mm

Time	pH (U.pH)	COD-Cr mgO_2/l	Cl^- mg/l	1,2 DCP mg/l	1,1,2 TCE mg/l	2 EH mg/l	ββ' ether mg/l
0	6.84	2016.0	18435.6	16.55	0.147	1.09	0.460
2	6.81	1920.0	18435.6	15.09	0.132	1.0	0.440
4	6.68	1824.0	18453.6	12.78	0.121	0.835	0.380
6	6.54	1728.0	18258.3	12.17	0.105	0.705	0.210
8	6.48	1632.0	18081.0	10.35	0.084	0.676	0.190
10	6.41	1536.0	18081.0	9.13	0.066	0.611	0.172
12	**6.37**	**1536.0**	**18081.0**	**7.77**	**0.053**	**0.564**	**0.167**

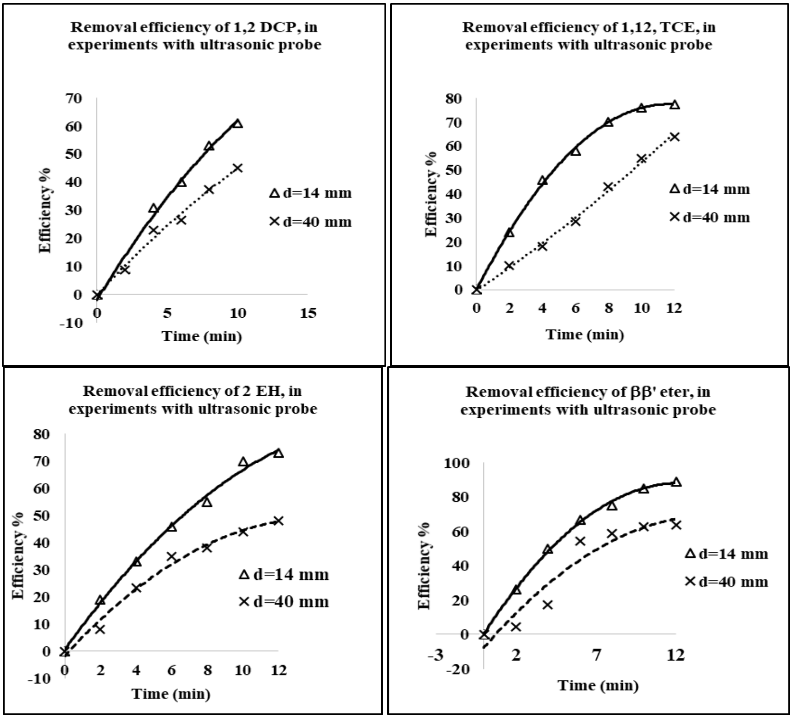

Figure 3. The evolution sonochemical decomposition efficiency of 1,2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether

Conclusions

The ultrasound degradation of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether from wastewater can be realized into a success manner using both ultrasound bath and sonotrodes. The efficiency degradation indicates good values for all components: 78.0% (1,1,2 Trichloroethane and β,β'diclordiizopropilic ether), 66.0% (1, 2 Dichloropropane) and 35.0 % (2-ethylhexan-1-ol) after 60 minutes of treatment in ultrasonic bath.

The experiments showed the best results for sonotrode with smaller diameter implicitly smaller surfaces. The explanation is the power intensity at the contact between wastewater and ultrasound irradiation surface. That imply higher amplitude and more sonochemical processes. The efficiency of β,β'diclordiizopropilic ether and 1,1,2 Trichloroethane degradation is much better with 14 mm diameter sonotrode (89.0% and 77.5%) than with diameter of 40 mm (64.0% and 64.0%). The experimental results for 1,1,2 Trichloroethane, showed a similar trend like for 1, 2 Dichloropropane. The degradation efficiency of 1,2 Dichloropropane and 2-ethylhexan-1-ol, showed a similar trend like for β,β'diclordiizopropilic ether and 1,1,2 Trichloroethane, 73.0% and 53.0% respectively 73.0 and 48.0%.

It can be concluded that sonochemical processes represents a promising technique that improves the detoxification of waters containing organic compounds especially considering the time required for detoxification (few tens of minutes) compared with conventional methods.

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POLLUTION ASSESSMENT & MANAGEMENT SYSTEMS

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ASSESSMENT OF THE ENVIRONMENTAL ASPECTS IN A CITY AREA AFFECTED BY HISTORICAL POLLUTION

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Abstract

The paper presents the results obtained by performing specific activities aimed to assess the quality of the soil and water components (surface and groundwater) in Copsa Mica, a small town from Romania, well known for the historical pollution recorded over several decades. It is known that the contamination was induced by the industrial activities carried out in the area, which is caused by sulfur dioxide air emissions and atmospheric particulate matters containing heavy metals, mainly cadmium, lead and zinc. The pollution of the city and the neighboring areas was mainly due to activities of two companies: SC Sometra SA (with a non-ferrous metallurgy profile, which before 1990 was considered the largest unit in the country) and SC Carbosin SA (with a chemical profile until its closing, in 1993). The assessment of the quality level of the environmental factors was carried out in 2016 through specific activities for soil and water quality investigation - sampling and physico-chemical analysis in R&D Institute for Industrial Ecology ECOIND laboratories, in order to highlight relevant elements of environmental quality of the above mentioned year, within a pre-established experimental field and targeting the limited area of the Copsa Mica city. As an important aspect, it is worth mentioning that the footprint of the pollution sources is still present in the area, even long after their activity has ceased. It is estimated that a soil and water monitoring could establish a dynamics of the quality parameters in the Copsa Mica area during the subsequent periods.

Keywords: *assessment, environment quality, heavy metals, pollution*

Introduction

Industrial polllution has been and continues to be a major factor causing the degradation of the environment (Muntean 2010). Copsa Mica city is located in the North-West of Sibiu County, at the confluence of the Tirnava Mare river with Visa. Crossed by DN14, the city is located 43 km from the county seat, 12 km from Medias and 33 km from Blaj on DN 14B (Szanto 2011). The city is bordered by Bazna commune and resort, to the North-East by Tirnava commune and Medias municipality, by the commune of Valea-Viilor to the East, by the Axente Sever commune to the South and the Micasasa commune to the West. The city is located in the depression corridor of the Tarnava Mare River, surrounded by hills (Figure 1).

The city of Copsa Mica is well known for the historical pollution induced by the industrial activities carried out in the area (over 60 years) which is attributed to gaseous emissions containing sulphur dioxide and atmospheric particulates containing heavy metals, mainly Cd, Pb and Zn. (Lacatusu 2010).

The ecological importance of the presence of heavy metals in urban soils is closely related to human health due to their high ecological transference reported as an indicator of urban environmental quality (Stanescu 2016). Recent studies underline the importance of the correlation between the state of terrestrial ecosystems and groundwater, considering that one of the basic principles in this field is based on groundwater protection policy against pollution and deterioration, as included in EU Water Framework Directive 2000/60 EC and Directive 2006/118/EC (Scradeanu 2016).

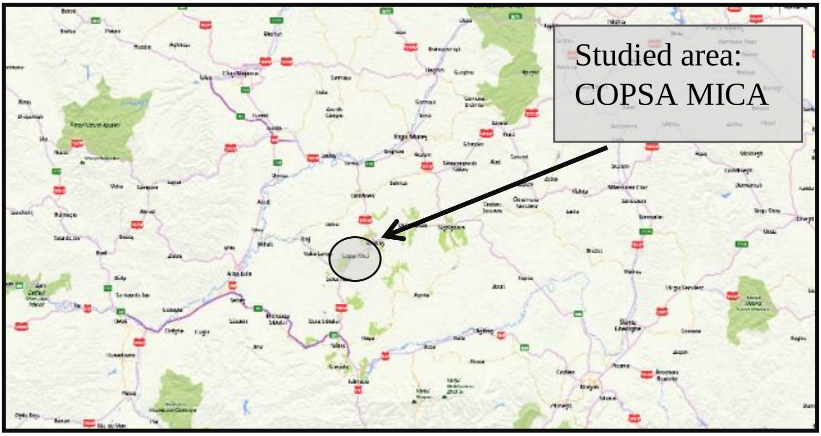

Figure 1. Localization of the studied area – Copsa Mica City

The pollution of Copsa Mica and neighboring areas was mainly due to two companies: SC Sometra SA with a non-ferrous metallurgy profile, which before 1990 was considered the largest unit of this type in the country and, until 1993, SC Carbosin SA, with a chemical profile.

Important issues were revealed by field visits in 2016 that highlighted the following:
- the current pollution sources are limited to heavy road traffic on DN14, a rehabilitated road in recent years, which has traffic values that can reach 30000 vehicles / 24 hours and sporadic activity and much diminished at SC SOMETRA SA, whose activity is regulated from the point of view of environmental protection;
- the only source of drinking water in the city is the underground water, provided by a public wells network distributed throughout the city. The water from the Copsa Mica water supply network is not used for drinking;
- the waste water in the city is cleaned in a station that is neither modern nor performant;
- public green areas in the city are numerous and have a neat look.

Experimental part

The soil quality survey in Copsa Mica consisted of sampling soil from an experimental field with an extended spatial distribution throughout Copsa Mica and beyond its limits to a distance of about 6 km. A total of 20 soil samples were taken from depths of 0-10 cm and 30-40 cm, resulting in a total of 40 soil samples. Hand-operated soil sampling equipment produced by the Eijkelkamp company was used. The GPS tracking equipment used is a Garmin portable GPS receiver, the GPSmap 60CSx. The location distribution of the sampling points is shown in Fig. 2.

For each soil sample, the following quality indicators: pH, humus, sulphates, phenols and heavy metals (Pb, total Cr, Cu, Zn, Fe, Cd, Mn, Ni, As).

The investigation of the groundwater quality in Copsa Mica consisted in the sampling activities according to of the distribution of fountains throughout the city of Copsa Mica and 2 distribution points (named "Cismea" 1 and 2). A total of 9 groundwater samples were taken, with the reference that for points F7 and F8 the underground water is captured, stored and pumped into two distribution points, locally identified as "Cismea".

For each water sample, the following quality indicators: pH, nitrates, conductivity, sulfates, phenols, oxidation and heavy metals (Total Chromium, As, Ni, Cu, Zn, Cd, Fe, Pb, Mn, Ni) were analyzed in the R&D Institute for Industrial Ecology ECOIND laboratories using the standardized test methods.

Figure 2. Distribution of sampling points (soil and water) – Copsa Mica City

Results and Discussion

Interpretation of the results of the laboratory tests made for the 40 soil samples taken from Copsa Mica, Sibiu county was done by comparison to the reference values of the Order 756 1997, respectively the reference values for chemical soil traces in soil for sensitive land use. Sensitive use is defined by Article 8 paragraph a) from the above mentioned regulation:

"Sensitive land use is represented by their use for residential and recreational areas, for agricultural purposes, as protected areas or restricted sanitary areas as well as the areas of land forecasted for such uses in the future."

The evolutions of some relevant quality indicators for the industrial activities carried out in the area of Copsa Mica are graphically presented below:

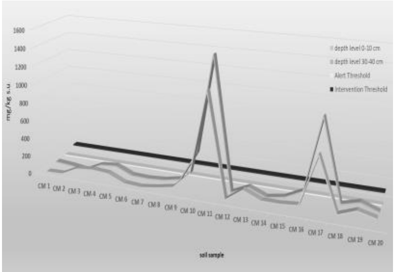

Figure 3. "Lead" content in soils samples from Copsa Mica

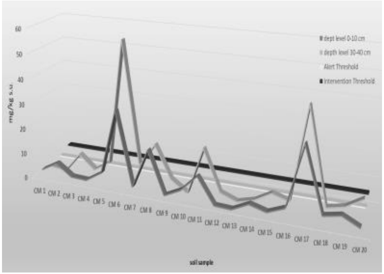

Figure 4. "Cadmium" content in soils samples from Copsa Mica

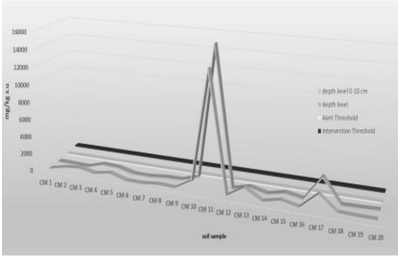

Figure 5. "Zinc" content in soils samples from Copsa Mica

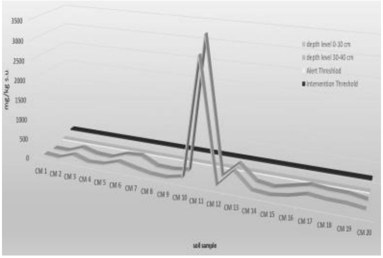

Figure 6. "Copper" content in soils samples from Copsa Mica

There are a number of negative aspects regarding the soil quality, which mainly consist in the frequent exceeding of the intervention threshold. An extremely unfavorable situation was recorded at sample "CM 11", located near DN14B, at approx. 700m in the South direction of the dumps of SC Sometra SA, which is the potential source of pollution with heavy metals. A general conclusion for the soil environmental component can be formulated as follows: the soil is still affected by the residual pollution of historical nature, induced by the industrial activities carried out in the area that had a significant impact on the environment.

The groundwater quality investigations, respectively 9 groundwater samples taken from the Copsa Mica area led to results that were interpreted by comparison with the reference values of drinking water quality (Law 458 2002).

The evolutions of some relevant quality indicators for underground water in the Copsa Mica area are graphically presented in figures 7 to 10.

This shows that the underground water supply in the analyzed area is not affected by the pollution identified in the case of soils, and under these conditions the groundwater can be considered much better in qualitative terms.

Interpretation of the results of the tests performed for the two samples of surface water taken from the area of Copsa Mica, respectively from the Visa and Tarnava Mare River, was performed using reference values according to Order 161 2006.

Analyzing the obtained results, it is obvious that both water bodies analyzed correspond to a "very good" ecological status, with one exception, respectively the "Ni" quality indicator whose values impose the "good" ecological status.

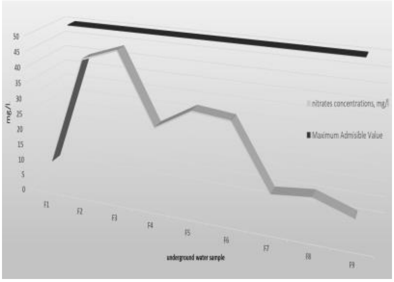

Figure 7. "Nitrates" content in underground samples from Copsa Mica

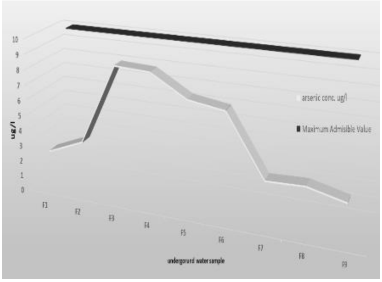

Figure 8. "Arsenic" content in underground water samples from Copsa Mica

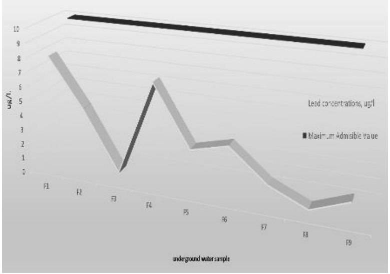

Figure 9. "Lead" content in underground water samples from Copsa Mica

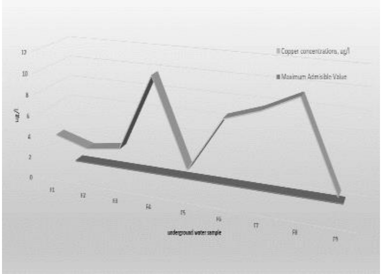

Figure 10. "Copper" content in undreground water samples from Copsa Mica

Conclusions

The project aimed to investigate the quality of the environmental components of soil and water (surface and underground water) in the Copsa Mica, a small city, known for the historical pollution recorded over several decades.

Specific soil and water quality investigations were conducted in 2016 in order to highlight the evolution and dynamics of environmental issues in a highly anthropic and polluted area (historical pollution). The experimental field will be used to highlight dynamic evolution starting from the baseline identified in 2016.

The conduct of several investigative campaigns within the proposed experimental field will create clear premises for obtaining a solid database regarding the quality of the environmental components and the evolution and dynamics of the environmental aspects for Copsa Mica, as the activities are in progress in 2017.

Acknowledgements

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ASSESSMENT OF WATER AND SEDIMENT CHARACTERISTICS OF THE NORTHERN DANUBE DELTA LAKES - MATIȚA, BABINA AND MERHEI, ROMANIA

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Abstract

At the end of its course of 2857 km running to the Black Sea, the Danube River - the longest river in the European Union shapes a river delta, an exclusive area consisting of a complexity of water and land, numerous lakes, ponds, marshes and unique waterways. The Danube Delta, considered the Europe's largest wetlands, is included in Unesco's World Heritage list, due to its outstanding importance conferred by the many natural habitats with their specific characteristics and bio diversities, preserved in a near pristine state. Even though considerable conservation efforts have been made lately, the Danube Delta is still subject to threats due to both natural and anthropogenic stressors that may alter its ecosystems. This study aims to investigate the water and bed-sediment general characteristics of some lakes from the Matița - Merhei Depression located in the fluvial delta plain, to assess the current quality status of water and sediments. A significant number of water and sediment samples were collected from each lake in October 2016, for determination of water physical-chemical parameters, lithological components and some heavy metals - analysed in random bed-sediment samples. The investigation results show that the water environment-related indicators fluctuated in terms of sampling sites and generally agreed with the Romanian environmental quality criteria. Average lithological composition of the bed-sediments indicates an autochthonous source for the recent accumulation of sediments. Overall, the technophyllic heavy metal concentrations of the bed-sediments were below the limits of the quality criteria. The exceptions were represented by local values, incidentally exceeding the recommended limit.

Keywords: *assessment, bed-sediments, environment, physical-chemical, surface water*

Introduction

The Danube Delta is mainly located in Romania, with sectors in Ukraine. The delta is developed and elaborated at the Danube River mouth, by the division of the three river branches that flows into the Black Sea. The deltaic edifice is divided into three main depositional systems: the delta plain, the delta front, and the pro-delta.

The delta edifice integrates two main compartments: the upper fluvial delta plain located on the west side, and the lower fluvio-marine delta plain that is evolved on the east side, and up to the Black Sea coastline. These units are partitioned by the initial littoral ridge: Jibrieni-Letea-Răducu-Ceamurlia-Caraorman-Sărăturile-Perișor-Lupilor (Panin 1996). The importance of the Danube Delta as Europe's largest remaining natural wetland derives from inestimable habitats for wetland wildlife and biodiversity, so it was conferred a triple international protected area's statute - Biosphere natural reserve (as part of the Man and Biosphere Programme), a World Wildlife Heritage Site accredited by UNESCO and a Wetland of International Importance (since 1990 as reported by Wetland Convention Ramsar). The Danube Delta acts as an environmental buffer zone between the Danube River and the Black Sea, filtrating the potential contaminants derived from changes as a result of uncontrolled past and current practices related to urban run-off and agricultural waste-water discharges at the upstream countries that influence the flow in the downstream region. To the same extent, the Danube Delta environment would be impinged by the ecological changes that occur in the Delta itself. As a result of these changes, it becomes essential to study the actual current quality status of its aquatic ecosystems. The lakes selected for this study, namely Matita, Babina and Merhei, belong to the Matita-Merhei Depression, one of the largest lake systems, which covers an area of 5700 ha (including 108 shallow lakes), being located in the fluvial Danube Delta plain. Matita (652 ha), Babina (338 ha) and Merhei (1057.5 ha) are the widest lakes from this depression (Gastescu et al. 2008). The purpose of this paper is the assessment of the physical-chemical characteristics of water and sediments from Matita, Babina and Merhei lakes.

Materials and Methods

Study Area and Sampling Stations

The Matita-Merhei Depression represents one of the largest lake systems in the Danube Delta being located between Chilia and Sulina arms, in the central region of the Letea fluvio-marine grind (Letea Island – sandy areas with dunes). The natural and artificial hydrographic network of inlets and canals is defined by Eracle, Lopatna, Dovnica, Raducu, Bogdaproste, Sulimanca and Rosca (Bondar et al. 2001). These lakes (*i.e.,* Matita, Babina and Merhei) belong to the category of lakes with a large aquatorium and relative active changes of waters, including a secondary hydrographic network, too. The great distance from the lakes to the Danube River arms led to the poor water circulation of these lakes. Even if they are geographically closely located one to each other, the Babina Lake, for instance, is situated in an area with a relatively active circulation of water, in comparison to Matita and Merhei lakes that are situated in an area affected by poor water circulation, specifically during the summer and autumn months, due to the low water levels (Gastescu et al. 2008). To some extent, the poor water circulation is also influenced by the siltation, a specific phenomenon that occurred within deltaic areas, and the abundant aquatic vegetation that both reduce and determines an impediment to some specific natural function as the water circulation of these lakes. Anywise, there are several waterways that provide the inputs and outputs into/from the Matita-Merhei complex:
Lopatna Stream, Eracle Canal, Radacinoasele Canal (NW of Babina L.), Stipoc Canal (W of Babina L.), Canal to the Miazazi Lake (S of Matita L.), Lopatna Canal (N of Matita L.) and the Suez Canal (NE of Matita L.).

Sample collection and analysis

The field measurement activities were performed aboard the"Istros" RV owned by the National Research and Development Institute for Marine Geology and Geoecology – GeoEcoMar, Romania. For the purpose of this study, 49 sampling sites (Figure 1) monitored during October 2016 were selected. A part of water quality variables were measured *in situ* at the sampling points (*i.e.*, depth, temperature, transparency, dissolved oxygen, pH, electrical conductivity etc.). After collection, the remaining *ex situ* water variables (*i.e.*, total dissolved solids, turbidity, nitrates, nitrites, orthophosphates, sulphates etc.), were promptly measured and analysed with portable sensors -WTW Multiline P4 Multiparameter, HACH 2100Q, HACH 5000 - UV-Vis – Spectrophotometer. The water and sediment environment-related indicators were mainly related to the Romanian environmental quality criteria (Order 161/2006, STAS 6323 – 88, Order 756/1997), but has also consulted other international environmental standards.

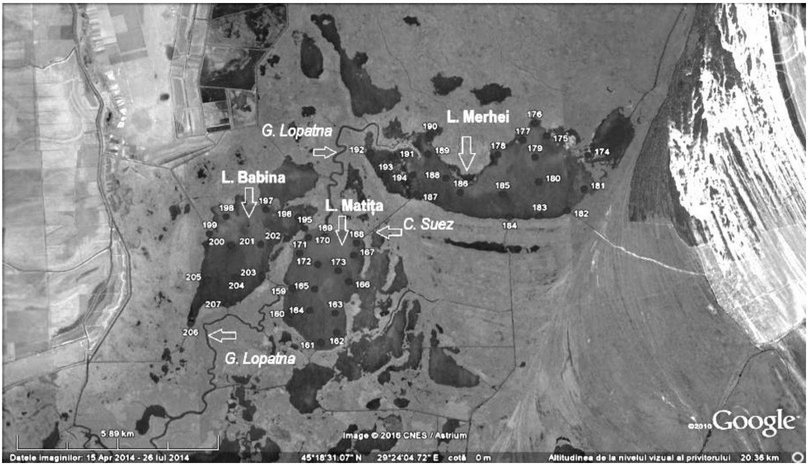

Figure 1. Map of the sampling sites of the study area

For sampling the bed-sediments (the upper layer – 0-20 cm of the sediment-water interface) was used a Van-Veen grab sampler. Determination of dry matter residue (% DM) and water content (% WC) were performed gravimetrically by the classical laboratory Loss On Drying (LOD) method. Loss On Ignition (LOI) analysis was used to assess the total organic content (% TOM), carbonates (% CAR) and siliciclastic fraction (% SIL) of bed-sediment samples (Dean 1974; Heiri et al. 2001; Santisteban et al. 2004). The distribution of some selected major, minor and trace elements (Fe_2O_3, TiO_2, Rb, Sr, Zr and V) was estimated in random bed-sediment samples by X-ray fluorescence spectrometry on a VRA – 30 XRF sequential spectrometer, fitted with an X-ray tube with chromium anode, directly on compacted powders. An analyser crystal LiF 200 was utilized to select the characteristic wavelengths, measurements being done with a Na (Tl) J scintillation detector. Titration methods were applied to determine CaCO3 (Black 1965) and TOC - total organic carbon (Gaudette et al. 1974). MnO, Cr, Zn, Ni, Co, Cu and Pb were tested by flame atomic absorption spectrometry and Cd by electro-thermal atomic absorption spectrometry on a Pye Unicam SOLAAR 939E double beam absorption spectrophotometer with deuterium lamp background correction.

Results and Discussion

Water characteristics

The physical and chemical characteristics of water samples from three lakes of the Matita-Merhei unit are shown in Table 1. The investigation results show that the water environment-related indicators fluctuated in terms of sampling sites and generally agreed with the Romanian or international environmental quality criteria. Water variables did not show significant variation among the three lakes. For example, the thermal regime and water acidification present normal values. The water temperature exhibited normal values that were consistent with seasonal climate variations encountered during the wet season. So, the mean value was quite similar in the three lakes as Matita (10.83^{o}C), Merhei (9.54^{o}C) and Babina (9.65^{o}C). The pH values in surface water varied from neutral to slightly alkaline. The dissolved oxygen content concentration displays the highest mean value (8.85 mg/l) in Matita Lake, while the lowest mean value was noticed in Babina Lake (7.59 mg/L). Some variations were noticed in nutrient regimes of investigated lakes.

For instance, the $N\text{-}NO_3^-$ concentration in all investigated surface water samples show values below the limit values established for Class I (Order 161/2006). Instead, some water samples gathered from all lakes showed that the $N\text{-}NO_2^-$ concentration exceeding the limit value settled for Class I and II according to limit values (Order 161/2006). The same tendency is also valid for $P\text{-}PO_4^{3-}$, observing elevated values in most of the samples exceeding the limit value settled for all quality classes as reported by environmental reference (Order 161/2006). Electrical Conductivity (EC) mean value increases from Matita Lake to Babina Lake and ranged between 388.27 μS/cm to 489.31 μS/cm. TDS indicator exhibited the highest mean value (244.65 mg/L) in Babina Lake, while the lowest mean value was recorded in Matita Lake (194.13 mg/L). For SO_4^{2-} were recorded values situated below the limit values established for Class I (Order 161/2006). The turbidity indicated values in the range of 1.55 mg/l and 13.3 mg/l, exhibiting the highest mean value (5.94 mg/l) in Matita Lake, while the lowest mean value was recorded in Merhei Lake (3,65 mg/l). The Total Suspended Substances (TSS) levels in tested samples were in line with the maximum permissible level for TSS in the freshwater environment. The SiO_2 content recorded values in agreement with the range of variation in natural waters (5 – 25 mg/L).

Sediment characteristics

The physical and chemical characteristics of the bed-sediments collected from three lakes (Matita, Merhei and Babina) of the Danube Delta are shown in Table 2.

The lithological analyses as content based on the total organic matter content (% TOM), the total carbonate content (%CAR) and siliciclastic fraction (% SIL) showed significant fluctuations among the three ecosystems. An overall assessment of the composition of lake sediments can be done according to the weight percentages TOM (%), CAR (%) and SIL (%), figured by the total weight of dry sediment (G. van der Veer 2006).

Table 1. The physical – chemical parameters of water characteristics collected from Matita, Merhei and Babina lakes

	The physical-chemical parameters							
MATITA Lake	Value	**Temp. (ºC)**	**pH (units)**	**O_2 (mg/l)**	**O_2 (%)**	**N-NO_2^- (mg/l)**	**N-NO_3^- (mg/l)**	**P-PO_4^{3-} (mg/l)**
	min	10.4	7,8	7,52	68	0,007	0,02	0,08
	max	11.5	8,34	9,22	82,8	0,031	0,09	1,77
	mean	10.83	8,09	8,85	79,03	0,018	0,04	0,96
	Value	**EC (µS/cm)**	**TDS (mg/l)**	**SO_4^{2-} (mg/l)**	**Turb (NTU)**	**TSS (mg/l)**	**VDS (m)**	**SiO_2 (mg/l)**
	min	368	184	26	2,36	5	0,7	0,47
	max	455	227,5	31	11,1	17	1,75	4,07
	mean	388,27	194,13	28,67	5,94	11	1,14	2,54
	The physical-chemical parameters							
MERHEI Lake	Value	**Temp. (ºC)**	**pH (units)**	**O_2 (mg/l)**	**O_2 (%)**	**N-NO_2^- (mg/l)**	**N-NO_3^- (mg/l)**	**P-PO_4^{3-} (mg/l)**
	min	8,7	7,95	7,42	66,8	0,007	0,01	0,05
	max	10,9	8,68	10,4	91,2	0,024	0,03	1,76
	mean	9,54	8,43	8,83	76,13	0,017	0,02	0,67
	Value	**EC (µS/cm)**	**TDS (mg/l)**	**SO_4^{2-} (mg/l)**	**Turb (NTU)**	**TSS (mg/l)**	**VDS (m)**	**SiO_2 (mg/l)**
	min	372	186	23	1,91	5	0,5	0,39
	max	535	267,5	34	6,15	8	1,25	3,89
	mean	439,71	219,86	28,25	3,65	6,14	0,85	1,72
	The physical-chemical parameters							
BABINA Lake	Value	**Temp. (ºC)**	**pH (units)**	**O_2 (mg/l)**	**O_2 (%)**	**N-NO_2^- (mg/l)**	**N-NO_3^- (mg/l)**	**P-PO_4^{3-} (mg/l)**
	min	9,3	7,65	5,74	52,3	0,007	0,01	0,06
	max	10,6	8,44	8,61	74,5	0,054	0,30	0,82
	mean	9,65	8,15	7,59	66,09	0,023	0,08	0,21
	Value	**EC (µS/cm)**	**TDS (mg/l)**	**SO_4^{2-} (mg/l)**	**Turb (NTU)**	**TSS (mg/l)**	**VDS (m)**	**SiO_2 (mg/l)**
	min	403	201,5	18	1,55	1	0,3	1,13
	max	699	349,5	37	13,3	17	1,25	10,08
	mean	489,31	244,65	31,13	5,03	6,38	0,80	3,24

Also, an empirical classification of lake sediments based on the percentage of the carbonate content was taken into consideration (De Bakker & Schelling 1989). Thereby, the TOM (%) showed highest mean concentration, over 50 % of the total weight of dry sediment, as in the Merhei Lake (84.27 %) and Babina Lake (79.77 %), while the lowest mean value was noticed in Matita Lake (62.48 %).

Table 2. The physical – chemical parameters of water characteristics collected from Matita, Merhei and Babina lakes

	Distribution of the main lithological parameters in bed-sediments					
MATITA Lake	Value	**TOM** %	**CAR** %	**SIL** %	**WC** %	**DM** %
	min	30,86	7,89	9,60	23,53	28,69
	max	78,77	38,36	56,14	71,31	76,47
	mean	62,48	16,68	20,84	34,93	65,07

MATITA Lake	Distribution of major constituents in bed-sediments								
	Value	**$CaCO_3$** %	**TOC** %	**Fe_2O_3** %	**TiO_2** %	**MnO** %			
	min	9,83	3,02	2,14	0,18	0,059			
	max	49,89	6,5	4,09	0,85	0,092			
	mean	32,79	4,98	2,81	0,40	0,08			
	Distribution of heavy metals in bed-sediments								
	Value	**Zn** µg/g	**Ni** µg/g	**Cr** µg/g	**V** µg/g	**Co** µg/g	**Pb** µg/g	**Cu** µg/g	**Cd** µg/g
	min	31,2	18,2	21,5	20	2,44	7,51	12,99	0,109
	max	47,3	25	56,6	97	6,57	13,24	25,23	0,152
	mean	39,90	22,38	33,33	47,75	4,14	10,15	18,63	0,13
MERHEI Lake	Distribution of the main lithological parameters in bed-sediments								
	Value	**TOM** %	**CAR** %	**SIL** %	**WC** %	**DM** %			
	min	24,11	0,11	1,34	12,89	77,65			
	max	98,55	13,10	63,76	22,35	87,11			
	mean	84,27	5,91	9,82	18,54	81,46			
	Distribution of major constituents in bed-sediments								
	Value	**$CaCO_3$** %	**TOC** %	**Fe_2O_3** %	**TiO_2** %	**MnO** %			
	min	13,95	1,19	1,83	0,12	0,056			
	max	35,56	7,13	3,48	0,62	0,094			
	mean	24,35	5,51	2,46	0,32	0,07			
	Distribution of heavy metals in bed-sediments								
	Value	**Zn** µg/g	**Ni** µg/g	**Cr** µg/g	**V** µg/g	**Co** µg/g	**Pb** µg/g	**Cu** µg/g	**Cd** µg/g
	min	22,9	13,7	19,9	14	1,35	4,28	9,1	0,053
	max	47,1	34,8	52,4	79	8,18	15,39	16,61	0,238
	mean	32,36	20,84	28,78	39,20	3,78	8,96	12,30	0,12
BABINA Lake	Distribution of the main lithological parameters in bed-sediments								
	Value	**TOM** %	**CAR** %	**SIL** %	**WC** %	**DM** %			
	min	60,46	1,46	6,07	11,30	68,49			
	max	88,62	15,37	34,93	31,51	88,70			
	mean	79,77	8,32	11,90	19,97	80,03			
	Distribution of major constituents in bed-sediments								
	Value	**$CaCO_3$** %	**TOC** %	**Fe_2O_3** %	**TiO_2** %	**MnO** %			
	min	8,5	3,25	2,52	0,21	0,047			
	max	39,43	7,36	6,15	0,94	0,132			
	mean	19,31	5,95	4,33	0,56	0,09			
	Distribution of heavy metals in bed-sediments								
	Value	**Zn** **µg/g**	**Ni** **µg/g**	**Cr** **µg/g**	**V** **µg/g**	**Co** **µg/g**	**Pb** **µg/g**	**Cu** **µg/g**	**Cd** **µg/g**
	min	45,4	28,3	27,1	19	3,73	10	26,38	0,236
	max	110,2	49	116,8	111	13,36	19,17	51,29	0,72
	mean	72,84	37,58	83,72	81,80	8,14	13,69	37,54	0,41

Withal, the CAR (%) content showed higher mean concentrations, over 1 % of the total weight of dry sediment, as in the Matita Lake (16.68 %) and Babina Lake (8.32 %), while the lowest mean value was recorded in Merhei Lake (5.91 %). What remains is attributed to SIL (%) fraction, that showed higher mean concentration in Matita Lake (20.84 %) and Babina Lake (11.90 %), while the lowest mean value was reported in Mehei Lake (9.82 %). On the basis of the obtained results it can be asserted that the sedimentary accumulations of these recent sediments within the three ecological sites (*i.e.*, Matita, Merhei and Babina) belong to the category of organic sediments (rich and very rich in organic matter), subsequently followed by organic-mineral sediments, and a noticeable higher carbonate content, too. The results mentioned in Table 2 show the concentration of the major constituents and heavy metals in bed-sediment samples collected from three lakes. Generally, the technophyllic heavy metal concentrations (Ni, Cu, Pb, Zn and Cd) of the bed-sediments were below the limits of the quality criteria. The exceptions were represented by local values, incidentally exceeding the recommended limit. So, Ni, Cu, Pb, Zn and Cd exhibited the highest mean concentration in Babina Lake (37.58 μg/g, 37.54 μg/g, 13.69 μg/g, 72.84 μg/g and respectively 0.41 μg/g) and Matita Lake (22.38 μg/g, 18.63 μg/g, 10.15 μg/g, 39.9 μg/g and respectively 0.13 μg/g), while the lowest mean value was recorded in bed-sediments collected from Merhei Lake (20.84 μg/g, 12.3 μg/g, 8.96 μg/g, 32.36 μg/g and respectively 0.12 μg/g).

Conclusions

The water and sediment quality deterioration is one of the most important environmental challenges currently facing around the world, originated mainly by several types of anthropogenic sources. This study shows that Matita, Merhei and Babina Lakes's water exhibit overall, normal values for oxygen content, electrical conductivity levels, total dissolved solids concentration, sulphates content, total suspended solids and silica content. Slightly pH elevated values indicate the slightly alkaline character of lacustrine water. The analysis shows that turbidity, nitrite nitrogen and orthophosphates were above the permissible limits in some investigated water samples. Probably, the slightly elevated turbidity values in some water samples and for a short period of time not be significant. Generally, increases in nitrate and phosphate levels can affect the algae blooms. Causes of water quality impairment may be due to inorganic nitrogen and phosphorus from anthropogenic sources (*i.e.*, fertilizer run-off) or, as a result of nutrient dynamics in lakes (remobilisation of nitrogen and phosphorus from lacustrine sediments).

Like freshwater, the aquatic sediments are an important natural resource, constituting an important compartment in the energy flux (bio-geo-chemical cycle) of aquatic ecosystems, but their quality could be impaired by several anthropogenic activities. The complex nature of lacustrine deposits is a result of numerous sediment sources originated from autochthonous (in-lake processes) and allochthons input, and different depositional and post-depositional processes generated by natural or human-related factors. The lithological analysis allowed to reveal a category of organic sediments (rich and very rich in organic matter), subsequently followed by organic-mineral sediments, and a noticeable higher carbonate content, too. Probably, the in-lake hydro-sedimentological processes of these standing waters have a considerable role in terms of the influx of autochthonous material contrary to allochthons material. Sediment quality has been acknowledged as an important indicator of water contamination. Sediments act as a repository and a source of contaminants (*i.e.*, heavy metals) in the aquatic environment, having a role in the migration and retention of potentially hazardous materials. The concentration of technophyllic heavy metals in the bed-sediments of different ecological sites from Matita-Merhei Depression were below the limits of the quality criteria. The exceptions were represented by local values, incidentally exceeding the recommended limit. The fluctuations encountered within this investigation are most likely due to local hydro-sedimentological actual conditions of three ecological sites as, sampling stations, seasonal changes in the water budget through hydrological network etc. that impact incidentally the water and sediment conventional variables. Generally speaking, it should not be omitted either the siltation process that constitutes one of the most important problems in deltaic lakes that could also be responsible for the degradation of the water and sediment lake's quality. Favourable conditions such as the position of lakes in the Danube Delta, high alluvial content, water regime of the Danube River, morpho-hydrographic conditions, abundant aquatic vegetation, include the danubian lakes in the category of lakes susceptible to progressive colmatation (long-term changes in the delta).

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EXPERIMENTAL MODELS OF CHARACTERIZATION AND ANALYSIS OF INDUSTRIAL WASTE

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Abstract

In the present paper we report, a series of experimental characterization and analysis models that can be applied to industrial waste samples in order to determine the heavy metals within them. During our studies we determined that both preparation and pretreatment of the waste sample are the two most important steps in the analysis process. Therefore, an increased attention was given in using appropriate procedures and methods for preparation and pretreatment. In order to ensure a correct and secure analysis were developed experimental models based on preparation and pretreatment stages and also on organic matrix decomposition method (digestion process with acid mixture under microwave). These experimental models were tested on a series of wastes coming from processing and finishing activities of metal surfaces and other materials. Metal concentration was analyzed by AAS (atomic absorption spectrometry) and XRF (X-ray fluorescence spectrometry). The obtained results proved that the proposed experimental models are suitable for analysis of different types of industrial wastes samples.

Keywords: *experimental models, heavy metals, industrial waste, microwave digestion*

Introduction

Knowing the waste composition is extremely important because based on it and depending on the waste nature and the hazardous substances content, the environmental contamination degree could be highlighted (Haţegan 2013; Guta et al. 2013). Also, knowing waste composition is important from a managerial point of view, which consists in collecting, transporting, capitalizing and waste disposal activities, as well as in terms of recycling, reuse or treatment (Arama et al. 2015; Arama & Kim 2016). It is well known that pollution of the natural environment with heavy metals is a universal problem because these metals are not biodegradable and many of them have toxic effects on living organisms and implicitly on human health (Zeng et al. 2016). Considering that most metal analysis techniques allow their determination in aqueous solution, the greatest difficulty and complexity of metal waste analysis is to bring them into a liquid form as an aqueous solution, given that each waste is different depending on the activity or product from which it was generated.

Currently they are many waste categories for which are no available methods of characterization, processing and, implicitly, heavy metal content analysis.

Given the current legislative tasks (Law 21 /2011; GD 856 2002; GD 34 /2005; GO 95 2005; GD 1061 2008), frequent requests come from those who own and / or manage wastes, regarding their characterization in order to determine the hazardous / non-hazardous character and further including them on waste list, filing the transport forms as well as to determine the type of deposit in which a waste can be accepted (Guta et al. 2013). All this steps involve primarily analytical determinations of waste specific quality indicators, hence the importance of the laboratory analysis quality made on wastes (Puiu & Cruceru 2016). Equally important is to carry out a correct sampling process and all preliminary operations of the actual waste analysis (packing, storage, preservation, transport, pretreatment etc.) (Stenvall et al. 2013; Dahlén & Lagerkvist 2008; Van der Sloot & Kosson 2012; Musee et al. 2008; Guta et al. 2013). In the literature there are presented a series of preparation methods for waste samples in order to determine the heavy metals from them, such as digestion in open systems and closed systems (Mester & Sturgeon 2003; Qi et al. 2007; Nóbrega & Donati 2011; Ramanathan & Ting 2015), combustion (Flores et al. 2007), ultrasonic extraction and solvent dilution (Nelson et al. 2015; Mello et al. 2012).

The paper presents two experimental models for the characterization and analysis of industrial wastes and their application for wastes samples preparation and pretreatment in order to determine heavy metals such as Cu, Zn, Ni and Pb. The study investigated the efficiency of the microwave digestion method by the variation of the oxidation agents and a comparative analysis of waste analysis by AAS and XRF.

Materials and Methods

The experimental characterization and analysis models were developed based on a series of sample characterization standards (ASRO 2009; ASRO 2013a; ASRO 2013b) and on an analysis protocol used to determine a waste total composition of by analyzing its components and constituents (Hennebert et al. 2013).

This protocol allows the user to obtain adequate information about organic and mineral substances contained within the waste and in the same time the determination of their properties in order to comply with the regulations in force or to ensure the recyclation process.

In Figure 6 and Figure 7, are given two models of preparation and characterization applicable on solid waste and solid-liquid mixture.

Due to the fact that each waste sample analysed was different we were able to consider them as unique tests. Therefore these models had to be adapted to the origin and composition of each individual waste. The models that were described above were applied to four wastes coming from processing and finishing activities of metal surfaces and other materials. The selected waste samples were solid (three of them) and semi-solid (one of them), their description (Figure 8) is given below:

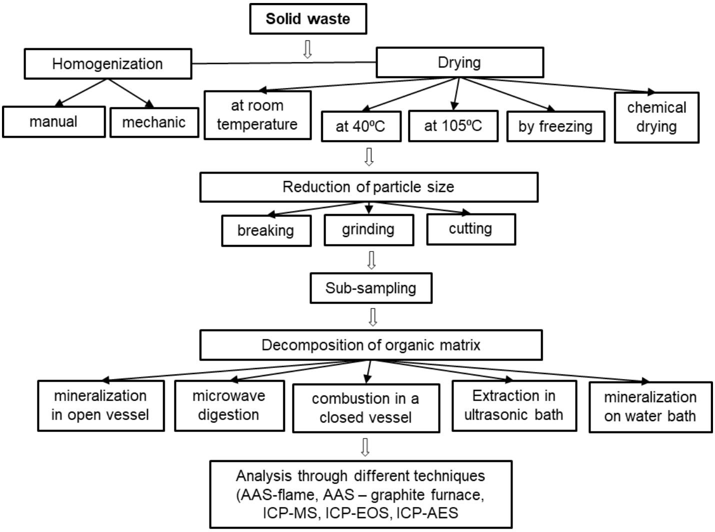

Figure 6. Solid waste characterization scheme

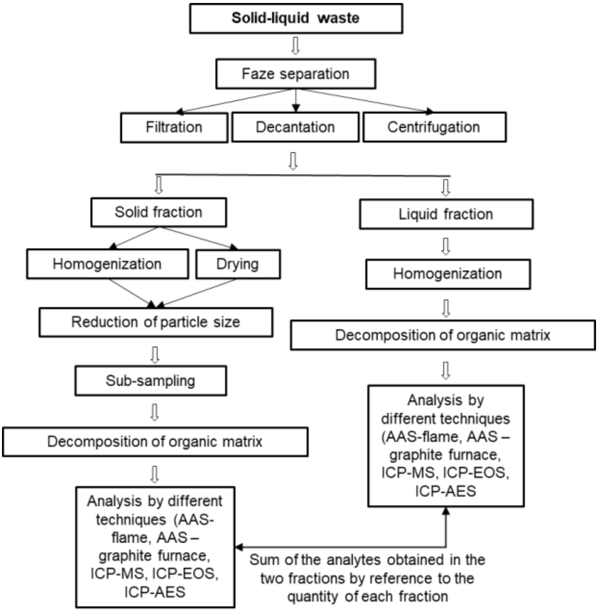

Figure 7. Solid-liquid waste characterization scheme

N1 - Soil and filter cakes containing dangerous substances, waste code 11 01 09 * - generated from nickel and chrome plating processes;

N2 - Soil and filter cakes containing dangerous substances, waste code 11 01 09 * - generated from electrochemical milling processes of metal parts using salt baths;
D1 - Powder coating waste - generated from the brake pad manufacturing industry;
D2 - Paint waste - generated from cleaning or mixing colors during painting process of aluminum profiles in electrostatic field.

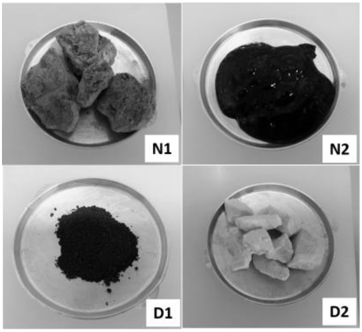

Figure 8. Study types of waste

Preparation of waste samples

The preparation of waste samples in order to ensure organic matter decomposition was carried out in several stages according to scheme presented in Figure 9.

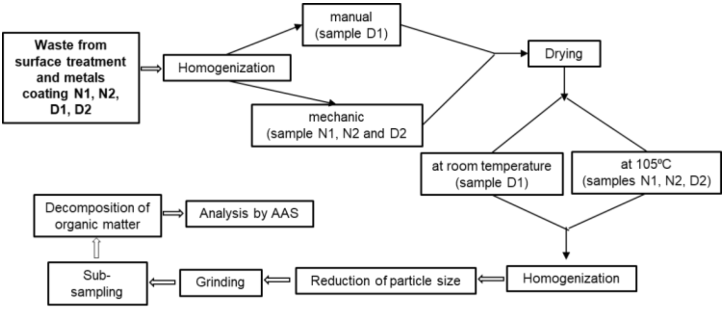

Figure 9. Sample preparation scheme

Organic matter decomposition

For sample mineralization was used microwave digestion according to the schedule in Table 6**.** Organic matter digestion was performed using ETHOS UP equipment provided by Milestone Company.

In order to track the mineralization efficiency, the used acids had different concentrations, and they were used separately or in mixture, according to EPA 3052 (EPA 1996) (Table 7). After the mineralization step, the obtained solutions were analysed using a flame atomic absorption spectrometer (AAS) using a calibration curve in the range 0.1 to 0.5 mg/L. The calibration curve was prepared based on mono-element certified reference material (CRMs) solutions having a concentration of 1000 mg/L in 2% HNO_3. All reagents used were of high analytical purity (Merck quality). Each experiment was repeated three times, the final result representing the mean of the three measurements.

Table 6. Microwave program

Microwave digestion program			
Steps	**1**	**2**	**3**
Temperature (°C)	100	200	70
Microwave power (%)	1500	1500	0
Time (minutes)	15	30	30

Table 7. Methods of mineralization

Methods of mineralization	Analyte	Analytical technique	Procedure
Method I. HNO_3	Cu, Zn, Ni, Pb	AAS	0.5 g of the sample is introduced into the digestion cell. Add 10 mL of HNO_3 (65%).
Method II. HNO_3 + HCl	Cu, Zn, Ni, Pb	AAS	0.5 g of the sample is introduced into the digestion cell. Add 3 mL HNO_3 (65%) + 7 mL HCl 37% (v/v).
Method III. $HNO_3 + H_2O_2$	Cu, Zn, Ni, Pb	AAS	0.5 g of the sample is introduced into the digestion cell. Add 6 mL HNO_3 (65%) + 4 mL H_2O_2 (30%) (v/v).
Method IV. $HNO_3 + H_2O_2$ +HCl	Cu, Zn, Ni, Pb	AAS	0.5 g of the sample is introduced into the digestion cell. Add 4 mL HNO_3 (65%) + 4 mL H_2O_2 (30%) + 2 mL HCl (37%) (v/v/v).

After complete digestion, the solutions were filtered through blue strip filter paper (porosity 3µ), and filled up to volume of 50 mL and were measured on AAS, using a calibration curve in the range 0.1 to 0.5 mg/L.

Results and Discussion

In Fig. 5-8 are presented the results obtained for all types of waste samples analysed. From the obtained results, it is found that the highest concentrations were obtained by applying mineralization method IV (mixture of HNO_3 65% + H_2O_2 (30%) + HCl (37%), even if the concentration differences between the four analysed wastes (N1, N2, D1, D2) were not very high.

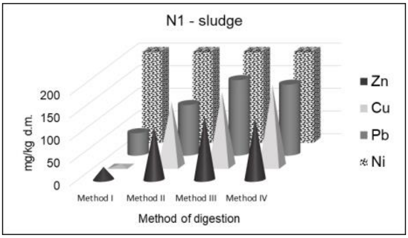

Figure 10. Experimental results for sludge N1

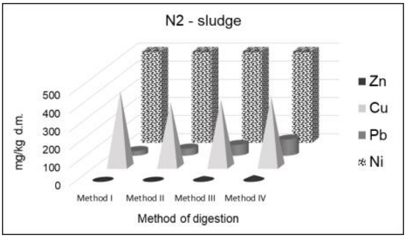

Figure 11. Experimental results for sludge N2

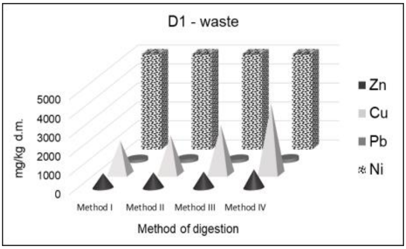

Figure 12. Experimental results for waste D1

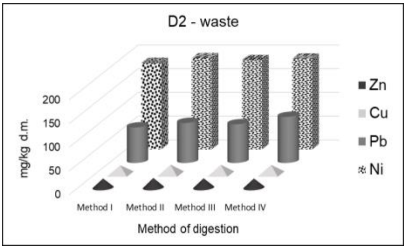

Figure 13. Experimental results for waste D2

The results obtained for the two types of sludge N1 and N2 (sludge and filter cakes containing dangerous substances) cannot be compared, even if analysed sludge are part of the same waste class. Therefore we could conclude that this aspect indicates that each waste has a different composition depending on the mode or processes which led to its generation.

Also there is a clear difference between the appearances of the two sludge: one being a paste, the other in the form of agglomerations. The only similarity between the two waste samples N1 and N2 is nickel loading (27224 mg/kg dry matter (N1) and 5117 mg/kg dry matter (N2)), concentrations obtained using method IV.

In terms of analysed metals, the composition of D1 and D2 wastes was different, and we concluded that it depends on their generation process.

For the paint waste sample it is found that the metal concentrations are much lower, indicating that the paint does not accumulate heavy metals in high concentrations.

Comparative study on heavy metals composition in waste samples

In order to verify the results obtained for all analysed waste samples (four types of waste) using AAS analysis, were carried out comparative studies on X-ray fluorescence spectrometry (XRF) equipment.

XRF analysis were performed using a Rigaku CG analyzer (Rigaku, Japan) equipped with a 50W X-ray source having a Pd anode and secondary Al, Mo, Cu and RX9 targets (highly oriented pyrolytic graphite HOPG polarizer).

The choice of secondary targets was done automatically, depending on the analysed items. Detection was performed using a silicon drift detector (SSD) maintained at optimum temperature via a Peltier system.

This technique does not require all sample preparation operations (operations applied for AAS), but only a part of them such as: drying at 105°C and homogenization by means of a mortar and sieving process, the sample being introduced in solid state into the equipment.

Approximately 1 g of each waste sample was introduced into a polypropylene cup (diameter 32 mm) equipped with a Prolene transparent film, after than the sample was analysed.

In order to perform the comparative analysis by the two techniques, the metal concentrations obtained by mineralization method IV were taken into consideration.

After comparing the results obtained by the two analytical techniques (Table 8), it is found that for all the analysed waste samples, the obtained concentrations values are comparative, being slightly higher when is used XRF technique. This fact is due to the way in which sample are analysed, in XRF technique the interference given by oxidation agents and compound losses resulting from the preparation and pretreatment steps are eliminated.

Table 8. Comparative results obtained through AAS and XRF

Waste sample	Metal	Values	
		XRF technique (mg/kg d.m.*)	**AAS Method IV** (mg/kg d.m.)
N1 - Soil and filter cakes containing dangerous substances, waste code 11 01 09 *	Zn	217	136
	Ni	30057	27224
	Cu	235	180
	Pb	174	157
N2 - Soil and filter cakes containing dangerous substances, waste code 11 01 09*	Zn	33.7	24.4
	Ni	5653	5117
	Cu	444	387
	Pb	106	89.3
D1 – Powder coating waste	Zn	85767	82000
	Ni	197	189
	Cu	1117	975
	Pb	4343	3713
D2 – Paint waste	Zn	207	191
	Ni	112	97.2
	Cu	21.8	19.6
	Pb	24.8	19.3

*Dry matter

Conclusions

From the obtained results it is found that even if there are no very high concentration differences between the four analysed wastes (N1, N2, D1, D2), the highest concentrations were obtained by applying method IV in digestion step. Metal concentrations obtained through this method were also verified using XRF analysis technique. The results obtained applying both analytical methods (AAS and XRF) are comparative and they highlight the fact that the models applied in samples preparation of are suitable for the characterization and analysis of these categories of wastes.

Acknowledgements

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GENERAL SCHEME TO EVALUATE THE DANGEROUSNESS OF WASTES IN ORDER TO MANAGE THEM BY PRODUCER/HOLDER ORGANIZATIONS

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Abstract

A general scheme for the assessment of dangerousness of waste is presented taking into consideration the new European and Romanian applicable laws in order to adequately manage them (storage, elimination with specialized firms - preparation for disposal/recovery, recovery, and final disposal). Some relevant examples from current practice will be reviewed emphasizing the interest aspects in applying the current legal provisions in order to adequately manage the waste in Romania in the spirit of sustainable development and protection of environment and human health on short, medium and long term.

Keywords: *dangerousness, disposal, elimination, recovery, wastes*

Introduction

The paper presents a general scheme for waste assessment based on current environmental and waste legislation as a methodological approach to be used in practice in order to make an appropriate waste management. Following economic development, our modern society is facing increasing amounts of wastes and consequently there is a strong necessity to adequately manage them in the spirit of sustainable development. In this respect, nowadays, any developed wastes' policies and strategies should be conceived in order to find balance between continuing economic development on one hand and decreasing natural resources consumption and wastes production in order to minimize their environment and human health negative effects on the other hand.

Materials and methods

The following assessment scheme presented in Figure 1 is based on the current environmental protection laws dedicated to the waste management. Waste, as is defined by legislation (Directive 2008/98/EC) is "*any substance or object which the holder discards or intends or is required to discard*". This legislation states that any waste assessment "*should be based, inter alia on the Community legislation on chemicals, in particular concerning the classification of preparations as hazardous, including concentration limit values used for that purpose. Hazardous waste should be regulated under strict specifications in order to prevent or limit, as far as possible, the potential negative effects on the environment and on human health due to inappropriate management*". European legislation states also that classification of any waste should be realized in accordance with the waste types list "*as last established by Commission Decision 2000/532/EC in order to encourage a harmonized classification of them and ensure also the harmonized determination of hazardous* *waste within the European Union and adequate management"*(Commission Decision 2000/532/EC).

Activities involved in the appropriate waste management are referring to the sorting, collection, and preliminary storage of waste pending its further collection, transport, recovery/disposal treatment and disposal. The Directive 2008/98/EC for waste at Chapter I, Article 2 (1) presents also exceptions from its scope. The proposed scheme is transposing and summarizing the current waste law requirements. It has been conceived in order to help waste management taking into account the large variety of the generated waste. The classification of waste as hazardous should be based on a series of dangerous properties presented in Annex of Regulation nr 1357/2014 and also considering the Regulation (EC) No 1272/2008. The Romanian transposing Waste European Legislation is as follows: Law nr. 211/2011 (republished) regarding the waste regime, modified through the Governmental Order nr.68/2016 in force from 28 of October 2016, Commission Decision 2014/955/UE, for the modification of Decision 2000/532/CE to establish a waste list (the European Waste Catalogue), EU Regulation nr.1357/2014 replacing Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives. The *EU Regulation nr.1272/2008 gives explanations of the legally used concepts in assessing "hazardous substances and mixtures and specify the hazard classes".* A *substance* or a *mixture* fulfilling the *criteria* relating to *physical hazards, health hazards* or *environmental hazards*, laid down in Parts 2 to 5 of Annex I is hazardous and shall be classified in relation to the respective *hazard classes* provided for in that Annex, where, in Annex I, *hazard classes* are differentiated on the basis of the route of exposure or the nature of the effects, the substance or mixture shall be classified in accordance with such differentiation". "

"A substance" means a chemical element and its compounds in the natural state or obtained by any manufacturing process".

Note 1: For waste classification purpose, the number from Chemical Abstract Services (English Abbreviation CAS nr.) for the corresponding element/compound/substance is recommended to be known so that, properties of interest can be verified.

"*A 'mixture"* means a mixture or solution composed of two or more substances".

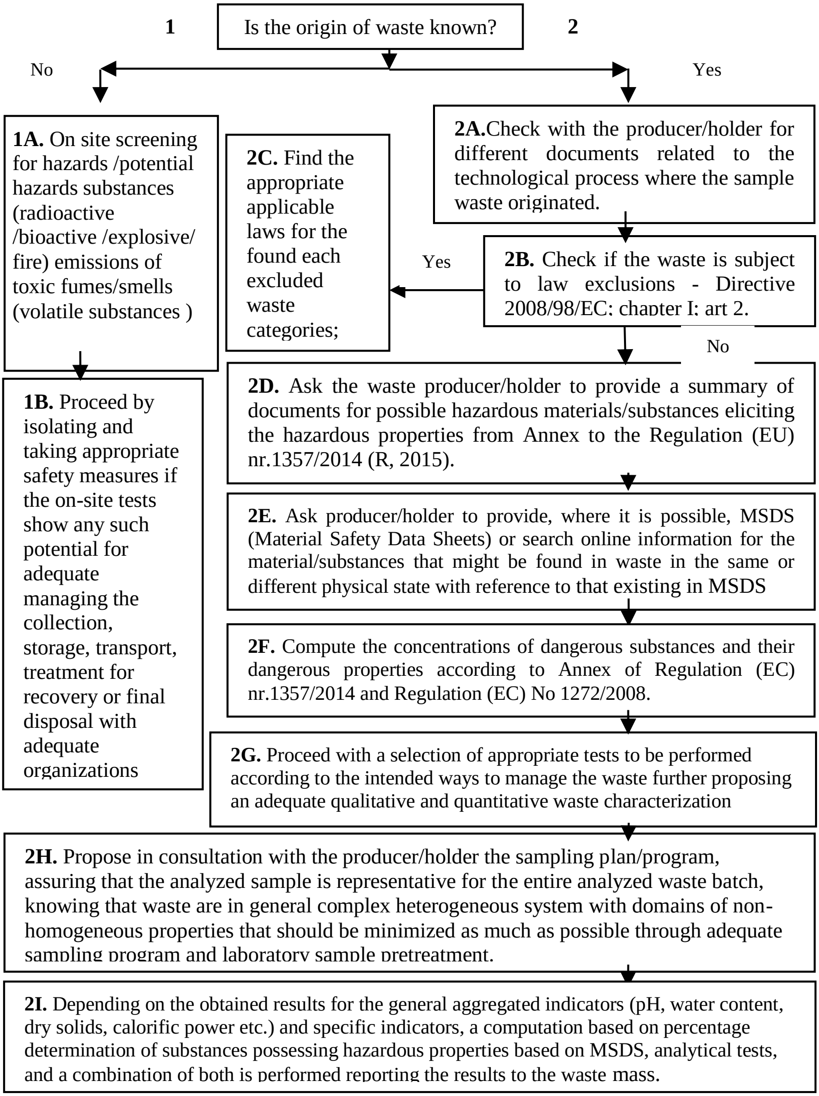
Note 2: In the context of waste classification we should mention that usually a non-homogeneous system (mixture) of two or more substances is called a mixture and a homogeneous system (mixture) of two or more substances is usually called solution.

Results and Discussion

Any endeavour related to waste characterization means actually a less or more extensive case study that necessitates organizing documentation from the producer/holder, in order to evaluate it and to elaborate a sampling plan for analytical relevant determinations (indicators) and finally, to assess all available data and information based on the applicable current waste legislation. According to our proposed presented scheme the waste should first be tested for its origin. If the origin is not known the branch 1 of the scheme Fig. 1 should be followed. If the origin is known, we will follow the branch 2 of the scheme. Procedural cassette 2A instructs to check with the producer/holder for different documents related to the technological processes where the waste originated. Afterwards, the cassette 2B is followed in order to check if that waste is subject to law exclusions stipulated in Directive 2008/98/EC; chapter I; art 2. If this is not the case, the procedural cassette 2D is followed. This cassette instructs to ask the waste producer/holder to provide a summary of documents for possible existing hazardous materials/substances eliciting the hazardous properties from Annex to the Regulation (EU) nr.1357/2014, in the context of mentioned current applicable waste laws. Then, assessment continues with the procedural cassette 2E that requires producer/holder to provide, where it is possible, MSDS (English abbreviation for Material Safety Data Sheets) or search online information for the material/substances that might be found in waste in the same or different physical state with reference to that existing in MSDS. Next, the procedural cassette 2F is followed. It instructs to compute the concentrations of dangerous substances with corresponding codes that can impart to the waste dangerous properties according to Annex of Regulation (EC) nr.1357/2014 and Regulation (EC) No 1272/2008. Those computations can be done from data and information included in MSDS and also from the process mass balances information. Following the cassette 2G a selection of appropriate analytical tests that should be performed can be realized according to the intended ways for waste management (sorting and storage for transport and management with a specialized waste management firm, pre-treatment for transport, recovery or final disposal). An adequate qualitative and quantitative waste characterization strategy can be planned and applied. That means that, from all obtained data and information, the relevant hazardous elements/compounds and substances should be assessed from the point of view of their inter-phases partition/distribution in the waste batch sample. Depending on the waste physical state and waste general exhibited properties it is decided the way that sampling program should be done according to the in place applicable current sampling standards so that the sample will have relevance for the type of waste or at least for the batch of analyzed waste. In the current practice, we are receiving waste characterization applications from a large diversity of clients both producers and holders who are trying to manage the waste, having a variety of origins according to the current law requirements. Most frequently encountered waste that can be analyzed for determination of different indicators is that in solid form with more or less humidity and of different granularity. In such waste, general indicators that can be usually analyzed are the so-called aggregated properties indicators such as: pH, humidity, suspended maters, dry solids, total organic carbon, total inorganic carbon, calorific power, elemental analysis, TPH, metals/heavy metals, leachable substances etc. All these indicators complement the MSDS specific information about the substances that can be finally found in each analyzed waste batch. The literature in the field related to the analytical balances determination in the waste analysis shows that an error of 10 % in mass analytical balances is usually accepted knowing that in any analyzed waste, transformations can occur modifying not only the physical state of the entered substances but also their chemical forms. Complex compounds of heavy metal for instance, that are found more in the humidity of a waste sample, are the most frequent case of elements transferable from solid phase in soluble form depending on waste pH . Analytic protocols allowing the user to gain appropriate knowledge of the organic and inorganic substances in a waste and to allow the determination of the properties for the regulatory or recovery purposes have been considered in order to improve the waste analytical determinations approach with a combination of quantitative/qualitative methods. Qualitative methods are usually applied for organic parameters. Global (aggregated) indicators determinations are another example that is used for characterization of parts of waste composition that remain undetermined.

Another very important issue in the case of analyzing a waste is related to its inherent heterogeneities which are difficult to be managed in order to have relevant results. Volatile compounds are those that will always tend to go in the atmosphere depending on the storage temperature. The relative solubility of different substances can change over the time along with rheological properties (viscosities and redistributions of substances between solid or liquid phases of a waste). The literature in the field (Hennerbert et al. 2013) states that using the combined type of methods, depending on each specific case, "it is possible to quantify *in* essential lines the composition of the waste batch sample in the terms of specific substances" taking into consideration that when performing computation of the hazardous properties "the level of concentration that impact the waste classification as hazardous through the contained present substances, in legislation, varies in a range of 0.1-10 % and at those concentrations the relative error of the semi-quantitative analysis seems to be reduced." Always the pre-assessment waste characterization phase is a work done in consultation with the client and within a multidisciplinary team of assessors and analysts. The quality assurance program in laboratory where those determinations are made is followed in order to have defendable results. (Pascu et al. 2015). The cassette 2 H from the scheme requires to have a short but comprehensive documentation related to the waste - technological process, raw and intermediate materials that can be found in waste, process material mass balances, operation technological parameters influencing the waste properties on short term but also on medium and long term. However, because in practice we are facing a large variety of waste, very well illustrated by all the waste codes existing in the European harmonized list of waste, we are not able to analyze all types of listed waste. For those types of waste that cannot be analyzed through usually laboratory procedures, the information from the MSDS of commercial used products' help us to make an appropriate characterization.

In Table 1 and 2, two examples of waste characterizations are presented next. In the tables are presented only few components, as an example, of some of the commercial used products. The used commercial products in the processes from where the waste is coming from, are more numerous than those presented in the Table 1 and Table 2. In a usual Report of waste characterization offered to our clients, all the relevant components are taken into consideration and what is presented in Table 1 and Table 2 for only few commercial products and their components is replicated for all relevant entered products in the process and their components. Properties HP1÷HP15 that might impart to waste hazardous properties are considered and a resolution for each property is given according to the made computation for all the found components with hazardous statements and categories codes. The present legislation especially the Regulation 1357/2014 is very helpful in summarizing the algorithm for computation of concentrations of waste compounds that present hazardous statements and category codes that might impart to the waste the hazardous properties identified as HP1÷HP15.The computed concentrations of those compounds are checked against the prescribed cut-off-values of each of HP1÷HP15 properties.



Is the origin of waste known?

1A. On site screening for hazards /potential hazards substances (radioactive /bioactive /explosive/ fire) emissions of toxic fumes/smells (volatile substances)

1B. Proceed by isolating and taking appropriate safety measures if the on-site tests show any such potential for adequate managing the collection, storage, transport, treatment for recovery or final disposal with adequate organizations

2A. Check with the producer/holder for different documents related to the technological process where the sample waste originated.

2B. Check if the waste is subject to law exclusions - Directive 2008/98/EC: chapter I: art 2.

2C. Find the appropriate applicable laws for the found each excluded waste categories;

2D. Ask the waste producer/holder to provide a summary of documents for possible hazardous materials/substances eliciting the hazardous properties from Annex to the Regulation (EU) nr.1357/2014 (R, 2015).

2E. Ask producer/holder to provide, where it is possible, MSDS (Material Safety Data Sheets) or search online information for the material/substances that might be found in waste in the same or different physical state with reference to that existing in MSDS

2F. Compute the concentrations of dangerous substances and their dangerous properties according to Annex of Regulation (EC) nr.1357/2014 and Regulation (EC) No 1272/2008.

2G. Proceed with a selection of appropriate tests to be performed according to the intended ways to manage the waste further proposing an adequate qualitative and quantitative waste characterization

2H. Propose in consultation with the producer/holder the sampling plan/program, assuring that the analyzed sample is representative for the entire analyzed waste batch, knowing that waste are in general complex heterogeneous system with domains of non-homogeneous properties that should be minimized as much as possible through adequate sampling program and laboratory sample pretreatment.

2I. Depending on the obtained results for the general aggregated indicators (pH, water content, dry solids, calorific power etc.) and specific indicators, a computation based on percentage determination of substances possessing hazardous properties based on MSDS, analytical tests, and a combination of both is performed reporting the results to the waste mass.

Figure 1. Scheme for waste assessment and classification

All existing or estimated substances to be found in wastes according to the entire available documentation and literature in the field, are screened and assessed for hazard statements and categories codes either in the presented MSDS or in the specialty literature according to the CAS number. Next, we give two examples of waste sediments coming from the physical-chemical step of treatment of the industrial waste washing waters, from two industries: car washing and food industries. Each of them contains detergent solutions. Both wastes have pH around 7 but have different humidity content. One waste has the humidity of approximately 30% and the sediment is mostly inorganic with only 2% TOC and the other one has the humidity of over 70% and has a greater organic content expressed as TOC of over 50%. Both wastes have been analyzed from possible existing dangerous substances considering all useful information and data obtained from the waste producer/holder. The commercial used products' MSDS have been consulted in order to obtain for each component/substance the CAS nr. (English abbreviation for Chemical Abstract Services nr.). This allows to check for the hazardous statements and categories codes and also all other important physical properties such as concentration, solubility, flash temperature etc.).

Conclusions

The assessed waste according to the scheme Fig. 1 has been done in a methodical way following the legal requirements. The quantitative determination of assessed hazardous properties HP4 presented for two examples of waste from two industries have shown that the waste in the form that has been transmitted by our client has no hazardous properties imparted by the concentrations of the contained substances tested against legal cut off values. The greatest challenge in environmental toxicology is to understand the toxicity of mixture when different pollutants are coexisting and manifesting synergistic effects that is precisely why the topic of correct classification is one that should be given the necessary attention both in research studies and in practice.

Table 1. Example 1 - Waste from washing and polishing cars activities

Commercial product type/Component of the comercial product identified by CAS nr.	**Component conc. in commercial product % (Min, Max)**	**Hazardous statement - Regulation nr. 1357/3014 (cut-off values)**	**Waste Hazarous Property (HP) according to Regulation nr. 1357/2014**	**Estimated compound in:** a)the monthly consumption of comercial product (Kg b) the humidity of the waste sample (Kg) **c) waste, in weight (%)**	**Test** (c1+c2**)** against **cut – off- value**s for **HP 4 -** ***skin irritant and eye damage***	**Yes/No hazardous waste conclusions** according to hazard statement
Liquid wax/Acetic Acid (CAS 64-19-7)	**<0.25**	**H314:** Skin corr 1 A (≥1 %)	**HP 4 „*Irritant – skin irritant and eye damage”*** waste which on application can cause skin irritation or dam age to the eye	a1) 0,011 b1) 1,221.10^{-5} **c1) 1,221x10^{-6}**	**1.161x10^{-3}** **< 1%**	***No hazardous waste***
Car detergent/ Sodium Hydroxide (CAS 1310-73-2)	**(≥3, <5)**	**H314:** Skin corr 1 A (≥1 %)		a2) 10,5 b2) 0.0116 **c2) 1,16x10^{-3}**		

Table 2. Example 2 - Waste from washing equipments and hygiene activities from food industry

Commercial product type/ Component of the comercial product identified by CAS nr.	**Component conc. in commercial product % (Min, Max)**	**Hazardous statement Regulation nr. 1357/3014 (cut-off values)**	**Waste Hazarous Property(HP) according to Regulation nr. 1357/2014**	**Analytically determined element conc. /Estimated associated compound in waste**	**Estimated compound in:** a) monthly consumption of comercial product (Kg) b) the humidity of the waste sample (Kg) **c) waste, in weight (%)**	**Test** (c1+c2**)** against **cut – off- values** for **HP 4 -** ***skin irritant and eye damage***	**Yes/No hazardous waste conclusions** according to hazard statement
Food detergent /Sodium Hydroxide (CAS 1310-73-2)	**(5, 10)**	**H314:** Skin corr 1 A (≥ 1 %)	**HP 4 „*Irritant – skin irritant and eye damage”*** waste which on application can cause skin irritation or damage to the eye	Sodium /NaOH	a1) 257 b1) 59 **c1) 1.03x10^{-2}**	**9,43x10^{-2}** **<1%**	***No hazardous waste***
Food detergent/- Sodium Hypochlorite (CAS 7681-52-9)	**(≤ 4)**	**H314:** Skin corr 1 A (≥ 1 %)		Potassium /KOH	a2) 254 b2) 58 **c2) 8.40x10^{-2}**		

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MECHANICAL RECYCLING: SOLUTIONS FOR GLASS FIBRE REINFORCED COMPOSITES

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Abstract

When it comes to reutilization of glass reinforced plastic composites (GRP), mechanical recycling is one of the most widely used methods. This research brings further insight to environmental assessment of mechanical recycling by comparatively analyzing three types of products (concrete block, plastic foil and ceramic sink) from an LCA perspective. Thus, a deeper relationship between theoretical LCA modelling, factual production and market potential can be established. Results show that re-utilizing GRP recyclate as replacement for petroleum-based products delivers most environmental benefits.

Keywords: *GRP, LCA, mechanical recycling*

Introduction

Recycling of glass reinforced plastic composites (GRP) has been gaining increasing attention. Available methods include incineration (as well as with energy recovery), co-processing, mechanical recycling and thermal recycling. Based on comparative research, mechanical recycling seems to be one of the best choices. For example, a study cross-referencing a variety of research projects on composite recycling technologies, reviewing thermal processing (pyrolysis and solvolysis) and mechanical grinding, concluded that mechanical grinding is most mature solution for glass-fibre applications (Rybicka et al. 2016). A study performed in 2009-2012, with support of the European Commission, compared incineration, mechanical recycling and thermal processing (pyrolysis and solvolysis) and revealed that solvolysis was not competitive with treatments like mechanical recycling or with incineration with energy recovery in terms of environmental impacts (EC-EURECOMP 2013). A Life-Cycle Assessment (LCA) study assessing incineration, co-processing, mechanical recycling and thermal recycling for recycling of GRP waste concluded that the mechanical approach had most environmental benefit (Vladimirov & Bica 2017). This paper brings further detail to environmental evaluation of mechanical recycling, providing insight into three types of products (concrete block, plastic foil and ceramic sink). These applications were chosen based on existing research and market availability in order to establish a relationship between theoretical LCA modelling, market potential and factual production.

Mechanical recycling

Mechanical recycling is one of the most widely used approach for recycling GRP, with its commercial start drawing back to the 1970s (Job 2013). Applications include concrete, artificial wood, rubber pavement blocks, reinforcement in asphalt, dense bitumen macadam, bulk/sheet (BMC/SMC) molding compounds, textile sandwich structures, sanitary ceramic objects and plastic applications. The process typically starts by reducing the particle size of waste through mechanical operations such as shredding, crushing or milling. The resulting scrap pieces can then be separated by using sieves and cyclones into powdered products (rich in resin) and fibrous products (rich in fibers) (Yazdanbakhsh & Bank 2014).

Figure 14. Fine ground GRP
Source: HOBAS

Advantages of mechanical recycling include a high variety of product applications and very positive variations of environmental indicators through recycling. Further benefits are relatively no atmospheric pollution by gas emission, simpler equipment required and no use of chemical solvents when compared with the ovens necessary for thermal processing (Ribeiro et al. 2014). Furthermore, mechanical recyclate has lower density and may contribute to lighter end-products (Pickering 2006). Drawbacks of mechanical recycling refer lack of consistency (and purity degree) of the grind material due to the many variety of GRP compound formulations. The recyclate addition to new products has tendency to negatively affect the mechanical properties of the final composite (i.e. consistency, strength, stiffness, the filler-matrix interface bond strength, etc.) and to negatively impact the cost balance (as operational costs with mechanical recycling and sorting outweigh the market value of the virgin products chopped glass fibre and calcium carbonate) (Yazdanbakhsh & Bank 2014). Due to lower mechanical properties powder recyclates have limited potential for reuse back into the thermoset compounds from which they originated (closed loop recycling). Another potential disadvantage is that the energy content is not recovered.

Mechanical reclaiming for concrete applications

One the most extensive research work has been carried out on Portland cement concrete in which mechanically recycled GRP waste have been incorporated either as reinforcement, aggregate or filler replacement (Ribeiro et al. 2014). The use of GRP waste in concrete can therefore contribute to cost savings associated with waste handling, transport, storage and traditional disposing methods such as landfill. GRP waste substitution to fine aggregates in concrete could save approximately 15% of the fine aggregate cost (Asokan et al. 2009).

Mechanical reclaiming for plastic applications

GRP recyclate could be used for a variety of plastic products, such as wood flooring in high density polyethylene (HDPE), PP under-floor vents or PE and PP plastic foil. In case of the foil, the powder is mixed with additives for increasing compatibility with the PE or PP base material. The addition leads to a thinner and stronger end-product used for several applications (roofing sheet, valley gutters and flat sheet for signage) (Job 2013). Thus, the manufacturer needs less virgin material to reach the same specifications and the new product is partly "green".

Mechanical reclaiming for ceramic applications

Mold applications can be obtained in preparing a mixture comprising fragments of fiberglass, polyester resin, titanium dioxide, microspheres of thermoplastic material and benzoyl peroxide with a catalyst. The mixture is poured into a mold and then hot-pressed to form an object. The ground material is usually 35-40% between 75% of weight (Wolf 2008). A similar method incorporates fine ground GRP (particles of up to 2,5 mm) into granular compounds with synthetic resin (i.e. unsaturated polyester, epoxy, polyurethane, vinyl ester, etc.), essences (chemical additives for odors), zinc stearate (facilitates mixture flow) and coloring agents (Bravo et al. 2014).

Methods

Calculations were made in accordance to EN 15804 with Module D. The model used as reference is one-meter GRP Pipe with a nominal diameter (DN) 1000 mm, pressure class one PN 1 bar and a nominal stiffness (SN) 10000 N/m². The environmental impacts were calculated as the sum of the following components (the "integrated formula: (i) primary material input, (ii) secondary material input, (iii) material recycling, (iv) energy recovery and (v) disposal. The following EN 15804 system stages were included: product stage (A1 raw material supply, A2 transport, A3 manufacturing, including treatment of factory waste), end of life (C2 transport, C3 waste processing, C4 disposal) and benefits and loads beyond the system boundary (module D). Module D was calculated as in the formula below (Wolf & Chomkhamsri 2014):

$$\text{Net benefit impact indicator} = \text{Yield} * \text{Amount} * [RR * (Ev' - Er') - RC * (Ev - Er)] \tag{1}$$

where RR = Recycling rate at the end-of-life (EoL stage), Ev' = Impacts of substituted virgin material production (EoL stage) (credit), Er' = Impacts connected to the recycling processes from beyond the system boundary (after the end-of waste state up to the point of functional equivalence), RC = Recycled content (product stage), Ev = Impacts of virgin material production (product stage), Er = Impacts connected to the recycling processes from beyond the system boundary of the life cycle that generated the waste flow (after the end-of waste state).

The system boundaries are presented in the figures below. Benefits from incineration with energy recovery of production waste were calculated for all scenarios.

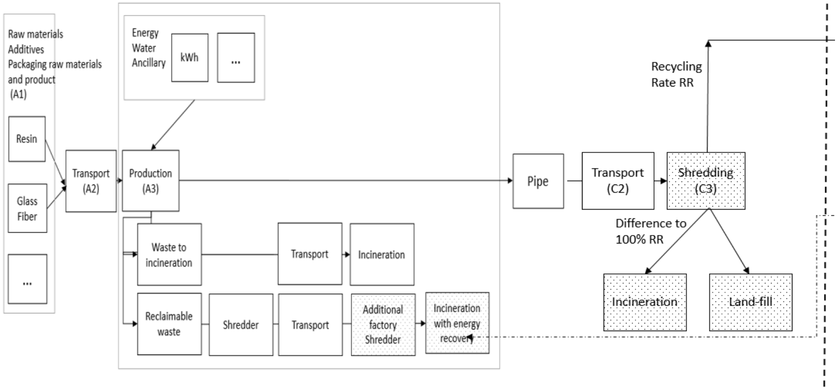

Figure 2. Base model (before Module D)

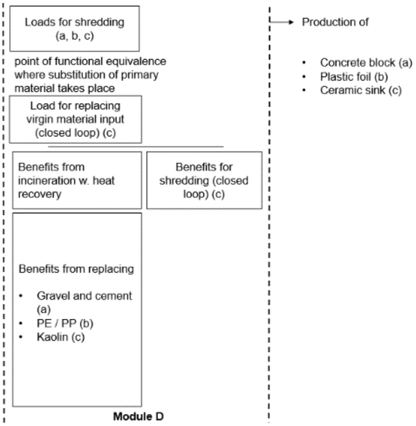

Figure 3. Module D

As the substitution of primary material by the secondary material is not 1 to 1, a yield of functional equivalence of 0.85 was defined. Within system boundary 100:0 allocation was used. A 95% recycling rate (RR) was considered to highlight the potential environmental benefits of the recycling methods. A 5% RR was also calculated for the plastic foil scenario, to clarify the influence of the recycling rate to the results. The remaining waste (difference to recycling rate) was treated as 55% to landfill and 45% to incineration (EC 2016). A 90% efficiency rate for the incineration process as well as a 300-km distance to the incineration plant / landfill / recycling plant were included in the calculations. For the ceramic sink, two additional scenarios were calculated: (i) open loop – close loop (OL CL) in which 5% (recycled content – RC) of the recyclate is used back to pipe production and (ii) using of recycled PET resin on the input side of the pipe production model. These two scenarios bring additional insight to the results, per life cycle assessment methodology.

Results and Discussion

Results of the scenarios are presented in the Table 2 and Fig. 4. The table shows the variation of the calculated values to the reference (scenario without recycling). The figure depicts weighted results, with equal weighting factor 1. The purpose is to facilitate the overall understanding of the results and support primary decision making amongst the discussed options.

Table 2. Results of the mechanical recycling modules

	non-hazardous waste	**acidif. potential**	**GWP 100a**	**eutroph. potential**	**high NOx POCP**	**depletion abiotic resources**
Concrete block (a)	131.91%	91.95%	82.23%	96.78%	96.96%	98.56%
Plastic foil (b)	111.26%	-69.23%	-41.10%	54.11%	-58.29%	-158.34%
Ceramic sink (c)	233.02%	92.04%	104.69%	87.99%	97.68%	92.68%
Ceramic sink PET (c)	120.90%	75.00%	84.49%	71.15%	73.95%	75.54%
Ceramic sink OL CL (c)	131.80%	90.80%	98.39%	80.79%	92.38%	93.09%
Plastic foil RR 5% (b)	774.60%	107.17%	150.50%	150.82%	131.74%	93.88%
Reference	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Reference	9.18E-02	3.35E-03	1.09E+00	9.17E-04	2.05E-04	1.01E-02

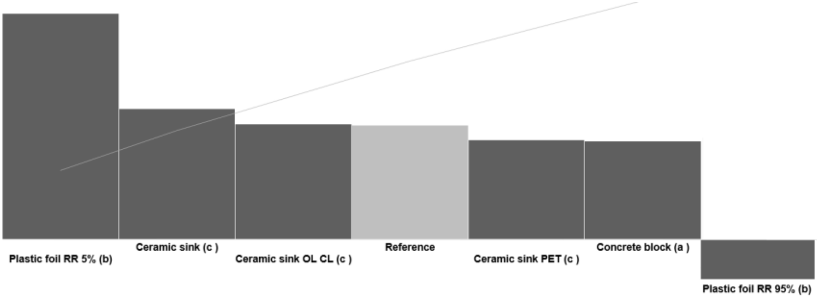

Figure 4. Weighted results (for decision making)

Results for mechanical recycling to concrete blocks (a) indicate overall indicators improvement and reinforce previous research, that recycling to concrete elements is providing valuable environmental benefits. Best variation is registered by CO_2, acidification and eutrophication potential indicators.

Results for mechanical recycling of GRP waste to plastic foil (b) tend to be very positive (best scenario), as most considered indicators have clear and positive net flows. Most benefit is obtained for depletion of abiotic resources, acidification potential and ozone depletion (as petroleum-based products are re-used instead of being acquired anew from nature). However, it should be noted that the very positive result is an indication of the optimal scenario, where recycling rate stands at 95%. A variation of the scenario is further included, considering a RR of 5%. The benefits in this case are not as significant. Mechanical recycling has a very high potential for GRP waste and efforts to increase the recycling rate throughout the industry would have definite beneficial results.

The results for mechanical recycling of GRP waste to ceramic sink (c) tend to be favorable, even if the positive net flows are reduced as compared with the plastic foil. The main reason is that PE and PP production is a process with heavier environmental load than that of kaolin, for which less processing is required, respectively the processing has lower environmental impacts comparatively. Most benefit is obtained for eutrophication potential, depletion of abiotic resources and acidification potential. In the close loop scenario (5% RC of the recyclate is used back to pipe production) results are similar with the already calculated ceramic sink model. Through application of Module D, credits were allocated for replacing kaolin and debits for shredding the pipe at EoL (open loop), as well as credits for shredding the pipe and debits for replacing virgin materials at pipe production input (close loop). A higher RC may influence total results positively, depending on the impacts of the recycling, compared to the functional equivalence process. In case of the GRP product, it is expected that this influence would be positive but moderate. In the variant where recycled PET resin is used for pipe production, results are better than of the original scenario "Ceramic sink", due to using recycled input. Most benefit is obtained for eutrophication potential, ozone creation and acidification potential.

Conclusions

Results for mechanical recycling of GRP waste are positive, especially at higher recycling rates. The most favorable method is recycling to plastic foil (as primary petroleum-based resources are saved), followed by recycling to concrete block and ceramic sink. Using of close loop and recycled raw materials brings further environmental benefits. Mechanical recycling remains a strong option for GRP recycling, especially from an environmental perspective. The main challenge remains identifying product applications that can incorporate the GRP powder to satisfactory product quality requirements (e.g. compressive strength, tensile strength, shrinkage, water absorption, density, microstructure, sort-term and long-term performance) and that have market potential (operational cost, demand and distribution channels).

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NEW ECOLOGICAL SOLUTION TO IMPROVE THE LAKES CAPACITY BY COMBATING THE EXCESSIVELY DEVELOPED VEGETATION

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Abstract

The paper presents a solution designed and tested hydroelectric lakes, which have the useful volume reduced by 80% since the commissioning. The experimental prototype perfectly ecologic may be applied into hydropower lakes with complex utilization, including water supply for human necessities and cities. At the beginning are mentioned some responsible factors as the climate, hydrological, physical, and chemical for the lake's eutrophication. The vegetation developed so rapidly, diminishes quickly the water volume of the hydropower lakes, meaning less produced electric energy. Further, are presented the previous solutions tested, without any effect. This new solution, proposed as patent, is realized and tested in the Lake Pangarati. The main steps, challenges, and main solutions, during the utilization, are mentioned. Finally, in images are presented the obtained results, the real differences between shores with and without the barrier utilization. This new ecologically and friendly environment solution, to combat the excessive vegetation has a considerable efficiency and low costs. The main purpose is to rehabilitate the area and to reestablish the previous environmental conditions, taking into account that these two lakes Pangarati and Vaduri are RAMSAR sites since 2006. Finally, are mentioned some conclusions, acknowledgments, and references.

Keywords: *biodegradation, environmental engineering, environmental monitoring, maintenance management, water conservation*

Introduction

In the last decades, the national hydropower system confronts a new problem, excessive vegetation growth of in hydropower lakes. It seriously affects the ecological balance in the area (most affected are the fish) by the drop of the useful volume, water volume capacity decrease with economic effects (Nistreanu 1999).

The excessive hydropower resources use in the last 20-30 years due to the low cost of produced MW, led to a chain of negative effects (Seteanu 1998, 2004). Many SMEs have been developed in the recent years around lakes, using, and then spilling the water, leading to increased nitrites and nitrates concentrations. This explains why currently more than 20 lakes have a useful capacity reduced by over 80% (Bockman 2008, Turbatu 2004). In this category the rivers Bistrita and Jiu are included.

In this study three lakes on Bistrita, respective Pangarati, Vaduri, and Reconstructia are analyzed. As a first objective in order to solve this problem, was analyzing the environmental parameters from the critical areas, which led in time to excess vegetation grown. Analyses of sediments, chemical structure, biological conditions, temperatures, water flowrate, type of vegetation were carried out, as to estimate the real situation.

During the past years different methods for combating the vegetation growth were experimented, but all of them failed. The adopted solution must be realized while taking into account the importance of continuous useful flow assurance through the transport channel (Radulescu 2004), the energy needed to be produced, but, also the water alimentation for the local population and for the downstream consumers.

The solution is an economic, ecologic, and efficient solution, by placing of "screens" above the plant roots, as to suffocate the existing vegetation. Shortly the vegetation turns into sludge, without regenerating, even in the next year. This means that even the seeds, the cuttings and the roots have been destroyed.

At each 3-4 weeks, the barrier is moved to a new location, adjacent to the old one. After one year, comparisons were made and the solution efficiency was evaluated by comparing the two shores (the one with the "screens" and the natural one).

Materials and Methods

Based on the tests realized during the last decade, it was observed that the excess vegetation development is due primarily to the existent sediments, as consequence of the repeated, registered floods between 2005-2012 (Rodhe 1969). Another cause is represented by the new appeared SMEs on the lake's shores. They use the water from the lake and render it, partially decontaminated. A particular problem occurs in the case of the companies that process the wood. The water which is returned to the lake contains a significant amount of nutrients, clearly advantageous for aquatic vegetation development (Smith, 1999; Horrigan, 2002).

Some remarks:

- The dissolved substances in water are the main arguments of aquatic vegetation development,
- The Carbon, after the Hydrogen and the Oxygen, represents the main component,
- The presence of the Phosphor assures a supplementary nutrient, larger than the presence of the Nitrogen compounds, due to the repeated floods,
- If large amounts of Phosphor are discharged into the hydrographical structure the phenomena induce a decrease of the Nitrogen compounds concentrations and consequently, Ciano-bacteria explodes in number (Bartram 1999),
- The Oxygen assures the reaction between the water and sediments; the cycle becomes repetitive and the excess bacteria appear. Moreover, there is only one-step to an excess vegetation growth.

In Table 1 some characteristics of the analyzed sediments are mentioned, as well as some average values obtained during the measuring campaigns. In Table 2 the available/necessary substances in the lake water for vegetation development are presented.

In these lakes the nutrients intake is too high, assuring the development of algae at this level, mainly due to the sediment transported from the upstream.

Many algae represent a first favorable aspect, the first step into developing of the aquatic vegetation. In short time, some species become dominant, with a major influence on the local ecosystems. The local flora becomes restricted, and some species of fish decrease dramatically in number.

In time, in the mentioned lakes different methods to combat the vegetation have been tested.

Table 1. The average measured values

Parameter	Lake I	Lake II	Lake III
Humidity (105^{0}C) %	55.46	53.38	55.66
pH (up H)	6.80	6.65	7.04
Organic Substances (%)	6.95	5,93	8,36
Mineral substances	93.05	94.07	91.64
NH^+_4 mg/100g	5.85	7.27	8.01
NH^+_4 mg/L	105.48	136.19	143.91
NO^-_3 mg/100g	0.33	0.41	0.19
NO^-_3 mg/L	5.95	7.68	3.41
PO^{3-}_4 mg/100g	0.068	0.072	0.086
PO^{3-}_4 mg/L	1.22	1.34	1.54
N- NH^+_4 + N - NO^-_3 mg/100g	4.61	5.74	6.27
P- PO^{3-}_4 (mg/100g)	0.022	0.023	0.028
$N_{dissolved}/P_{dissolved}$	209.54	249.56	223.93

Table 2. The available/necessary values of chemical components

Element	Symbol	Consume (vegetal) %	Water offer %	Consume/offer (approx.)
Oxygen	O	80.5	89	1
Hydrogen	H	9.7	11	1
Carbon	C	6.5	0.0012	5.000
Silica	Si	1.3	0.00065	2.000
Azoth	N	0.7	0.000023	30.000
Calcium	Ca	0.4	0.0015	<1.000
Potassium	K	0.3	0.00023	1.300
Phosphor	P	0.08	0.000001	80.000
Magnesium	Mg	0.07	0.0004	<1.000
Sulpha	S	0.06	0.0004	<1.000
Chlorine	Cl	0.06	0.0008	<1.000
Sodium	Na	0.04	0.0006	<1.000
Iron	Fe	0.02	0.00007	<1.000
Boron	B	0.001	0.00001	<1.000
MangaN	Mn	0.0007	0.0000015	<1.000
Zinc	Zn	0.0003	0.000001	<1.000
Cuprous	Cu	0.0001	0.000001	<1.000
Molybdenum	Mo	0.00005	0.0000003	<1.000
Cobalt	Co	0.000002	0.000000005	<1.000

Chemical products

1. Algaecides. Recommended to be used as the effective derivative of copper products on the surfaces covered by algae for their fast reaction. A mixture is uniformly sprayed over the infested water surface, preferably on a calm sunny day. The heavy infestations were treated, but only for small surfaces, in different stages, at intervals of 5-7 days, with rest between treatments as to avoid the oxygen depletion. The re-treatment during the growing season is required, and it is most efficient if it is used when a new growth cycle begins. In the hydropower lakes, *this solution could not be applied,* due to the water use, as supply for the population.
2. Herbicides – Represent an effective systemic solution for the control of the aquatic vascular plants. This solution is effective when the water flow and discharge are

minimal. The application is easy, by discharging into the water body at several locations. During the application plants should be actively growing, with the water temperatures above 15^{o}C. Moreover, the solution does not destroy algae and some other species. In many countries, this solution *is completely forbidden.* In the hydropower lakes, this solution could not be applied, due to the water use, as supply for the population .

Biological additives
Generally, the use of bio-augmentation inhibits algae growth, reduces odors, and reduces the sludge deposits while improving the water quality. These highly concentrated cultures of naturally occurring microbes destroy the algae. This solution, as the previous ones, could not be applied, due to the water use, as supply for the population. The solution was tested ten years ago in the lake but the Commissions of the Environmental Protection and of The Commission of Public Health have rejected it immediately.

Mechanical control
There are two different solutions:
1. Harvesters - remove the plants from the water and restore the water quality problems associated with a partial decay of the cut plants. These machines, after cutting, may remove the vegetation from the water with a conveyor system, and dispose of the collected plants onshore. They operate in depths of about 1 m. Some of them are large enough to haul up to 13 tons of vegetation. Densely packed, the aquatic vegetation can weigh up to 200 tones for a lake with a surface of 100 m^2. Sometimes, it is necessary to separate the shuttle barges from the harvester with an additional boat for the matter transport to the shore, while the harvester continues to work. Unfortunately, the machine also kills the fish, amphibians, reptiles, birds, and other wildlife by including them in the harvested material.
In the lakes Pangarati and Vaduri, considered for application, this solution cannot be applied; the lakes are Legal protected by the Decision 1266/2000. They were declared RAMSAR sites in 2006, included in Nature 2000 based on the EU Birds Directive, having the RoSPA0048 code.
2. Rotovator - uses the rototiller with blades to collect at 0.5-0.8 m of the bottom water, by extracting most of the plants. They are primarily used for plants that have buoyant roots, crowns. The loose floating plants and with roots are then collected and removed by an attachment to the machine, by the harvester, or by hand. Rotovators can clean large surfaces per day. Most often they should be used in winter or during spring when the plants have died. The control generally lasts two of the growing seasons. Rotovation is expensive and has large dimensions. The machines are difficult to be handled, consequently the bottom obstacles are problematic (as the rocks or in the areas where the bottom of the lake is variable). The rotovation severely disrupts the sediments, and can produce negative environmental impacts such as increased water turbidity, the release of nutrients from the sediments, the release of the toxic residues bound in the sediments, and disruption of the bottom dwelling of the aquatic animals, for fish, the spawning, and the migration. There are many countries where rotovators are not used. In the mentioned lakes, this solution cannot be applied; the lakes are Legal protected by Decision 1266/2000. The mechanical solutions are

expensive and not efficient. Shortly, the floating vegetation develops new roots and starts a new cycle, being stronger than before and in a larger number (as grass cut in one-year next year is getting stronger, denser). Generally, the natural species are developing in natural rhythm; the invasive species grow faster.

The Carp of grass
The solution was tested by importing some carp species from China. The control and the use of such biological solution it is not well tested worldwide. In Romania, the solution was not efficient. Populating lakes with such fish was tried twice in Romania. They need an almost constant temperature to survive, of around 18-24^{0}C. In the mentioned lakes, for more than 7 months/year the temperature is around 10^{0}C and generally, the surface freezes in winter; in these conditions, the fish died.
It was, therefore, necessary to find another solution, accepted by all users and without disturbing the environment.

Results and Discussion

The proposed solution is ecological and efficient, consisting is bottom barriers. Each panel is formed from three subsidiary ones, covering a surface of 72 m^2. There are three years since the solution is tested with favorable results, for the water depth of 2-4 m, the main area where the vegetation grows. Such barrier or benthic barrier covers the sediments and the vegetation roots as a blanket, compressing the aquatic plants, and blocking light almost totally. The material that was used is Texel, a special material, a heavy plastic, used especially in highways; nowadays it has a new destination. In Fig. 1 one barrier is presented during transport, at the testing area the Lake Pangarati. The solution is compact and easy to be transported, manipulated, being modulated.

Figure 1. The bottom barrier

When the barrier is placed over vegetation must be checked that the natural water current or different animals do not move the panels. It must be anchored at corners, and at least in six other places. In order to decrease the final costs local stones are used as anchors, by being placed in special realized bags, from the same material (Texel). In order for the solution to be efficient, the material has to be black or dark material as to assure the impossibility of light penetration. The Texel is black. The time period for each lake bottom segment was selected at the beginning, of three weeks. The first barrier was made of compact material. In short time, due to the vegetation, which is "suffocated," large gas bubbles appeared, which couldn't be evacuated. On a routine inspection, the damages were observed. Initially, it was thought that some water animals destroyed the barriers. Only later, in an area where the released gases were still accumulated during the routine inspection and the barrier was entire, the cause of the damage was determined. In a second phase, the barrier was realized with many holes, as in Fig. 1-b. Time proved that the adopted solution is correct. The orifices must be small enough, to not let the light enter and to allow it to grow through the orifices (otherwise in time it will destroy the barrier) but large enough to let the gases to be evacuated at the lake surface.

This method may be used even from the beginning of the vegetation, early in March (Figure 2) especially for Elodeea Canadensis (the mainly developed aquatic plant) until the end of the November.

Figure 2. Image from the first site

In hydropower systems the massive vegetation appears at shallow waters, from the shores until 3-4 m. A boat and two divers carried out the barriers transportation. The first barrier was placed at the beginning of May 2014 and was left in the same position for a month. During the time it resulted that for May-June the barriers should be maintained in the same position for 3 weeks; during July-October the necessary time-frame is of one month (the vegetation already have grown and longer time is necessary for it to be destroyed). In this time, even the Elodea is destroyed. An area with a large amount of vegetation was selected. After a week, the first photos were made. Moreover, where the barrier was fixed, the vegetation changed its color. It does not grow, and it is not developing like into the rest of the lake. In June, the barrier was transported to another location. Once the anchors removed, the barrier floats at the surface. It is important to know the area of the barrier's influence. Through the barrier's holes partially destroyed vegetation appears. In Fig. 3-b, c the former vegetation, collected from the vicinity of the barrier is presented. The vegetation lacks roots and the color has already changed, the vegetation has another aspect, it is not fully green as a month before, and it became brown in many places, destroyed.

Due to the holes, the emanated gases during the decomposition process were evacuated, and the barrier looks well (Figure 3-a). After three weeks all types of plants have been suffocated and transformed in mud, due to darkness and the high temperature developed under the plastic material of the barrier (Figure 4-a). Even for a few meters around the barrier the vegetation is partially destroyed. The places where the barrier was installed are marked, in order to observe if next year the vegetation reappears. In places without the barrier, the vegetation grows normally. A massive amount may be observed, increased up to 20-30 cm of the surface. Basically, the divers fail to lift the arms with the vegetation that they can gather, in one motion (Figure 4-b).

Figure 3. Vegetation partially destroyed after one week

Figure 4. Images with and without barrier

In Figure 4-c, an image taken two months after the replacement of the barrier from the initial place is presented. During this time, the vegetation didn't develop, remaining destroyed. In the area where the barrier was placed, a small amount of water free of vegetation can be observed (Figure 4-c).

Conclusions

The solution was developed and implemented in silted lakes at a rate of more than 80%, in order to restore the ecological balance, without disturbing the environment. The solution is environmentally friendly meaning it does not affect the water quality. Under these circumstances, it can be used in the hydroelectric lakes where are catchments for water supply for cities and villages.

For the mentioned areas there are no other known classical solutions that could be used to control vegetation growth. In the areas where the bottom barriers were placed, in the following two years the vegetation didn't reappear, so basically a lake with clean water remains. This means that even the seeds have been destroyed. In a period of three - four weeks an area of about 100 m^2 has cleaned, which remains clean at least for two years. There appeared no new development of aquatic vegetation. Using this solution boosted the fish regeneration, consequently of the animals that inhabited near water. No other solution with the same efficiency and with so low costs is known to date for this cases.

Acknowledgements

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NEW SOLUTIONS IN RECALIBRATION OF RIVER BEDS IN NATURAL CONDITIONS, CONFRONTED WITH REPEATED FLOODS

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Abstract

Due to irrational exploitation of water reserves from some hydropower systems and due to improper maintenance of the natural river beds, in present days, in conditions of abundant rainfall, the whole area into river vicinity are in a real danger. The present paper is dedicated to estimate the real capacity of transport of natural riverbeds in permanent correspondence with the zone reality during and after repeated floods. A numerical model based on experimental measured local data is elaborated. In these conditions in 2005, 2010 and 2012 in the Siret basin, on Bistrita and Cracau rivers area, nine floods considered major were mentioned, followed by human victims, lost animals, and huge terrains under water for more than five weeks. First is presented an actual documentation concerning the situation of functioning, producing, transport and exploitation of hydro systems from the affected areas, based on local experimental measurements. A new numerical modeling of the free surface water flows is realized, taking into account the possibility of permanent changing of lateral surfaces (river beds) during floods, due erosion and sediment transport. It must be considered that during the floods may appear also zones with uncontrolled deposition of the moved and transported sediments. Finally, an optimum management of the flow rate on short and medium term, to assure the environmental protection of the affected areas and some conclusions are mentioned.

Keywords: *environmental protection, measurements, numerical modeling, repeated floods, sediments transport*

Introduction

In Romania, in the past 20-25 years was no complex plan for ecological and energetic rehabilitation for riverbeds, channels, and their vicinity realized. Considering the last decade, for the analyzed area (Siret basin) some places, more or less the same, are confronted with repeated floods. In 2005, 2010, 2015, and even 2017 twelve floods have been registered, nine of them considered critical. Moreover, in time, constant modifications of the riverbeds are recorded. Punctual erosions, followed by uncontrolled of sediments deposits elsewhere, coastal slides, have turned those zones in areas at risk (Nistreanu & Nistreanu 1999).

The EU laws concerning environmental protection impose that after every special hydrological event (for floods are dedicated four paragraphs) a rehabilitation of the entire affected area should be realized. If not, secondary phenomena appear, harder to be controlled. In time, without a management plan, for short or medium term, as to assure optimal ecological and safety energetic power conditions, the entire environment is affected.

There are places near the analyzed area where meander phenomena, sediment deposits, or uncontrolled coastal erosion appear, which in time lead to landslides, followed by the roads, houses, and agricultural terrains destruction. Years 2005 and 2010 are considered to have values way over the annual average from a hydrologic point of view, followed by floods, human, and animal losses, and severe material damages: houses, bridges, agricultural lands, and forests. In 2006, two severe ecological accidents have been recorded, due to cyanide leak from the settling basins in the water treatment plants. The phenome was followed by long-term environmental perturbations, with over-border pollution. It took approximately 2 months to reach the water, in the Danube Delta. The fact that most of the rivers from Moldavia area are part of the Siret hydrographic basin, reaching finally the Danube shouldn't be overlooked. At the current moment, the analysis of the natural rivers beds' transport capacity is only realized in areas with massive destruction and serious damages. Any technical research of the entire area, analyzing the phenomena in the whole basin, inter-connected, hasn't been carried out. Nowadays the international commitments impose complex analysis and arrangements for the entire hydrological basins.

The numerical model of sediment transport, consider the mass balance of the incoming and outgoing sediments. Consequently, considering the cross-sections, an action plan for tracking the changes of the geo-morphological basin can be estimated. It solves a recent problem, due to the actual conditions, regarding the flows in natural or critical regimes (high waters or lasting drought) in near vicinity of areas affected by repeated floods (Radulescu & Nistreanu 2004). By knowing the flow rate, by direct reading from the measurements sections, establishing the risks zones far away from the river borders will be possible.

Materials and Methods

Set in the Cracau – Bistrita Depression, the analyzed area, respectively Pangarati - Vaduri - Reconstructia is characterized by a continental climate. In terms of the climate, Neamt County has a specific climate, typical for plains and meadows. The main features of the microclimate are the following:

- The annual average temperature: 8.5°C,
- The average January temperature: - 4.5°C, due to the cold air coming from the north and east part to the lower areas,
- the average temperature in July is 20 ° C; can be explained by the possibility of hot, continental air circulation, especially from the South and East part,
- The relative humidity: 80%,
- The average annual rainfall amounts: 500 - 600 mm,
-The greater variety of precipitation is in July – November; the precipitations are higher than on the plateau, the annual average precipitation quantity in the hot season is 450 mm,
- The average wind speed at 10 m height above the ground: 3 m/s.

Bistrita River has springs that start in the southeastern part of the Rodna - Ineu mountain and the northern Călimani massif, gathering the water from the Dorna Depression. Bistrita was the first river entirely designed and engineered on the middle and lower course, and was built during 1951-1960. Bistrita is a tributary of the Siret, with an average flow rate of 45 m^3/s, over a length of 125 km, resulting in a vertical difference of 372 m and average energetic potential of 1200 kW/km. The dam of the Mountain Spring lake makes the multi-annual flow rate regularization. The minimum flow rate increases from 0,4 x Qm during the dry years to 0,7 x Qm in normal years. In Table 1 flow rate measurements carried out during a year in 5 measurement points are presented. The 12 hydropower plants on River Bistrita, downstream the Bicaz plant to its confluence with Siret River have a total installed capacity of 244 MW with and an energy production of 918 mil. KWh. The Mountain Spring Dam Catchments cover 4070 km^2, with a significant hydroelectric potential.

The analysis was accomplished based on in-situ measurements, taken from more than 60 places crossing the rivers Cracau, Bistrita, Siret, on both sides, during 2006-2016. The obtained hydro-chemical data prove the fact that the sediments are moved more than 45 km during a flood as the ones from the spring of 2005 (MacDougall 1993).

Table 1. The average flow rates measured values Q [m^3/s]

Sections / Q [m^3/s]	**SH Carnu**	**SH Pangarati**	**SH Vaduri**	**SH Piatra Neamt**	**SH Bacau**
X	27.96	33.25	33.52	33.85	37.99
XI	26.42	30.99	31.23	31.50	40.40
XII	21.48	25.36	25.57	25.81	33.83
I	17.96	21.25	21.38	21.59	28.49
II	18.13	21.46	21.63	21.85	27.05
III	32.11	38.41	38.77	39.19	44.61
IV	80.30	97.35	98.11	99.28	107.17
V	92.21	109.53	110.47	111.55	118.18
VI	73.15	87.65	88.41	89.34	96.22
VII	59.37	70.91	71.49	72.22	76.38
VIII	43.96	52.56	53.02	53.56	57.15
IX	33.10	39.51	39.85	40.29	41.87
Annual Average	43.85	52.35	52.79	53.34	59.11

An update of the flow characteristics of the interest sector was made considering a characteristic hydrologic period of 50 years (1960-2010). The values used in the study were based on the measurements made at Carnu, Pangarati, Vaduri, Neamt, and Bacau stations. These values were processed by the known statistical methods and insurance curves were drawn.

The calculated average annual flow of river Bistrita during the mentioned period is of 43.85 m^3/s at Izvorul Muntelui, 52.35 m^3/s at Vaduri, 53.34 m^3/s in Piatra Neamt, and 59.11 m^3/s at Bacau section. Lake Pangarati is the first lake from the analysis area, and provides partial regulation of the flow for the entire river basin. Lake Piatra Neamt is designed to assure the flow for the upstream turbine Q_I = 180 m^3/s, and for the downstream at Q_I = 84 m^3/s, where Q_I, is the installed flow rate.

The seasonal and annual adjustment possibilities of the Izvorul Muntelui accumulation leads to a redistribution of the water volumes, in different floods schemes, during spring and summer to a reduced leakage, at autumn and winter, for Pângăraţi Lake. The year 2005 was a year with large hydrologic variations from a month to another. Before July 12, due to the occurred floods, a bridge of large woods formed (inserts having even 60 cm in diameter). In these circumstances, in order to destroy the "bridge", the downstream power plants were stopped (Vaduri and Batca Doamnei). On August 12, another flood changed the main river flow channel (Figure 1). In Fig. 1 - the erosion and deposition of sediments can be seen, having as effect the main river course altering. On September 22 a new flood was registered. The water evacuated from the hydropower lakes, Fig. 1-b covered in large land areas downstream, Fig. 1-c. In Fig. 2 images from February 2017 and in April 2017 are shown. In these conditions, the average hydrological data, taken from the previous years (1997-2002) became just informative, without any relevance.

Figure 1. Images during floods in 2010

In many days of 2005-2006, the rainfall exceeded the annual average. In 2007, the average was within the features of the dry years. The period from May to August, was considered the driest of the last 40 years. For the first time in Romania, in the summer months, code red has been established, as well as code orange during two months (July-August). Next years, until 2010, they have similar structures as dry years.

In these conditions, massive deposits of sediment appeared in the wider areas of the river cross-sections, where the flow rates are lower. In 2010, there were large quantities of water from snow melting, and the floods occurred. They repeated each time when the rainfalls were more abundant.

Even this year there were floods in the Siret valley (Figure 2). In the analyzed sector, the riverbed Bistrita generally provides a flow easement of 2.8 m^3/s. This flow is maintained until the river Bistrita meets Cracau River and the flow rate increases with an average of 2 m^3/s.

A particular interest is represented by the upstream hydrological regime.

In fact, the hydro channels III, IV, V, and VI, are a constituent part of the basin hydrological Bistrita. The characteristics are directly influenced by the upstream sector due global leakage, floods, the water chemical composition. It has a major impact, through both its specific construction and by its functional characteristics. By analyzing the water supply from the natural intakes and the precipitation, and the consumption and losses, it is possible to estimate the hydrologic stability. The water balance is a possibility to estimate the water reserves.

The monthly average flow has the highest values in the warm season of the year, primarily between the months of March to October, but mainly from April to August. It is achieved when 85% (or 70%) of the annual average flow is reached. From the statistics of the past 20 years (except 2005 and 2007) 18.4% was achieved in July and 16.2% in August. In winter, November to February, the rates drop considerably, reaching a minimum 0.212 m^3/s in January, representing about 2.3% of the annual average.

Figure 2. Images during floods in 2017

The hydrologic balance represents the difference between lake effluent and evaporation. Generally, the evaporated water is compensated by the precipitations fallen directly into the lake. If we consider the ratio of precipitation and evaporation, it results that these lakes belong to an area with excessive humidity. The seepage losses can be located as more important in the downstream left bank of the Bâtca Doamnei accumulation, built in the embankment. It also influences the clogging, by deposition of the suspended material entrained during the floods (Seteanu, I et al. 1998).

Results and Discussion

The numerical model analyzes the unsteady free surface flow rate in rivers with natural riverbeds, considering the sediment transport balance (entered, transported or deposited). The cross sections have arbitrary shapes. For the study case Cracau river was selected (Ackers & White 1993).

It has an average flow rate of 2 m^3/s, but sometimes in spring the flow rate may increase at 45 m^3/s (registered in 2005). Eight cross sections were measured during the 2014 campaign, representing the basis for the simulations. As it may be observed in Figure 3-a, cross-section numbered 2, in the left side of the riverbed there is practically no shore.

Here it is obvious that at high flow rate values, flood may appear and rehabilitation is necessarry. Some cross-sections, for five profiles are presented in Table 2 (Seteanu & Radulescu 2004).

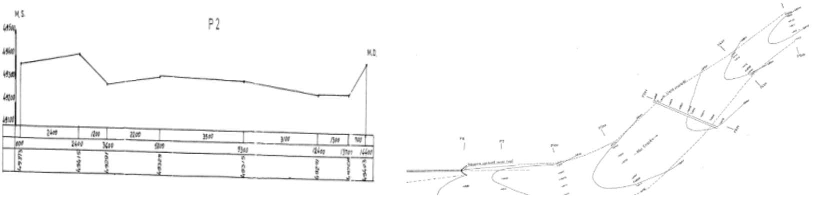

Figure 3. Cross-sections into the riverbed Cracau

In Table 2, x is the horizontal coordinate, measured from the right shore to the left one and y is the altitude, reported to the sea level. An example is presented in Fig.3-a. For Cracau River, there is no database containing long term flowrate values. The maximum values selected for Siret River, Table 3, are correlated with the statistical calculation for hydrograph floods, for Cracau river (Guangqian et al. 2008).

Table 2. The coordinates in cross-sections on Cracau river

Profile 1av		Profile 2av		Profile 3av		Profile 4av		Profile 5av	
x	y	x	y	x	y	x	y	x	y
0	491.06	0	490.33	0	489.88	0	488.31	0	487.43
2	490.14	3	489.53	10	489.78	1	487.02	3	486.25
15	490.25	20	489.93	26	489.23	6	487.32	7	486.45
20	490.86	23	489.27	43	489.27	23	487.52	13	486.95
25	490.73	32	489.38	57	489.08	28	487.09	15	486.45
36	490.46	60	489.3	61	488.24	31	487.82	20	486.51
50	490.14	66	489.58	77	488.37	36	487.87	30	486.81
60	490.87	72	490.1	81	488.04	40	488.31	42	487.65
64	492.1	78	490.07	93	488.09				
		84	490.92	109	488.98				

Table 3. Values of Q_{max} on Siret River

Year	Q(m^3/s)	Year	Q(m^3/s)	Year	Q(m^3/s)	Year	Q(m^3/s)
1970	3186	1983	1420	1996	1612	2009	1984
1971	1966	1984	2460	1997	1040	2010	4470
1972	1842	1985	1400	1998	1380	2011	3872
1973	1535	1986	334	1999	830	2012	2480
1974	1260	1987	275	2000	447	2013	1972
1975	1860	1988	1620	2001	435	2014	2257
1976	630	1989	1370	2002	2200	2015	4680
1977	889	1990	275	2003	796	2016	3342
1978	1320	1991	3270	2004	727		
1979	1280	1992	2045	2005	4650		
1980	989	1993	1020	2006	1375		
1981	2040	1994	604	2007	785		
1982	901	1995	1120	2008	2068		

The mathematical model used in the calculation scheme considers as data necessary for numerical modeling:
- The initial cross-sections profile through the rivers beds (Figure 3-a),
- The distances between the sections and the geographic variation of altitude (Figure 3-b),
- The roughness of the river beds on the analyzed distance,
- The maximum flow rate, the floods hydrograph,
- The time evolution of sediments, concentrations, and dimensions.

In each analyzed section the entered and the transported sediments to the next section were considered. Balances for the deposited sediments are made and appear into the final form of the cross-sections.
To simulate the real, natural flow, it is necessary to know the physics of the phenomena, to establish the significant parameters and the relations between them.
Further, in Fig. 4 some results obtained in the cross-sections are presented.
The areas where sedimentation appeared are mentioned, as well as the erosion sones. Eight cross-sections were considered. For each one the free surface level was determined, in 4 cases of transported flow rate with 10%, 5%, 2% and 1% assurance. In Fig. 4 the results of Sections 2, 4, and 5 at flow rate assurance of 2% and 1% are presented.

In Section 2, the flow channel is deeper than at the beginning. In Section 4 a sedimentation zone appears. Some deposits create an island. The active flow section decreases. In Section 5 two flow channels appear due to the accelerated erosion.

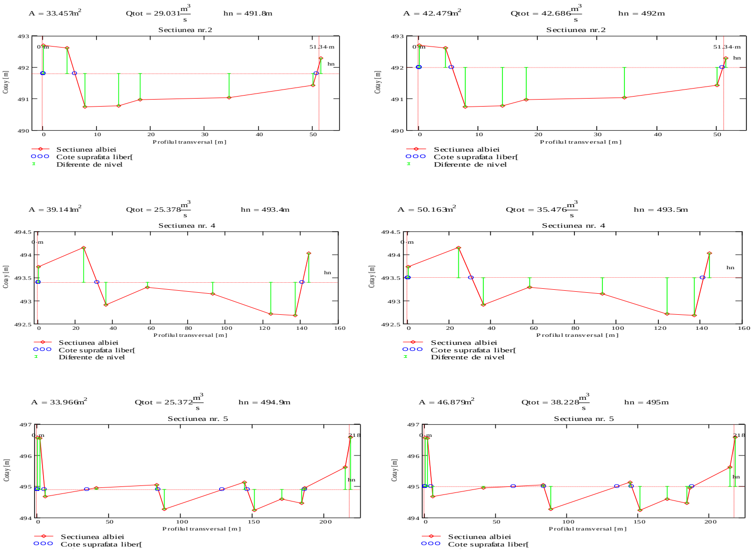

Figure 4. Results into Sections 2, 4 and 5 at two flow rates

For each section the sediments balance was determined. For each flow rate four cases of the roughness were considered. In three case, sedimentation appears on the left shore, especially in sections 5-7. The importance of knowing the exact sediments dimensions must be mentioned. Due to this parameter, during the same flood, in some cross- sections sedimentation appears and in others erosion.

Conclusions

The sediment transport is a current concern related to water management, a complex spatial planning of environmental protection. How this process unfolds, the phenomenon scale, the large significant number of parameters, the direct and indirect practical consequences, having as result often damages, requires the use of computational tools to enable qualitatively forecasting of the sedimentation process. Siret River catchments area was analyzed, well known for the problems concerning the repeated flooding. The numerical model analyzes the free surface non-permanent flow in variable cross- sections of arbitrary shapes. Riverbed-fluid interaction is modeled by three relations referring at the size fractions in the bed before the change of the area of influence, the liquid stream movement transported to the solid phase and the global recovery.

The weights of the initial particle sizes were chosen in accordance with the obtained data from the in-situ measurements. The available data for the solid flow highlights the strong character of the alluvial riverbed of the River Cracau. There is a significant suspensions weight with an excess of small diameter fraction (cvasicoloidal, 0.002 mm). Further sedimentation tendency of the bed, with a surplus of deposits in sections 5-7 appears. A lateral plugging is observed along the valley. It is expected that clogging will continue to evolve, being accompanied by new meanders and islands formation, as a result of solid stock agglomeration in the local concentration points (the induced vegetation increased in some areas).

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I would like to thank my colleagues from the SC Hidroelectrica SA, who presented me the problems appeared into the Siret basin, on Bistrita and Cracau Rivers, and supported me into physical measurements of the cross-sections, necessary to calibrate the numerical model.

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STUDY ON ELECTROMAGNETIC WAVES AND THEIR EFFECT ON THE ENVIRONMENT AND POPULATION HEALTH

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Abstract

Electromagnetic fields (EMF) are a combination of invisible electrical and magnetic fields of force. EMF is present in all places where electricity is used and surrounds every charged electric object. The impact of the electromagnetic field on the environment and people's health has begun to awaken more and more the interest of research in this field. This is due to the widespread development of various devices that emit electromagnetic waves on different frequencies. This paper presents comparative studies on the level of electromagnetic waves. Determinations have been made both at source so as to highlight the dispersion of electromagnetic waves and their effect on the population in the studied area.

Keywords: *electromagnetic field, electromagnetic waves, frequency, source*

Introduction

The exposure of live organisms to electromagnetic field generating equipment and devices has steadily increased in recent years, given the increasing number and power of these facilities and devices. The human body has developed different adaptation mechanisms, but exposure to high radiation and long periods of time may pose a health hazard. Many people claim sensitivities such as headaches, insomnia, depression or lack of concentration due to the influence of electromagnetic radiation on the human body. Many research shows that exposure to electromagnetic fields does not pose a health risk, but there are still many controversies and limitations in knowing the long-term negative influences. (Magureanu 2003; Marin et al. 2017; Marin et al. 2015).

What we can say with certainty is that we live in a radiation environment. Thus, there is a natural level of radiation but also secondary and artificial sources with the same effect on health. Knowing these effects is absolutely necessary for the development of biological protection conditions. The probability of occurrence of any effect is in direct correlation with the radiation dose received (Mai 2011; Bucur et al. 2016; Bucur et al. 2017) .

Electromagnetic waves are transversal waves with two components: a magnetic component and an electrical component, the electric and magnetic vectors being perpendicular to each other and to the propagation direction.

Non-ionizing radiation covers the visible spectrum up to very low-frequency radiation (ELF- Extremely Low Frequency) such as waves produced by base stations of mobile telephony, are non-ionizing radiation (Zagar et al. 2014; Albert et al. 2005; Bernhardt 1992).

It is recognized that exposure to non-ionised electromagnetic fields in the 300 MHz to 300 GHz range is unfavorable to human health. (Vijayalaxmi & Scarfi 2014; Heynick et al. 2003; Meltz 2003; Vijayalaxmi & Prihoda 2008; Verscha 2009).
The data presented in the paper are part of a larger study dedicated to assessing the level of electromagnetic radiation emissions and the possible effect on health and it includes the results of the tests performed in two areas characterized by two distinct sources emitting electromagnetic radiation on different frequencies.

Experimental

Location
The tests were conducted in two locations located near electromagnetic radiation sources: a GSM antenna Fig. 1-a and electric power transformer station Fig. 1-b located in residential areas of Bucharest. The determinations for the electromagnetic radiation level were made near the source for the case of the source 1- Fig. 1-a and also for the case of the source 2 – Fig. 1-b the determinations were made in two directions: magnetic field determination in the direction (A) without attenuating wall and magnetic field determination in direction (b) with attenuating wall as shown in the sketch of Fig. 2.

(a) (b)

Figure 1. The two sources for which electromagnetic radiation determinations have been made

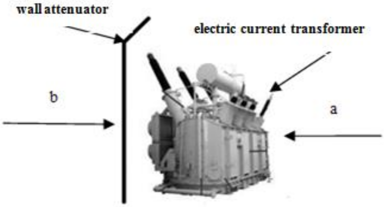


Figure 2. Outline of magnetic field determinations

Measured methods, equipment and indicators
In order to determine the level of electromagnetic radiation measurements were carried out respecting the requirements of the regulations and the standards in force (Romanian standard 50364:2010), (Romanian standard 50385:2003) (Government

decision 520/2016), (Government decision 1136/2006), (Government decision 1193/2006).

In order to assess the exposure of the human body to electromagnetic radiation, the most relevant parameters are the intensity and the power of the radiation. Exposure coming from multiple sources, power will be a result of the powers of the fields that propagate in several directions. To measure the power of the electromagnetic field, SPECTRAN HF 60105 was used to measure high frequency electromagnetic radiation (GSM mobile antenna) and SPECTRAN NF 5035 for measuring low frequency electromagnetic radiation (Figure 3) with specific detection sensors.

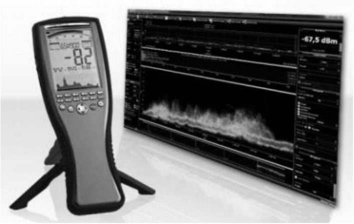


Figure 3. SPECTRAN NF 5035 Analyzer for Electromagnetic Wave Power Measurement

According to the relation (1) the amplitude of the electric field of incidence is the result of the vector composition on the three axes (Figure 4):

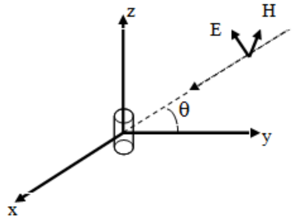


Figure 4. Sketch of the triaxial sensor of the SPECTRAL analyzer

$$|E| = (E^2{}_x+E_y{}^2+E_z{}^2)^{1/2} \qquad (1)$$

E is the amplitude of the electric field of incidence and θ is the angle between the sensor axis and the electric field direction, the detected signal is proportional to $| E | \cos \theta$. The overall amplitude of the field is expressed as:

$$|H| = (H^2{}_x+H^2{}_y+H^2{}_z)^{1/2} \qquad (2)$$

In the case of the magnetic field, it is characterized by two parameters: the field strength (H), which is measured in A / m and the flux density (B), which is measured in gauss (G) and tesla (T).

$$1T = 1(V*s)/m^2 \qquad (3)$$

(V =volt, s =second, m = meter), (5 October 2011)

Measurements were made under the following conditions: the 200 kHz resolution band; Scanning time 250 ms; 1MHz frequency step; Detector distance from the reference plane 1.5m. Table 1 lists the magnitude reference values for the electromagnetic field in the frequency range 0-300Hz considered dangerous for the human body.

Table 1. Reference levels for parameters characteristic of electromagnetic fields

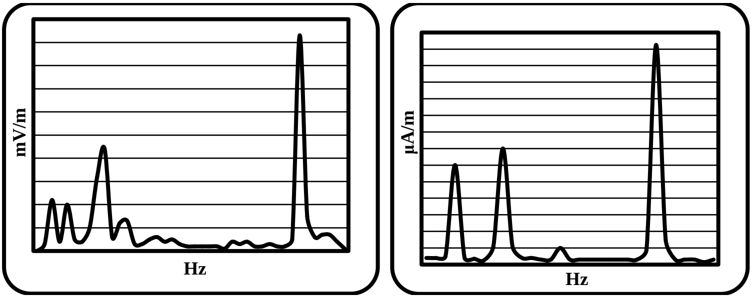
Frequency range	Intensity electric field E(V/m)	Intensity magnetic field H(A/m)	Magnetic induction B (μT)	Power Density for Equivalent plane wave Seq(W/m2)
0-1 Hz	-	$3,2*10^4$	$4*10^4$	-
1-8 Hz	10000	$3,2*10^4/f^2$	$4*10^4/f^2$	-
8-25 Hz	10000	4000/f	5000/f	-
0,025-0,8 kHz	250/f	4/f	5/f	-
0,8-3 kHz	250/f	5	6,25	-
3-150 kHz	87	5	6,25	-
0,15-1 MHz	87	0,73/f	0,92/f	-
1-10 MHz	87/f	0,73/f	0,92/f	-
10-400 MHz	28	0,073	0,092	2
400-2.000 MHz	$3f^2$	$0,008f^2$	$0,01f^2$	f/40
2-300 GHz	61	0,16	0,20	10

*f – frequency, Hz

Results and Discussion

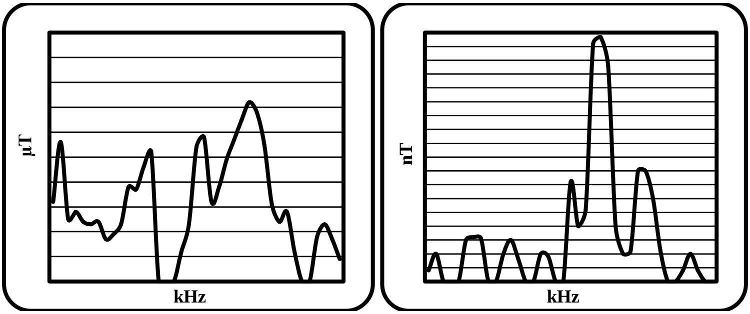
The values of the electromagnetic field measurements for the source 1, respectively the mobile antenna, are shown in the diagram in Fig. 5-a and 5-b. Characteristics: tower 20 m height and antenna power 60 W. Measured parameters: electric field intensity E (V/m) and intensity of magnetic field H (A/m). Also the maximum peak values for the two measured parameters are presented. Fig. 4a shows the intensity variation of the electric field, E function of the frequency, measured at the source. A maximum value determined for the field strength of 99.30 mV/m at a frequency of 953.5 Hz is observed. Calculating the reference level for the f=900 Hz frequency according to the relationship in Table 1 gives the value of 41.25 V m.

Fig. 4-b shows the intensity variation of the magnetic field H. In this diagram, a maximum magnetic field strength of 268.9 μA/m is observed. Calculating the reference level according to Table 1, a value of 0.111 A/m is obtained as the magnetic field exposure limit value. Thus, the values determined for the field strength and the magnetic field strength measured at the GSM antenna source are below the reference level calculated at the 900Hz frequency according to Table 1. For source 2 determinations for induction of magnetic field are shown in Fig. 6-a without attenuating wall and Fig. 6-b with attenuating wall. Also in Fig. 7-a and 7-b the magnetic field dispersion for the studied source 2 is presented.



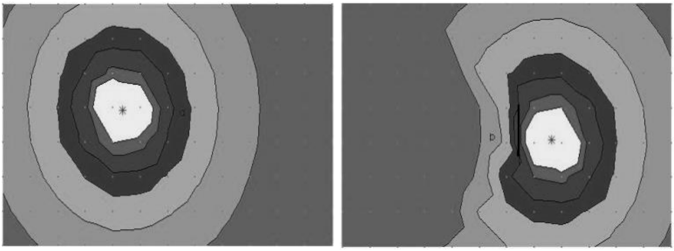
(a) (b)

Figure 5. Variation of the intensity electric field (a) and intensity magnetic field (b) at the GSM antenna



(a) (b)

Figure 6. Frequency variation of magnetic field intensity for the two situations at source 2 without attenuating wall (a); with attenuating wall (b)



(a) (b)

Figure 7. Mathematical modeling of the magnetic field dispersion according to frequency for the two situations at source 2 without attenuating wall (a); with attenuating wall (b)

It is observed that in the case of determining the induction of the magnetic field at the electric transformer source, for the case (a) without attenuating wall a maximum value of 7.2 μT was obtained at a frequency of 50 kHz so it is a value that exceeds the level for the 3-150 kHz range according to Table 1. When determining the attenuator wall point (b), a magnetic field inductance value of 442 nT resulted in a value below the reference level according to Table 1.

Conclusions

Today's world is subject to an ocean of electromagnetic waves due to a large number of sources of radiation both in and outside homes. The sources studied in this GSM antenna paper and electric current transformer are sources that the electromagnetic radiation emitted may affect the health of the people in the area. Thus, in the case of the GSM antenna, measurements were made to determine the level of electromagnetic waves at the base of the source. The intensity of the field and the intensity of the magnetic field were determined. Also, for source 2, the magnetic field intensity was measured in two directions with no attenuating wall and attenuator wall and the results were compared with the reference level presented in Table 1 and calculated at the frequency at which the determinations were made. Thus, for the source 1 for the 2 parameters determined, values below the reference level calculated according to Table 1 were obtained since the GSM antennas are mounted at a height of about 20 m so that it can not affect the population due to the electromagnetic radiation. In the case of source 2, according to the diagrams in Fig. 6, a high high level of 7.2 μT at a frequency of 50 kHz exceeding the reference level in Table 1 for the case of attenuating wall determinations is observed. Measurement in the attenuator side caused 442 nT values to be below the reference level according to Table 1 so that it is useful to construct this attenuating wall between the power transformer and the living quarters.

Acknowledgements

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THE ASSESSEMENT OF DANGEROUSNESS OF WASTE. CASE STUDY: WASTE ORIGINATING FROM DRILLING MUDS

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Abstract

This paper continues the presentation of the case studies on waste dangerousness assessment. Due to the particularities that shows many of the waste generated in industry, in particular, each analysis represents a special case. The application of the methodology for determining the dangerousness of waste (carried out and used by our institute, still in the absence of rules for the implementation of legislation on waste management), often faces challenges regarding the estimation (with an error as low as possible) of the concentration for the potential components from the waste, necessary to establish the hazardous/non-hazardous character of the waste and, implicitly, for its correct classification in the waste list. In this respect, the case study presented is that of a waste from drilling muds.

Keywords: *hazardous, quality assessment, the waste classification, waste*

Introduction

In order to determine the dangerousness of a waste and to classify it in the European Waste List, first must be sought out a waste stream, in the waste list, which matches it unreservedly. If this cannot be established, an in-depth analysis of the waste should be made. Such a case is that of the waste analysed in the present paper, waste from reconditioning mud and for which there are 6 possible entries in the Waste List. The methodology for determining the dangerousness of waste (carried out and used by our institute) includes nine steps (Guta et al. 2013; Arama et al. 2014; Technical Guidance 2015). First step consists in establishing identification data for the sample waste (waste type, the process from which the waste comes from, the obvious features of the waste such as physical state, appearance etc.). Secondly, it is necessary to obtain as much information as we can about the waste, and the third step is to identify a waste stream, typical for the waste in question, in the list of waste. If you can identify, without reserve, a good flow, it is possible to classify the waste without the need for further analysis. If, however, you cannot do this or if it is not sure that the waste is non-hazardous, analysis of the waste is continued. It follows the fourth step which consists in establishing the potential constituents of waste in order to set the indicators to be determined. Analytical determinations of the quality indicators that have been set and their registration is the next step of the methodology; it is very important to correctly determine the quality indicators, but equally important is to have a good sampling program and chain of custody (storage, transport, pre-treatment) for the waste before the analysis.

The sixth step is to identify the risk statements for the waste components; the waste components are determined analytically or estimated on the basis of all information available, and the risk statements - using reliable sources. The last three steps of the methodology consist of: assigning of dangerous properties based on identified risk phrases for the waste components, quantifying the level of hazardous properties and the evaluation of the results.

Materials and Methods

At the basis of the analysis were: the waste sample, on which analytical determinations have been made; information on how the waste is generated; the existing regulations on the characterization and classification of waste.

According to the waste legislation in force (L 211/2011), hazardous waste is defined as any waste that presents one or more of the hazardous properties stipulated in the current legal provisions (namely in Regulation (EU) No. 1357/2014) (R 1357/2014). This Regulation indicates in the appendix the 15 properties of the waste that make it hazardous and regulates the limit values for the HP4, HP5, HP6, HP7, HP8, HP10, HP11, HP13 hazardous properties. The quantification of these properties is based on the concentrations of the components presenting a particular hazard statement, responsible for a particular hazardous property. Concentration levels are compared with limits set by law, and the result of comparison indicates whether the sample analyzed waste can be classified as hazardous waste or nonhazardous. For the rest of the properties, the Regulation either does not provide limit values, or specifies the need for specific testing. Also for HP 1 ("Explosive"), HP 2 ("Oxidants"), HP 3 ("Flammable"), there are mentioned: "If the presence of a substance indicates that the waste is explosive (or oxidising or flammable, etc.), it is classified as hazardous waste type HP 1 (or HP 2 or HP 3).

The waste analyzed comes from drilling mud (recovered - by centrifugation and flocculation - from exhausted drilling mud) remaining on the containers walls~~.~~

Characterization of the waste was done on the basis of:

1. the results of the analytical determinations (the indicators, representative of the analyzed waste, were established based on the analysis of the waste information); in order to demonstrate the importance of the quality of information to identify representative indicators, it should be noted that there were problems with collecting the relevant information because the waste generator had not communicated at the outset that the drilling mud from which the waste originated was obtained by processing exhausted drilling fluids;
2. information on potential chemical compounds in waste and their related hazard statements provided both by the drilling liquids safety data sheets used for the drilling mud preparation, as well as the literature (Chemical Book) and dedicated legislative documents (R 1272/2008).

These data led to estimateing the waste composition, to identify the potential hazards posed by waste / components of waste and to establish the hazardous / non-hazardous nature of waste.

Results and Discussion

The indicators and the results of the analytical determinations for their quantification are presented in Table 1.

Composition of the waste is further analyzed simultaneously with the dangerousness of waste. For the quantitative estimates of the HP4, HP5, HP6, HP7, HP8, HP10, HP11, HP13 properties, the potential compounds in the waste were taken into account. In the present case, they may be components of the materials used in the preparation of drilling mud (presented below), as well as compounds that pollute mud derived from previous drilling muds, assuming that their removal from the mud (through centrifugation and flocculation) can not be done complete.

Table 1. Results of analytical determinations carried out on waste

No.	Indicators	M.U.	Values	Methods
1	pH	Unit. pH	7.2	SR EN 10390 :2015
2	Dry matter (d.m.)	%	95.9	SR ISO 11465:1998
3	Loss of calcination	% d.m.	9.31	SR EN 15935:2013
4	Barium	mg/kg d.m.	412852	SR EN ISO 17294-2:2005
5	Calcium	mg/kg d.m.	16305	SR ISO 7980: 2002
6	Iron	mg/kg d.m.	3721	SR 13315 :1996/C91 :2008
7	Sulfates	mg/kg d.m.	263635	SR ISO 11048:1999, 3.6
8	Chlorides	mg/kg d.m.	400	STAS 7184/7-87, 4.2
9	Carbonates	mg/kg d.m.	< 17	STAS 7184/7-87, 4.1
10	Silicon	mg/kg d.m.	38453	SR EN 15309:2008
11	(TOC)	mg/kg d.m.	71000	SR EN 13137:2002 SR EN 15936:2013
12	THP	mg/kg d.m.	92215	ISO 14507:2003
13	THP C10-C40 Fraction	mg/kg d.m.	14072	SR EN 14039:2005

Taking into account the way the waste was generated, its physico-chemical state and the visual examination of the sample, it is appreciated that the waste does not have the properties (defined according to Regulation (EU) No. 1357/2014 (R 1357/2014) that can induce the HP1 ("Explosive"), HP2 ("Oxidants"), HP3 ("Flammable"), HP12 ("Acid Toxic Acid Release") and HP15 («Wastes capable of developing one of the other 14 defined properties which the original waste does not present directly").

The drilling fluid waste analyzed, according to the information provided by the waste holder, contains mainly two products (synthetic drilling fluids). Safety Data Sheets of these products show~~s~~ the following composition:

- *for Drilling Synthetic Fluid (1)*: anhydrous calcium chloride in a concentration of 4-8%; Quartz (crystalline silica) in a concentration not exceeding 5%; Calcium hydroxide at a concentration of 1 - 2%; Iso-alkanes (42-72%); Barium sulphate (5-25%); Water (7-25%); C10-C18 alkanes (6-24%); Unsaturated fatty acids C14-C18 and C16-C18 (1-2%).
- *for Drilling Synthetic Fluid (2)*: 1-tetradecene ($C_{14}H_{28}$) 14% concentration; Anhydrous calcium chloride 4-8% concentration; 1-octadecene ($C_{18}H_{36}$) 2-3% concentration; Barium sulfate (42%); Water (10-15%); 1-hexadecene ($C_{16}H_{32}$) 5% concentration; 1-dodecene ($C_{12}H_{24}$ 1-2% concentration; Clay (clay) (1-2%); Gilsonite (compound with CAS 12002-43-6, which, according to the literature (Chemical Book) is a resin used as an additive in liquids used in the drilling technique).

In addition to these known compounds, as we have already mentioned, impurities can be found in the waste resulting from the previous uses of the drilling fluids subject to reconditioning. These impurities consist in organic compounds such as petroleum hydrocarbons, as well as other inorganic compounds (other than hydroxide and chloride) based on calcium (silicates, sulfates, carbonates).

Specialty literature indicates for these compounds the hazard statements presented in Table 2. The inorganic compounds possibly present in the waste were quantitatively evaluated based on the results presented in Table 1. This evaluation is synthetically presented in Table 3 and only takes into account inorganic compounds likely to exist in the analyzed waste and which may influence the dangerousness of the waste, based on the arguments presented above.

Table 2. Potential compounds in waste, hazard phrases and imposed limit concentrations that make the difference between dangerous and non-dangerous wastes

Compounds	Hazard statements	Significance of hazard	Limit value (%)
Calcium chloride	H319	Causes serious eye irritation (Eye Irrit. 2)	20
	H302	Harmful if swallowed (Acute Tox. 4)	25
Crystalline quartz*	H350	May cause cancer (Carc. 1B)*	0.1
	H335	May cause respiratory irritation (STOT SE 3: Specific target organ toxicity/aspiration toxicity)*	20
	H372	Causes organ damage in case of prolonged or repeated exposure (STOT RE 1) *	1
Calcium hydroxide	H314	Causes skin burns and eye damage (Skin Corr.1B)**	1
	H318	Causes serious eye damage (Eye Dam.1)**	10
Iso-alkanes	the literature does not indicate danger phrases		
Barium sulphate	H302	Harmful if swallowed (Acute Tox. 4)	25
	H312	Harmful in contact with skin (Acute Tox.4)	55
	H332	Harmful in case of inhalation (Acute Tox.4)***	22.5
	H315	Causes skin irritation (Skin Irrit. 2)	20
	H335	May cause respiratory irritation (STOT SE 3: Specific target organ toxicity/aspiration toxicity)***	20
1-tetradecene	H304	May be fatal if swallowed and enters airways	10
	H319	Causes serious eye irritation (Eye Irrit. 2)	20
1-octadecene	H304	May be fatal if swallowed and enters airways	10
1-hexadecene	H315	Causes skin irritation (Skin Irrit. 2)	20
1-dodecene	H304	May be fatal if swallowed and enters airways	10
	H317	May cause an allergic skin reaction (Skin Sens.1)	10

*) - in this case, quartz being in a mixture in the form of mud, we consider that these phrases of danger are inapplicable;

**) - Because: 1) The pH determined for waste (7.2 pH units) indicates a practically neutral value, which means that the calcium hydroxide, potentially present in the waste, does not induce corrosion of the waste, so it can be assumed that it is found in waste in a small proportion, possibly under the 1% limit; 2) Can not distinguish between the calcium bound as calcium hydroxide, calcium chloride and other combinations such as calcium sulphate, carbonate or calcium silicate (compounds which may exist, along with the synthetic drilling fluid components, in the analyzed mud obtained from the mud already used) - in these conditions, therefore, we can consider that most of the calcium is in the form of chloride, sulphate, carbonate and silicate; because calcium sulphate, carbonate and calcium silicate can induce danger only if it is in a dry state (which is not the case of the analyzed waste), only the calcium chloride was considered in the waste hazard assessment analysis;

[***]) - inapplicable, because barium sulfate is not pulverulent in the analyzed sample.

The results of the waste assessment, presented in Table 3, reveals that both for the property HP4 - "Irritants - skin irritation and eye lesions" and for the property HP6 - "Acute Toxicity" (properties corresponding to compounds in waste that have the potential to induce danger) the limits were exceeded due to the presence of barium sulphate, classified as H315 (Causes skin irritation) and as H302 (Harmful if swallowed) and H312 (Harmful in contact with skin), respectively. Consequently, according to these results and to the definition for the hazardous waste given by Law no. 211/2011 - Annex no. 1, item 11 ("any wastes presenting one or more of the hazardous properties listed in Annex 4 to the Act"), it results that, in relation to inorganic compounds, the analyzed waste constituted from recovered mud is DANGEROUS.

Besides the inorganic compounds, as can be seen from the above description, organic compounds are also found in the waste; their presence in the waste was quantitatively estimated by the TOC (total organic carbon), THP (total petroleum hydrocarbon) and C10-C40 hydrocarbons (without being able to analytically determine the constituent chemical compounds).

Considering:

- the TOC of 7.1% in waste (which translates to a much higher percentage of organic compounds, corresponding to this carbon content);

the value of the THP concentration of 9.2% and the fact that THP is a complex mixture of petroleum products (according to SR-EN 14039: 2005: n-alkanes, isoalkanes, cycloalkanes, alkylbenzene, naphthalene alkyl, aromatic polycyclic compounds; according to other technical sources, petroleum hydrocarbons may include: hexane, benzene, toluene, xylene, naphthalene and fluorene, other constituents of petrol, mineral oils); some of these compounds (such as benzene, toluene) are characterized by hazard phrases that have very low concentration limits of 0.1% - 0.3%);

- the determined value of 1.4% for the concentration of the C10-C40 hydrocarbon fraction from the waste;
- the impossibility of detecting THP constituents by analytical determinations,

Table 3. Data for waste assessment based on analytical determinations and potential inorganic compounds from waste

No.	**Criterion for classification in hazardous waste category, according to Law no. 211/2011 and Regulation (EU) No. 1357/2014**	**Determined element / associated compound**	**Determined element, mg/kg d.m.**	**Associated compound, %**	**Checking the criterion**	**The result of evaluation based on the criteria analyzed**
1	HP4 Property - «Irritants - skin irritation and eye injuries» Total concentration for materials classified as H315 and H319: ≥ 20%	Chloride / $CaCl_2*6H_2O$	400	0.10	**61.57%>20%**	**The waste is irritant due to the compounds with the H315 and H319 hazard statements**
		Sulfate / $BaSO_4$	263635	61.47		
		TOTAL		**61.57**		
2	HP6 Property «Acute Toxicity» Total concentration for materials classified as: H302≥25% H312≥55% H332: ≥22.5%	Chloride / $CaCl_2*6H_2O$	400	0.10	**61.57%>55%**	**The waste shows acute toxicity due to compounds classified as H302 and H312**
		Sulfate / $BaSO_4$	263635	61.47		
		TOTAL		**61.57**		

it follows that THP and C10-C40 components (characterized by danger phrases corresponding to the very low concentration limits - 0.1%, 0.3%, 0.5%) may be found in the waste in concentrations that exceed the above-mentioned concentration limits. In addition, the possible presence of mineral oils in the analyzed waste, irrespective of their percentage in the waste, causes the waste to be classified as an oil-containing drilling mud, thus as hazardous waste (Guidance 2015).

Therefore, by reference to the organic compounds in the waste, there may be at least one dangerous property for which the concentration limit of the compounds possessing that property is exceeded. As a result, again taking into account the definition of hazardous wastes mentioned above, it results that by reference to organic compounds, the waste analyzed is DANGEROUS.

Conclusions

Considering the above considerations, it results that both organic and inorganic compounds can induce danger to the analyzed waste.

In the European Waste List (EWC 2002; CD 955/2014), the entries for drilling muds are in number of 6, of which two are drilling muds with a dangerous character (*oil-containing drilling muds and wastes* and also *drilling muds and other drilling wastes containing hazardous substances*). As it is obvious that drilling mud analyzed contains barium sulphate in a very high concentration, but in addition the waste contains mineral oil, we believe that the appropriate entry in the list of the waste for the analyzed waste is *oil-containing drilling muds and wastes*.

Of the entire analysis presented it follows that the analized waste is dangerous and can be assigned the code 01 05 05* - *oil-containing drilling muds and wastes*.

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THE USING OF PRINCIPAL COMPONENT ANALYSIS FOR THE ASSESSMENT OF WATER QUALITY IN KIRMIR BASIN

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Abstract

Water is one of the most important nutrient for human and also for aquatic organism. Poor water quality has adverse effects on human health and aquatic life. Hence, protecting the water resources from pollutants and the monitoring of water quality is important. In recent years, some kind of methods such as water quality index model, regression analysis, factor analysis, principal component analysis, cluster analysis, etc. has been developed for easy assessment and interpretation of large amount of water quality data. Among these methods, multivariate statistical analysis has an advantage of giving an idea about possible sources of pollution. In this study, the assessment of water quality of 10 different sampling station in Kirmir Basin which is one of the most significant drinking water resources of Ankara, the capital city of Turkey has been investigated by using multivariate statistical methods (principal component analysis-PCA and factor analysis-FA). 18 water quality parameters were analysed for each sampling station and used for the statistical analysis. The correlations between parameters and sampling stations were evaluated by using statistical techniques in terms of underlying factors. FA/PCA identified water quality parameters in five groups. The results revealed that Kirmir Basin was mainly affected from agricultural activities, urban land uses and livestock activities. The improving of the water quality in this region can be achieved by controlling these activities.

Keywords: *factor analysis, multivariate statistic, water pollution*

Introduction

Water is an essential nutrient for living organisms. The amount of freshwater resources is very limited in the world. However, water resources are open to pollution due to the growth of population, technological development and increasing industrial activities. Pollutants may disrupt the aquatic ecosystems at a certain concentration. Thus, preserving the quality of water is crucial for the wellbeing of humanity and aquatic organisms. Water quality can be defined by using physico-chemical and biological parameters. Measuring the physico-chemical and biological parameters and comparing the results with the limit values given in standards/ guidelines is a general approach during water quality assessment. However, this approach is very exhaustive and also time consuming due to the evaluation of large number of measured variables (Akkoyunlu & Akiner 2012; Sánchez et al. 2007; Tezcanli Guyer & Genc Ilhan 2011; Tunc Dede et al. 2013).

Different kinds of methods have been developed for easy assessment and interpretation of water quality data such as water quality index methods and statistical multivariate analysis (regression analysis, factor analysis, principal component analysis, cluster analysis, etc.) (Akkoyunlu & Akiner 2012; Boyacioglu & Boyacioglu 2007; Malik & Nadeem 2011; Mazlum et al. 1999).

Among these methods, statistical multivariate analysis for data classification and modeling has an advantage of getting additional information about possible sources of pollution in addition to its capability of handling large amount of raw data (Boyacioglu & Boyacioglu 2007). Principal component analysis (PCA) and factor analysis (FA) aim to explain the relationship between the parameters in terms of the underlying factors, which are not directly observable. These analyses deal with the grouping of the correlated parameters and calculation of the new factors based on data set (Boyacioglu & Boyacioglu 2007). The only difference between PCA and FA is that PCA assumes that all variance is common and all unique factors set equal to zero while FA assumes some unique variance. Parameters can be either positively or negatively correlated. Parameters that are highly correlated means they are influenced by the same factors. PCA provides data reduction by selecting the parameters which represent the whole dataset and summarize the statistical correlation between parameters in water while keeping the original data loss at a minimum level. The main objective of the factor analysis is to determine the common factors affecting the parameters in the data set and to find the relation between the factors and the parameters (Boyacioglu & Boyacioglu 2007).

In this study, the water quality assessment of Kirmir Basin was studied and water quality data was evaluated by using factor analysis (FA) based on principal component analysis (FA/PCA).

Materials and Methods

Kirmir is among the most important branches of Sakarya River. It is third longest basins near Ankara, the capital city of Turkey and located between districts of Kızılcahamam and Beypazarı. 67% of the drinking water of Ankara is supplied by the main resources (Çamlıdere, Eğrekkaya and Akyar Dams) located in this basin. However, Kirmir basin is open to pollution due to livestock and agricultural activities, urban land uses, human activities and geothermal facilities (Tunc Dede et al. 2013; DEIAP 2016). For the assessment of surface water quality in Kirmir, water samples were collected on a monthly base from 10 different stations in this area for one-year period from June 2009 to May 2010. Sampling was conducted in accordance with "Standard Methods 1060 Collection and Preservation of Samples" (Eaton & Clescen, 2005). The analysis of water quality parameters was conducted according to Turkish Standards, Standard Methods and U.S. Environmental Protection Agency (EPA) methods. Factor and principal component analyses were employed to evaluate water quality data. Statistical analyses were done using Excel 2016 (Microsoft, 2016) and STATISTICA version 6.0 (SPSS, StatSoft, Inc., USA, 2001) software. The selected parameters for the estimation of surface water quality characteristics were: pH, electrical conductivity (EC), dissolved oxygen (DO), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl), sulphate (SO_4), biological oxygen demand (BOD), Total coliforms, *Escherichia coli*, manganese (Mn), arsenic (As), boron (B), titanium (Ti), vanadium (V) and barium (Ba).

Results and Discussion

In this study, multivariate statistical techniques including factor and principal component analysis were applied to data set obtained from Kirmir Basin and its tributaries in Ankara, Turkey. Selected parameters and their descriptive statistics are given in Table 1.

Table 1. Selected parameters for water quality evaluation and their descriptive statistics

	Unit	**Mean**	**Median**	**Mode**	**Std. dev.**	**Variance**	**Min. value**	**Max. value**	**Limit values**
pH	-	8.16	8.20	8.20	0.47	0.22	7.17	9.17	6.5 ≤ ≤ 9.5
EC	µS	456	423	549	247	60985	77	1210	2500
DO	mg O_2	8.31	7.80	7.70	1.18	1.40	6.50	11.80	$>8^{a1}$
Na	mg L^{-1}	35.65	22.11	11.40	37.41	1400	3.20	188	200
K	mg L^{-1}	6.99	5.94	4.60	4.49	20.15	1.40	23.97	3700^{a2}
Ca	mg L^{-1}	30.22	25.95	18.40	19.2	366	0.17	97.47	1000^{a3}
Mg	mg L^{-1}	19.26	16.30	5.60	13.41	180	2.10	62.86	200^{a3}
Cl	mg L^{-1}	20.41	12.05	2.00	22.14	490	0.80	90.20	200^{a1}
SO_4	mg L^{-1}	15.29	13.37	12.00	10.38	108	2.76	59.06	250
BOD	mg O_2	10.53	6.10	5.00	9.87	97.41	2.80	59.10	$<3^{a1}$
Total coliforms	no/100 mL	1483	800	3000	1937	3752790	50	9600	50^{a1}
Escherichia coli	no/100 mL	194	11	0	608	370238	0	3200	20^{a1}
Mn	µg L^{-1}	17.15	10.03	n.a.	18.69	349	1.17	87.35	50
As	µg L^{-1}	25.34	18.28	n.a.	25.37	643	0.86	127	10
B	µg L^{-1}	390	168	n.a.	551	303379	11.87	3222	1000
Ti	µg L^{-1}	10.39	2.63	n.a.	19.90	396	0.56	88.81	n.a.
V	µg L^{-1}	6.03	4.96	3.62	3.58	12.83	1.39	17.75	n.a.
Ba	µg L^{-1}	73.55	76.13	n.a.	37.72	1423	20.36	197	100^{a1}

Notes: All limits values were given based on TS 266 except: ^{a1} (TurkishRegulation 2012); ^{a2} (WHO 2009); ^{a3} (WHO 2011); no: number; n.a.: not available

In Table 1, standard deviation for some parameters are at high values which demonstrate the variability during the sampling periods due to the anthropogenic effects and variation in precipitation and flow. In order to evaluate mean differences among annual mean values, standard deviation, minimum and maximum values of parameters for all sampling stations, analysis of variance (ANOVA) was employed. Covariance values were found higher than 0.5 which means that the relationship between these 18 parameters are important and application of factor analysis is meaningful. Water quality parameters were grouped by using factor analysis. Factor and principal component analysis was applied in three phases:

1. Preparation of the correlation matrix for all parameters,
2. Extraction of the initial set of factors by using an extraction method (centroid, maximum likelihood, principal component and principal axis extraction, etc.),
3. The rotation of the factors, aiming for increasing the relationship between some of the factors and parameters for simple and easy interpretation. Varimax procedure was

used for the rotation. Varimax factors with eigenvalue 1 were retained. After rotation, the correlation between each parameter and each factor was obtained (Boyacioglu & Boyacioglu 2007; Malik & Nadeem 2011).

The correlation matrix of parameters was generated and five factors were extracted with principal component analysis method rotated by Varimax with Kaiser Normalization. The variance statement ratio of the factors has been optimized so as to be closer to each other by applying six rotations. Results of factor analysis including factor-loading matrix, eigenvalues, total and cumulative variances are presented in Table 2.

Table 2. Factor-loading matrix, eigenvalues and total and cumulative variance values (Marked loadings > 0.5)

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Na	**0.922**	0.017	-0.079	0.026	-0.037
B	**0.914**	-0.120	0.023	0.121	0.085
As	**0.881**	0.015	-0.069	0.117	0.232
EC	**0.841**	0.151	-0.157	0.287	0.287
Cl	**0.812**	-0.043	-0.092	0.152	0.046
K	**0.745**	0.199	-0.135	0.225	-0.134
Ba	**0.582**	0.252	-0.179	0.196	0.258
V	0.148	**0.898**	-0.031	-0.060	0.005
DO	-0.015	**0.891**	-0.119	0.043	-0.089
Escherichia coli	-0.009	0.016	**0.802**	-0.097	0.061
Ti	-0.202	-0.129	**0.758**	-0.218	-0.251
pH	0.201	0.222	**-0.698**	-0.191	-0.217
Mn	0.194	-0.005	-0.053	**0.729**	-0.196
Mg	0.183	**0.535**	-0.19	**0.642**	0.228
SO_4	**0.505**	-0.134	-0.048	**0.597**	0.224
BOD	0.371	-0.480	0.128	**0.520**	0.175
Ca	0.252	-0.127	-0.187	-0.082	**0.780**
Total coliforms	0.040	0.036	0.406	0.093	**0.706**
Eigenvalue	5.356	2.363	2.074	1.908	1.632
Total variance%	29.75	13.13	11.52	10.60	9.06
Cumulative variance %	29.75	42.88	54.40	65.00	74.06

To confirm the results obtained during factor analysis, principal component analysis was applied to the water quality parameters data set. A scree plot showing the sorted eigenvalues as a function of the principal components number is given in Fig. 1.

As seen from the figure, PCA generated five significant components with eigenvalues greater than 1 (according to the "eigenvalue-one" criterion) (Azhar et al. 2015). The breakpoint in the graph (component:5, eigenvalue:1) will also show us the number of the factors. And the group components are the same as in the factor analysis. Next, five significant factors which explained 74.06% of total variance of original variables were generated by using the factor analysis (Table 2):

Factor 1 (FAC1): Na, B, As, EC, Cl, K, Ba, SO_4
Factor 2 (FAC2): V, DO, Mg
Factor 3 (FAC3): *Escherichia coli*, Ti, pH
Factor 4 (FAC4): Mn, Mg, SO_4, BOD
Factor 5 (FAC5): Ca, Total coliforms

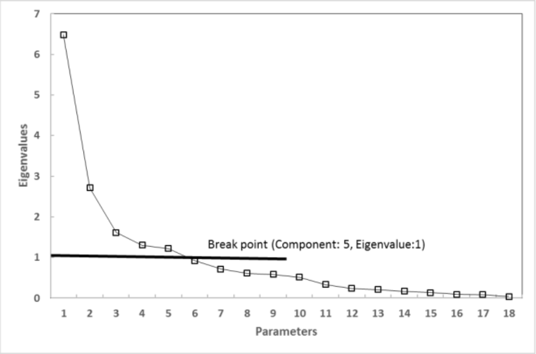

Figure 1. Scree plot of the eigenvalues

Based on factor loadings, FAC1 explained 29.75% of the variance and was strongly correlated with Na, B, As, EC, Cl, K, Ba and SO_4. The elements Na, K and Cl are essential for living organisms and they are among the most abundant elements on earth. Water may expose to serious amounts of Na, K and Cl due to the urban land use. The higher amounts of these elements can cause serious health problems. For example, the excess amount of chloride may result in hearth and kidney problems and also corrosion in the pipes of water distribution systems (TSE 1998; WHO 2011). Atmospheric activities, deposition from sedimentary rocks, sewage effluents and agricultural runoffs can be the reason of Cl in surface waters. Anthropogenic activities may increase K amount in water.

As is also an abundant element in Earth's crust and can be found in the form of sulfides and metal arsenide or arsenates. Exposure to high concentrations of arsenic can cause widespread health effects in humans. Volcanic rocks can be the reason increasing in arsenic amount in water. B occurs naturally in groundwater due to the rocks and soils containing borates and borosilicate. Surface water can be contaminated with boron as a result of wastewater discharge. Excess amounts can cause serious health problems (Malik & Nadeem 2011, TSE 1998, WHO 2011).

EC is an indirect measurement of total dissolved solids (TDS) which often is associated to waste water discharge and increase in dissolved salt amount cause increase in EC. Unexpected increase in EC is an indicator of the anthropogenic pollution in water (Akkoyunlu & Akiner 2012; Akoteyon et al. 2011).

SO_4 can be found naturally in the environment at high concentrations. Soil and industrial effluents can cause the sulfate contamination in water. High amounts of sulfate in drinking water can cause bowel problems in humans and also bad taste in water (Akoteyon et al. 2011).

High amount of Ba contributes to hardness of water. The main sources of hardness in water is due to the sedimentary rocks and also some runoff from soils. Ca and Mg are the principal elements found in many sedimentary rocks and can cause hardness in water, too. High values of hardness cause aesthetic problems in water (WHO 2011; TSE 2000).

In general Cl and SO_4 indicate some biological and anthropogenic activities in the environment (Avtar et al. 2011).

FAC2 was marked by V, DO and Mg. This factor explained 13.13% of the total variance. DO indicates inorganic pollution in the water. DO is one of the important parameters for aquatic life. Water containing high amounts of organic and inorganic substances results in oxygen depletion due to oxygen consumption (Malik & Nadeem 2011; Boyacioglu & Boyacioglu 2007). FAC3 explained 11.52% of variance and related with the parameters *Escherichia coli*, Ti and pH. The bacteriological monitoring (*Escherichia coli*, Total coliforms, etc.) is one of key components in water quality evaluation. Livestock activities, animal wastes and domestic waste water discharges may cause bacteriological pollution in water. pH is another important factor as an operational parameter. While it was reported that pH has no direct effect on consumers, pH level in surface water may affect respiration in aquatic life (WHO 2011).

FAC4 was correlated with the parameters of Mn, Mg, SO_4 and BOD. 10.60% of the total variance was explained by this factor. BOD is another important parameter for the determination of the quality of water and related with the oxygen demanding capacity of organic materials. It indicates organic pollution. High BOD concentration may cause death of fish and increase eutrophication (Akkoyunlu & Akiner 2012; Cude 2001). Mn is also one of the most abundant and essential elements in the world. High concentrations of manganese cause color problems in water and health problems in human. FAC4 represents the agricultural land use characteristics shown by presence of Mg and SO_4.

The last factor FAC5 was related with the parameters Ca and Total coliforms and explained 9.06% of total variance. High Ca concentration yields high Mg amounts. High metal contents in water are due to runoff carrying metals from municipal wastewater, urban areas and agricultural lands.

Conclusions

This paper introduces assessment of water quality data based on 10 monitoring stations in Kirmir Basin around the capital city of Turkey, Ankara by using statistical multivariate analysis (factor and principal component analysis). FA/PCA identified water quality parameters in five groups. The results revealed that Kirmir basin is mainly deteriorated with non-point pollution sources including mainly agricultural activities, urban land uses and livestock activities. Minimization and controlling these activities will be helpful for improving the water quality and providing better ecology for living organisms in Kirmir Basin. Multivariate statistical analysis was successfully applied for the assessment of water quality in Kirmir basin. In comparison to other techniques, this method has an advantage of providing additional information about potential pollution sources while analyzing large amount of raw data.

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POLLUTION CONTROL AND MONITORING

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A STUDY OF THE CONTENT IN VOLATILE OILS AND THEIR COMPOSITION OF VARIOUS AROMATIC HERBS FROM ECOLOGICAL SOILS

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Abstract

Volatile oils (aromatic essences) have been well known since ancient times, both as food flavors and as a treatment solution for sanitary and cosmetic purposes.

In order to highlight the content in the volatile oils and their composition, a number of fresh aromatic plants have been studied, as: lavender (*Lavandula angustifolia*), rosemary (*Rosmarinus officinalis*), sage (*Salvia officinalis*), thyme (*Thymus vulgaris*) and oregano (*Origanum vulgare*), all originated from the organic crops of the Hofigal Company.

Essential oils were obtained by using the water vapor extraction technique, while for the identification of volatile oil components was used gas chromatography coupled with mass spectrometry (GC-MS).

The experimental results present the volatile oil content of the studied aromatic plants and also the important and specific chemical components of each volatile oil. Likewise, the soils used for plants growth have been analyzed for organochlorine content by using gas chromatography with electron capture detector (ECD). The concentration of these organic compounds is below the maximum allowable limit established by specific law (Order no. 756/1997) for soils of Romania.

These volatile oils from organic sources will be used as raw materials for obtaining food supplements and cosmetics products.

Keywords: *aromatic plants, GC-MS chromatography, volatile oil*

Introduction

Volatile oils, products of secondary plant metabolism, are mixes of several chemical compounds which are characterized by a fragrant scent and by therapeutic proprieties. Volatile oils can accumulate in all organs of the herbs, in varying amounts. These compounds can be found in roots, stems, leaves, flowers, fruits, seeds or in the bark of different plants. Usually the concentration of volatile oils in plants is very low (below 1%), rarely could have values above 10-15% or more. The complex chemical composition of volatile oils (thousands of chemical compounds) is based on mono and sesquiterpene constituents, and aromatic compounds. Physical proprieties of essential oils are defined by volatility at ambient temperature, with a specific scent and a burning taste (European Pharmacopoeia 2017).

In order to highlight the volatile oils from fresh plant products, different extraction procedures are used as distillation and hydrodistillation, extraction with volatile nonpolar solvents, extraction with liquid or solid fats, extraction with supercritical fluids or pressing procedure (Topala & Tataru 2016, Berechet 2015). Choosing the suitable extraction method is function of the amount of volatile oil from several parts of the plant, and of its physico-chemical proprieties. In the present study was applied hydrodistillation techniques, a widely used extraction method for an expected amount of volatile oils, while pressing procedure is used especially for plants with a high concentration of essential oils (for example, citric pericarp) (Aumeeruddy-Elalfi 2016). The objective of the study consists in the determination and evaluation of essential oil's chemical composition, which was obtained by hydrodistillation from medicinal plants, according with the European Pharmacopoeia and the Romanian Pharmacopoeia.

Due to its phytohormones content, volatile oils are real anti-wrinkle and seboregular treatments in cosmetic preparations, with a very high hydration and regeneration capacity (Aumeeruddy-Elalfi 2016,). Also, these compounds used in some diseases at a suitable dose, represent the fastest and most effective remedy for aroma and phyto-therapy (de Sousa 2015, Manea 2016). In order to maintain these medical applicability, it is necessary that the organic food and supplements come from unpolluted soils, which are untreated with chemical fertilizers, synthetic pesticides, stimulants and plant growth regulators. For these experiments, none of the plants were treated with synthetic chemical compounds. However, historical presence of some pesticides in soil increases the risk of contamination. For the safety of the results, were performed determinations of organochlorine pesticides from plant soils, within the Romanian law (Order 756/1997).

Materials and Methods

The selected plants for the actual reasearch (lavender, rosemary, sage, thyme and oregano) are provided from Hofigal Company ecologic crops, preserved and deposited according to standards requirements, then analyzed for volatile oils content and composition. Gravimetric analysis was used for essentialcuantification after steam extraction. Regarding the quality of the extracts, it was carried out a screening of samples in hexane by using gas chromatography mass spectrometry (GC-MS) equipment from Thermo Electron Corporation, type Focus GS with a DSQ II mass spectrometer detector and a chromatographic column of fused silica, 30 m in length, 0.25 mm internal diameter, having a Macrogol 20.000 R as stationary phase and 0.25 µm film thickness. The chemical compounds present in the volatile oils were identified using a NIST spectra library. The various retention times for the same compound are given by different harvest moments and GC performances changes among the analysis.

The quality of soils used for studied plants growth was assessed by quantitative analysis of the presence of organochlorine pesticides. 10 g of each type of soil was extracted with hexane and analyzed by a gas chromatography Agilent 7890A, equipped with an electron capture detector and a 5% phenyl-95% dimethylpolysiloxane column, 60 m, 0.25 mm internal diameter and 0.25 µm film thickness. The extraction method and performance parameters were accomplished as it is stated in EN ISO 10382/2007 for organochlorine pesticides.

Results and Discussion

The quantity of volatile oils obtained by hydrodistillation extraction from studied herbs, expressed in mL/kg dry matter, it is presented in the Fig. 1.

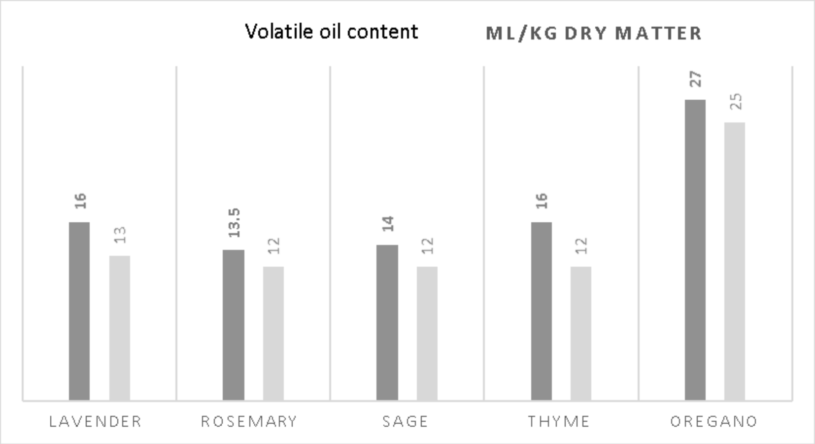

Figure 1. Content of volatile oil [mL/kg] from fresh plants

All the obtained results correspond with the volatile oil quantities requested by the European Pharmacopoeia, edition in force, with near 10% higher than minimum amount: lavender (*Lavandula angustifolia*) minimum 13 mL/kg, rosemary (*Rosmarinus officinalis*) minimum 12 mL/kg, sage (*Salvia officinalis*) minimum 12 mL/kg, thyme (*Thymus vulgaris*) minimum 12 mL/kg and oregano (*Origanum vulgare*) minimum 25 mL/kg. All the results are reported for dry matter of the samples.

The main compounds identified by using NIST library spectra, from the extracted volatile oils, are shown in the chromatograms from Fig. 2 and Tables 1-5.

Table 1. Chemical composition of volatile oil from lavender

No.	Name	Retention time	Area %
1	Cineole	13.63	2.3
2	α-Pinene	15.43	6.0
3	3-Carene	16.08	1.7
4	**Linalool**	**25.24**	**34.6**
5	**Linalyl acetate**	**25.45**	**37.8**
6	Caryophylene	26.22	3.8
7	α-Terpineol	26.49	1.3
8	Lavandulol acetate	26.69	3.5
9	α-Farnesene	28.11	1.5
10	Terpineol	28.78	2.9

For lavender and sage volatile oil, the compounds of interest (Table 1, 3) are between the limits given by European Pharmacopoeia, respectively 20-45% for linalool and 25-

46% for linalyl acetate in lavender oil, and 20-60% for thujone trans and cis isomers, 1-20% for camphor, in sage volatile oil. But for the other herbs, the limits were excedeed as: over 60% for thymol and carvacrol from oregano, over 13-21% camphor from volatile oil from rosemary and more than 28% for o-cymene in thyme volatile oil. The other compounds of interest (represented with bold text in Table 2,4,5) were below the given value.

Table 2. Chemical composition of volatile oil from rosemary

No.	Name	Retention time	Area %
1	**α-Pinene**	**5.87**	**16.1**
2	Camphene	7.60	6.2
3	β-Pinene	9.84	2.7
4	Limonene	15.78	4.4
5	**Cineole**	**16.14**	**12.2**
6	**Camphor**	**31.29**	**28.6**
7	β-Linalool	33.36	2.3
8	Caryophyllene	34.64	4.7
9	Verbenone	38.96	3.8
10	Borneol	39.03	7.0

Performing soil analysis, organochlorine pesticides as HCH isomers, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endosulfan were below the quantification limit of the method, 0.01 mg/kg dry matter, which is within the recommended alert limit value given by soil legislation (Order 756/1997).

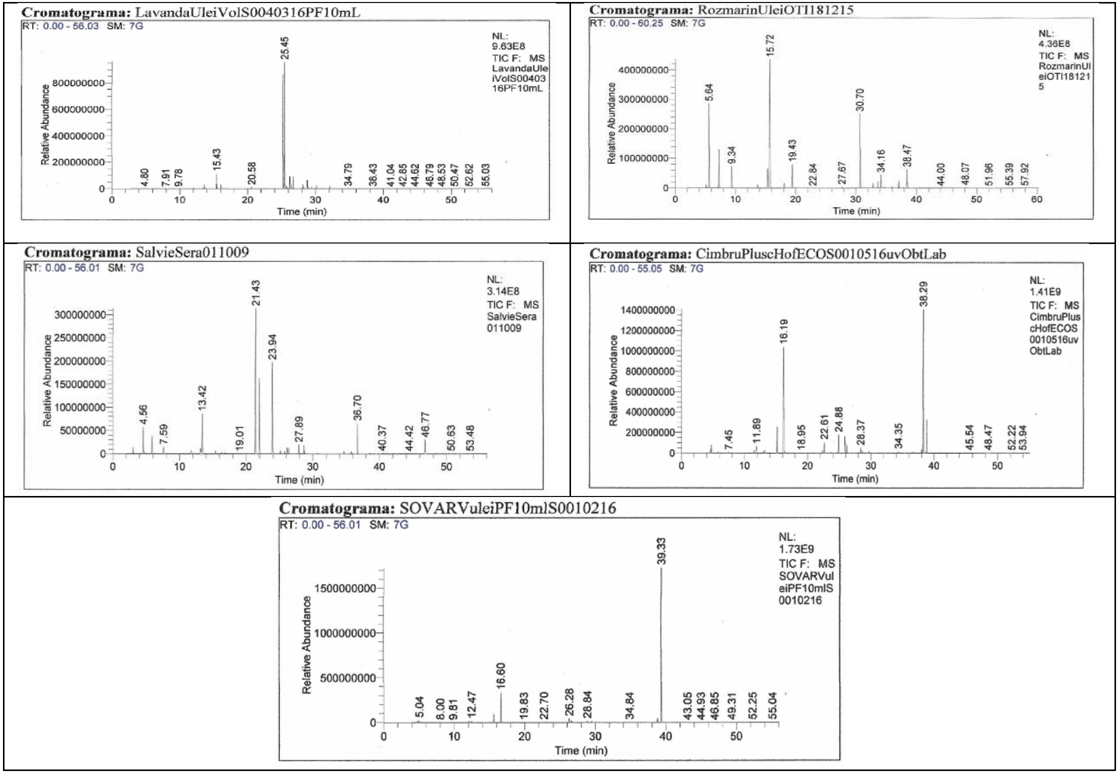

Figure 2. GC-MS chromatograms for studied volatile oils

Table 3. Chemical composition of volatile oil from sage

No.	Name	Retention time	Area %
1	α-Pinene	4.55	4.9
2	Camphene	5.87	4.1
3	β-Pinene	7.59	2.0
4	Cineole	13.13	1.5
5	Limonene	13.42	10.5
6	**Thujone trans**	**21.43**	**34.6**
7	**Thujone cis**	**21.98**	**13.1**
8	**Camphor**	**23.93**	**16.0**
9	Viridifloral	36.70	4.5
10	Epimanool	46.77	2.4

Table 4. Chemical composition of volatile oil from thyme

No.	Name	Retention time	Area %
1	Phellandrene	4.73	1.6
2	4-Carene	11.89	2.1
3	Terpinene	15.13	5.8
4	**o-Cymene**	**16.18**	**32.5**
5	Terpineol	22.61	1.9
6	Linalool	24.88	3.2
7	Caryophyllene	25.86	4.4
8	Thymol methyl ether	26.18	1.8
9	**Thymol**	**38.28**	**37.0**
10	**Carvacrol**	**38.80**	**5.0**

Table 5. Chemical composition of volatile oil from oregano

No.	Name	Retention time	Area %
1	α-Pinene	4.84	0.9
2	Phellandrene	5.04	1.3
3	Myrcene	12.10	1.4
4	Carene	12.47	1.1
5	γ-Terpinene	15.61	4.8
6	m-Cymene	16.60	14.5
7	Caryophyllene	26.28	1.6
8	Borneol	28.84	0.9
9	**Thymol**	**38.82**	**1.7**
10	**Carvacrol**	**39.33**	**69.7**

Conclusions

The quantity of volatile oil obtained through hydrodistillation from studied herbs: lavender (*Lavandula angustifolia*), rosemary (*Rosmarinus officinalis*), sage (*Salvia officinalis*), thyme (*Thymus vulgaris*) and oregano (*Origanum vulgare*), and the main compounds identified through GC-MS from each essential oil sample are appropriate to the values given by European Pharmacopoeia, edition in force. The soil free of organochlorine pesticides was suitable for medicinal plants growth. As a result, the volatile oils from studied plants can be used to obtain organic food and cosmetics.

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CHEMICAL CHARACTERIZATION OF WET DEPOSITIONS IN URBAN AND RURAL AREA

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Abstract

The aim of this study was to determine the chemical composition of wet depositions in two locations from urban and rural area near Bucharest from January to May 2017. For all the samples, pH, conductivity, anions, cations and heavy metals were determined. For anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Ca^{2+}, K^+, Mg^{2+}, Na^{2+}) determination an ion chromatographic method was used. Heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) were determined using AAS with flame and graphite chamber. Results showed the presence of the interested compounds in wet depositions samples with SO_4^{2-} and Ca^{2+} as the dominant anion and cation. Heavy metals concentration followed the trend: Zn > Mn > Cu > Pb > Ni > Cr > Co. Analysing the results obtained the potential sources of ambient air pollution were also suggested.

Keywords: *atmospheric deposition, heavy metals, wet depositions*

Introduction

According to EU Directive (Directive 2004/107/EC), transposed in our country through Law 104/2011, the atmospheric deposition (total or bulk deposition) are referred as being the total mass of pollutants which is transferred from the atmosphere to different surfaces (e.g. soil, vegetation, water, buildings, etc.) in a given area within a given period of time. Pollutants are removed from atmosphere either by precipitation (rain, snow, graupel and hail) in the form of wet deposition either as a result of complex atmospheric processes (turbulent diffusion, sedimentation, inertial forces, electrical migration) known as dry deposition. (Amodio et al. 2014). The characterization of the chemical composition of atmospheric deposits is relevant for the assessment of ambient air quality, providing information on the nature of atmospheric pollutants (natural or anthropic), regional and long-distance transport and impact on ecosystems. Wet deposition can include a wide variety of natural and anthropogenic pollutants, including inorganic elements and compounds (e.g., cations, anions, mercury and other metals) and also organic compounds (e.g., pesticides and herbicides). Different techniques can be used to determine these elements (Petrescu et al. 2016, Vasile et al. 2017, Tudorache et al. 2017, Vasile et al. 2016, Marin et al. 2017, Calinescu et al. 2016). There are countless studies around the world on the composition of wet atmospheric depositions (Deboudt et al. 2004, Agnieszka & Borowski 2015, Xing et al. 2017, Tiwari et al. 2016).

Acid rain is defined to have a pH of less than 5.61. Decreasing of pH values in rainwater is the result of major inorganic acids such as: sulfuric, nitric and organic acids, including carboxylic acids, carbonic acids, acetic acid, formic acid, etc.; resulting from homogeneous and heterogeneous complex reactions in the atmosphere

(Sillapapiromsuk & Chantara 2010). This shows that the wind-carried dust and soil play important roles in the chemistry of wet deposition.

The present study aimed to determine the chemical composition of wet depositions in two locations from urban and rural area near Bucharest from January to May 2017. For all the samples, pH, electrical conductivity, anions, cations and heavy metals were determined. For anions (Cl^-, NO_3^- and $SO_4^{2-)}$ and cations (Ca^{2+}, K^+, Mg^{2+}, Na^{2+}) an ion chromatographic method was used. Heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) were determined using AAS with flame and graphite chamber.

Experimental

Sampling sites and sample collection

The wet deposition samples were collected for a period of five months from January to May 2017 from two sites as indicated in Fig. 1.

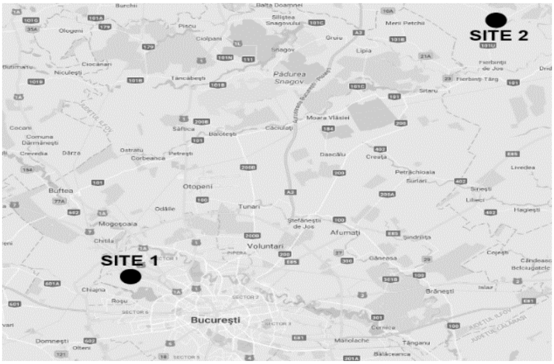

Figure 1. The sampling sites used in wet deposition, were: Site 1- Giulești (44°28'22.5"N 26°00'41.5"E) and Site 2 – Maia (44°44'14"N 26°23'58"E)

The first site, Giulesti (44°28'22.5"N 26°00'41.5"E), is located on the outskirts of Bucharest; a landfill is situated at approximate 2,25 km from the site, in Rudeni, Chiajna witch could represent a potential source of pollution. In general, the area is characterized by small constructions (1 or 2 floors), low traffic and little industry.

The second site, Maia (44°44'14"N 26°23'58"E), is a commune located in Ialomița County, Romania. The main activity carried out in this area is predominantly agricultural.

Both areas are located on the south-east of Romania, with an excessive continental climate, where there is an influence from the air masses from east-continental, west-oceanic and south-mediterranean. This type of climate is characterized by pronounced contrasts from winter to summer, with high temperature differences (above 50°C). The average temperatures are between 10 and 11°C, the warmest month being July (above 30°C) and the coldest being January (-3°C). In winter, the dominate winds come from North and North-East. The precipitations have a continental character, with differences from year to year, the average quantity being 400 – 600 mm/year.

For wet atmospheric deposition sampling we used bulk collector, exposed only during precipitation events in order to avoid the collection of dry atmospheric deposits. The methodology for sampling and analysis of the chemical composition of wet atmospheric depositions was in line with the requirements of the Romanian standard SR EN 15841:2010 and are harmonized with the guidelines from EMEP (EMEP 1996) and WMO/GAW (WMO 2004). The type of collector used is shown in Fig. 2.

Figure 2. Sample collector

Wet depositions were sampled in open areas with no trees or buildings; and, in order to avoid contamination of ground samples during rain episodes, the collector height was at least 1.5 m above the ground. Field blank samples were also determined.

Chemical analysis

After sampling, the samples were labelled and transported to INCD ECOIND Air Pollution Control Laboratory to determine their chemical composition. pH and specific conductivity were immediately determined by using the Seven_Excellence multimeter, Mettler Toledo, equipped with the electrode In Lab^{TM}Expert Pro-ISM and In Lab^{TM} 741-ISM, Seven Compact^{TM} conductivity Sensor. The samples were filtered with 0.45 µm acetate cellulose membranes and stored at 4°C for the determination of anions, cations and heavy metals. For the determination of major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, K^+, Mg^{2+} and Na^+) we used an ion chromatography system model Dionex ICS-5000+ Integrade Reagent Free, equipped with a conductivity detector and Anion Self-Regenerating Suppresor (Dionex AERS 5000 2mm). For anion separation, we used IonPac AS 18 analytical column with electrolytically regenerated suppressor model Dionex AERS 500 2 mm and 20mM potassium hydroxide for elution; IonPac-CS12A column with electrolytically regenerated suppressor model Dionex CERS 500 2 mm and 10mM methyl sulfonic acid for elution were used for determination of cations. Heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) in wet precipitation samples and digested solutions were determined by an atomic absorption spectrophotometer (Varian 280FS equipped with GTA 120) according to the standard SR EN 15841:2010. National and international legislation does not provide limits on wet deposition quality.

Results and Discussion

Relationship between pH and precipitation amount and relationship between conductivity and precipitation amount are shown in Fig. 3 and 4.

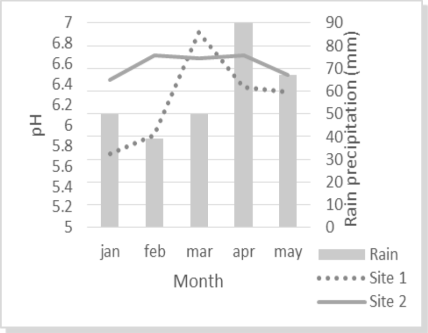

Figure 3. Variation of monthly precipitation amounts and pH mean value

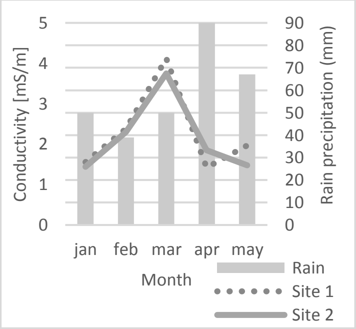

Figure 4. Variation of monthly precipitation amounts and conductivity mean value

For site 1 the mean value of the pH was 6,24 (min. pH=4,6 max. pH =7,02) and for site 2 the mean pH was 6.59 (min. pH =5,86 max. pH =7,50). The samples with pH values above 6.0 may suggest various inputs of alkaline species into precipitation (Sillapapiromsuk & Chantara 2010). Specific conductivity values varied between 1,42 and 4,12 mS/m for site 1 and were situated between 1.44-3,75 mS/m for site 2. The mean concentrations of major ions (Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^{2+}) are shown in Fig. 5 for site 1 and Fig. 6 for site 2.

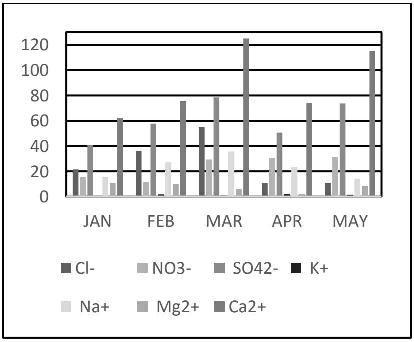

Figure 5. The monthly concentrations of ions in wet deposition samples - Site 1

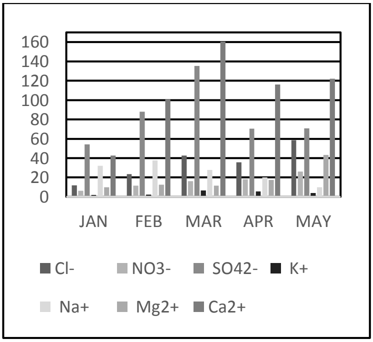

Figure 6. The monthly concentrations of ions in wet deposition samples - Site 2

The highest average fluxes found for the ions in site 1 were: $Ca^{2+} > SO_4^{2-} > Cl^- >$ $>NO_3^- > Na^{2+} > Mg^{2+} > K^+$, and the ions in site 2 were in the order: $Ca^{2+} > SO_4^{2-} > Cl^-$ $> Na^{2+} > Mg^{2+} > NO_3^- > K^+$.

The mean concentrations of heavy metals (Co, Cr, Cu, Mn, Ni, Pb and Zn) are shown in Fig. 7 for site 1 and Fig. 8 for site 2.

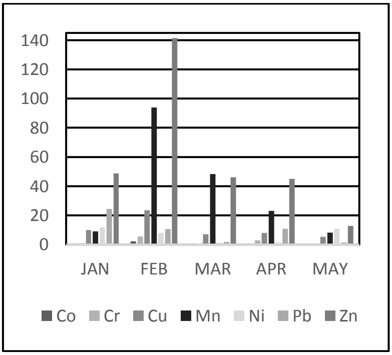

Figure 7. The monthly concentrations of heavy metals in wet deposition - Site 1

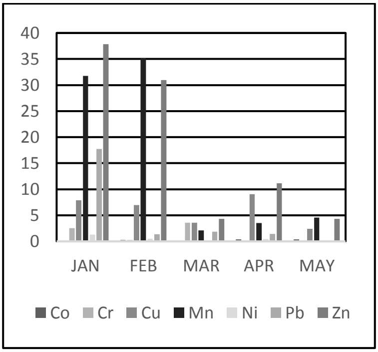

Figure 8. The monthly concentrations of heavy metals in wet deposition - Site 2

The highest average fluxes found for the ions in site 1 were in the order: Zn > Mn > Cu > Pb > Ni > Cr > Co.
The highest average fluxes found for the ions in site 2 were in the order: Zn > Mn > Cu > Pb >Cr > Ni > Co.

Statistical Analysis
In order to determine the associations among ions and heavy metals in wet deposition as well as the possible sources of pollutants, correlations are calculated and listed in Table 1 and Table 2 for site 1 and Table 3 and Table 4 for site 2. Spearman correlation coefficients (r) is a useful technique to characterize relationships among the ions present in wet deposition (Kanellopoulou 2001, Arsene et al. 2007).

Table 1. Spearman correlation coefficients between ions for site 1

Ion	K^+	Na^{2+}	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
K^+	1.000						
Na^{2+}	0.100	1.000					
Mg^{2+}	-0.600	-0.300	1.000				
Ca^{2+}	0.000	0.400	-.400	1.000			
Cl^-	-0.500	**0.700**	0.300	0.500	1.000		
NO_3^-	0.200	-0.500	-0.600	0.300	-0.600	1.000	
SO_4^{2-}	000	.400	-.400	**1,000**	0.500	0.300	1.000

All values in µeq/L

A correlation was seen between SO_4^{2-} and Ca^{2+} (r=1.000) indicating they originated from similar sources. Other relatively good correlations were observed between Cl^- and Na^{2+} with correlation values of r=0.70 (marine sources).

Table 2. Spearman correlation coefficients between heavy metals for site 1

Ion	Co	Cr	Cu	Mn	Ni	Pb	Zn
Co	1.000						
Cr	0.100	1.000					
Cu	-0.600	-0.300	1.000				
Mn	0.000	0.400	-0.400	1.000			
Ni	-0.500	**0.700**	0.300	0.500	1.000		
Pb	0.200	-0.500	-0.600	0.300	-0.600	1.000	
Zn	000	0.400	-0.400	**1,000**	0.500	0.300	1.000

All values in µg/L

A correlation was seen between Zn and Mn (r=1.000), Ni and Cr (r=0,700), indicating they originated from similar sources.

Table 3. Spearman correlation coefficients between ions for site 2

Ion	K^+	Na^{2+}	Mn^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
K^+	1.000						
Na^{2+}	-0.500	1.000					
Mn^{2+}	-0.300	-0.700	1.000				
Ca^{2+}	**0.900**	-0.600	0.400	1.000			
Cl^-	**0.700**	-0.800	**0.700**	**0.900**	1.000		
NO_3^-	0.600	-0.900	**0.900**	**0.700**	**0.900**	1.000	
SO_4^{2-}	0.600	0.100	0.100	**0.700**	**0.500**	0.200	1.000

All values in µeq/L

A correlation was seen between SO_4^2 and Ca^{2+} (r=0.70) indicating they originated from similar sources. Similar, a strong correlation was seen between Ca^{2+} and K^+ (r = 0.90), suggesting the common source of these ions was a natural source (e.g. crustal origin). Other relatively good correlations were observed between Cl^- and Na^{2+}, between NO_3^- and Mg^{2+}, between NO_3^- and Ca^{2+}-, and between SO_4^{2-} and Ca^{2+}, with correlation values of r=0.80, r =0.90 and r =0.70.

Table 4. Spearman correlation coefficients (r) between heavy metals for site 2

Ion	Co	Cr	Cu	Mn	Ni	Pb	Zn
Co	1.000						
Cr	-0.872	1.000					
Cu	-0.205	-0.300	1.000				
Mn	0.051	-0.100	0.100	1.000			
Ni	-0.395	0.051	**0.667**	**0.718**	1.000		
Pb	-0.872	0.600	0.500	-0.200	0.462	1.000	
Zn	-0.205	-0.100	0.600	**0.800**	**0.975**	0.300	1.000

All values in µeq/L

A correlation was seen between Zn and Mn (r = 0,80), Zn and Ni (r = 0,975), Ni and Cu (r = 0,667), Ni and Mn (r = 0,718) indicating they originated from similar sources.

Conclusions

During the winter months, the concentrations of SO_4^{2-} were higher in the rural area due to the use of coal as a source of heating for the living quarters. There were no acid rain phenomena due to the relatively high cation content (almost double to the urban area), pH samples in the rural area being much more alkaline than the urban area. The application of Spearman correlation coefficients analysis suggested that Ca^{2+}+ is likely to be the major neutralizing agent for SO_4^{2-}.

The samples with pH values above 6.0 may suggest various inputs of alkaline species into wet deposition. Zn and Mn were the dominant heavy metals found in the wet deposition; these may have sources in the soil resuspension and the building's rooftops in both areas.

The results presented in this paper are preliminary result in a study we intend to continue for a longer period.

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CONTROL OF INORGANIC AND ORGANIC CONTAMINATION, ASSESSMENT OF WATER QUALITY IN HYDROPOWER LAKES ON JIU RIVER

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Abstract

In the last decades near the hydropower lakes, have developed numerous private companies and settlements that constantly uses water from these lakes. In many cases, the spills are not controlled and are not decontaminated properly or even at all. In the Jiu hydrographic basin, there are 225 localities with a population of more than 2,000 peoples. Only 32 of them are equipped with sewer systems and only 2 of them in accordance with Directive 91/271/EEC. As consequence of the pollution with organic and inorganic substances (nutrients) has appeared the eutrophication of the lakes. From the total 12-hydropower lakes with a surface over 50 ha, eight of them are clogged in the proportion of 60%, and 3 of them in a proportion of 80%. In the first part of the paper are analyzed the main punctual and diffuse sources of organic and inorganic pollution, with a decisive factor in the development of the aquatic vegetation. During 2010-2016, a systematic campaign of measurements was done. They were determined the protection zones that need to be tracked, the catchments zone for the human consumption, the zones for protected fish or of those species economically important, the natural protected areas, and the zones vulnerable to nitrate and nitrites. The obtained results are presented for the most affected hydropower lakes from the selected area. Finally, are mentioned some possibilities and measures necessary to be followed as to reduce the inorganic and organic pollution, some conclusions, acknowledgement and references.

Keywords*:* *environmental engineering, hydroelectric power generation pollution, water*

Introduction

The central objective of the Water Framework Directive is to achieve the "good status" for all the water bodies, both for the surface and for the underground. To solve this problem must determine the types of pollution: with organic matter, the nutrients pollution, the pollution from priority substances/dangerous and the morphological alterations. The river Jiu, unlike other rivers, lacks major tributaries and the sediments are transported almost uniformly throughout its entire course.

The hydro-energetic structure of the river Jiu consists mainly of the hydropower plants: Valea de Pesti, Motru, Tismana, Vadeni, Tg-Jiu, Turceni, Isalnita, and some smaller as Tismana Aval, Clocotis, Suseni, Valea lui Iovan, Izbiceni, Dumitra. Of these power plants for analysis are chosen Vadeni, Tg. Jiu and Izbiceni, currently clogged more than 80%. The vegetation that grew in excess in these lakes gets its necessary substances to develop from the current sediments.

The physical and chemical parameters influence both the nutritional values of the ecosystem changes, but also the induced modification of the anthropogenic activities of the natural river basin. These properties are the result of the interaction between water and minerals from the systems geochemical water-rocks and water-sediment. Have been identified structures of phosphorus and nitrogen. The analyzes were performed on samples taken at different times during the years 2010-2016.

Some observations

1. The substances dissolved in the water synthesize the tissues of the aquatic algae
2. Structural, the carbon is the main compound, after hydrogen and oxygen
3. Under natural conditions, the phosphorus is the main nutrient, which provides the synthesis of the new tissue, being classified before the nitrogen and the carbon. The phosphorus is called "the limiting factor." This chemical element is the main factor contributing to the vegetation development. It can influence the increase or decrease of the algal proliferations. First, is metabolized the nitrogen found in the air, and then those from the aquatic environment.

In Table 1 are presented the localities from the Jiu hydrographic basin and the level of the water decontamination. There are 214 municipalities with more than 2000 inhabitants which are not equipped with water decontamination stations. From the total eight stations, only two are realized in conformity with current legislation. In the Jiu basin does not exists localities < 2000 inhabitants equipped with collecting systems in a centralized form (Carpenter 1998).

Table 1. Actual Situation of the water decontamination – organic load

Dimension	Nr.	Waste water treatment	Organic load (i.e.)	Organic load collected (i.e.)	Organic load collected (%)	Cleaned Organic load (i.e.)	Cleaned Organic load (%)
>150000	1	0	385000	331100	6	0	0
15000-150000	11	4	573567	408943	29	253268	44.2
10000-15000	9	1	110500	47698	16	10857	9.82
2000-10000	204	3	819696	11879	44	5076	0.61
Total	225	8	1888763	799620	42.2	269201	14.3

Table 2. Actual situation of the water decontamination of N and P

Localities	**CCO**	**BCO$_5$**	**Total Nitrogen**	**Total Phosphorus**
	t/year	t/year	t/year	t/year
> 100000	8061.4	3428.2	1836.4	868.7
10000-100000	1166	569.7	217.8	18.3
2000-10000	63.3	38.3	14,8	1.5
< 2000	-	-	-	-
Total	9290.7	4036.24	2069	888.5

Table 2 shows the quantities monitored by organic substances, expressed as CCO-Chemical Consumption of Oxygen and BOC$_5$- Biochemical Oxygen Consumption at 5 days at 20^{0}C, and the nutrients as total nitrogen and total phosphorus, measured in 2010, reported at different categories of human agglomeration. Table 3 shows the results obtained from the sediment samples, collected in 2016 from the three lakes under analysis. In Table 4 are mentioned the same parameters as in Table 2, but produced of the industrial capacities (Integrated Prevention Pollution Control IPPC), and in Table 5 another substances due to the local industry.

Table 3. The chemical sediment components

Parameter	Lake Vadeni	Lake Tg. Jiu	Lake Izbiceni
Humidity (105^{0}C) %	56.246	58.88	57.64
pH (upH)	6.78	6.66	7.16
Organics (%)	8.15	8.93	9.36
Inorganic (%)	92.75	96.17	93.68
NH_4^+ (mg/100g)	6.53	7.52	8.82
NH_4^+ (mg/l)	111.23	158.09	146.16
NO_3^- (mg/100g)	0.7	0.81	0.79
NO_3^- (mg/l)	6.25	7.87	6.12
PO_4^{3-} (mg/100g)	0.12	0.09	0.11
PO_4^{3-} (mg/l)	1.78	1.84	1.77
$N - NH_4^+ + N - NO_3^-$ (mg/100g)	5.63	5.97	6.83
$P - PO_4^{3-}$ (mg/100g)	0.05	0.053	0.058
$N_{dissolved}/P_{dissolved}$	212.74	257.71	243.73

Table 4. Actual situation of the water decontamination

Type	**CCO**	**BCO$_5$**	**Total Nitrogen**	**Total Phosphorus**
	t/year	t/year	t/year	t/year
Industry IPPC	12933.1	2904.4	31.4	12.83
Industry Non-IPPC	1313.6	322	16.3	26
Total industry	14246.76	3226.3	47.7	38.8
Other sources	171	8.6	8.5	0.056

Table 5. Other parameters of the contamination, due to the industry

Type	Cu	Zn	Cd	Ni	Pb	Hg	Cr
	kg/year	kg/year	kg/year	kg/year	kg/year	kg/year	kg/year
Industry IPPC	-	-	-	-	-	-	-
Industry Non-IPPC	0.9	1.9	-	-	0.1	-	0.1
Total industry	0.9	1.9	-	-	0.1	-	0.1
Other sources	0.1	0.1	-	-	0	-	1

In the Jiu River Basin, from the 39 significant industrial and agricultural local point sources of pollution, 17 have installations covered by the IPPC Directive. The improper waste management in localities is a local source of diffuse pollution, as same as the un-proper collection/disposal of the sludge from the wastewater treatment plants (Horrigan 2002).

Materials and Methods

During the measurements of 2010-2016, has been observed that if some species of cyano-bacteria grow, reducing the proliferation of the algae. They have an ability to proliferate rapidly due to the physic-chemical conditions mentioned above. Considering a small scale of time and space, after scientific experimentation, it was observed that the nitrogen deficiency is a limiting factor, but on a global scale for the Jiu basin, the phosphorus is responsible, triggering the biological nitrogen fixation. The cyano-bacteria are of a size and toxicity that opposes to the potential predators (herbivorous zooplankton) or of to other consumers. These bacteria dominate many algae, modifying the functionality of the food chain.

The development in the anoxic conditions in bodies of water removes all superior life forms, as the fresh water fish such as salmonids.

At the interface between water–sediment, anoxia maintains the reduction of iron compounds. The existence of cyanobacteria poses specific problems related to the toxins, which they secrete. A trend of intense phosphorus pollution is manifested in the waters where the flow rate is reduced, at the end of the hydroelectric lakes. They are considered sensitive areas. The data from the Table 2 demonstrate that the actual sediments from these hydropower lakes have the physical-chemical characteristics similar to each other.

The mineral nutrition is favorable in the light and depends on the temperature, the hydrodynamics, and other environmental conditions. The bioavailability of nutrients presented in the water, the gas dissolved or the minerals in solution are factors favorable to the proliferation of aquatic vegetation (micro-algae, macro algae, or floating macrophytes). The report of consumer/demand requirement is a function of the composition of the living organisms, Table 6 (Seteanu 2004).

The average composition of the aquatic vegetation, algae, and aquatic plants comprise the carbon as a major constituent, together with hydrogen and oxygen. It should be considered the silicon, which is ubiquitous in the water world, in the diatoms. Nitrogen is the following chemical element, then calcium, potassium, and phosphorus (0.08%), and ends the enumeration with magnesium, sulfur, and chlorine. These constituents, provide nutritional support necessary to proliferation of the aquatic vegetation in the absence of the polluting substances that inhibit the growth of these plants.

The upstream lakes are not contaminated anthropogenic than an insignificant extent and this correlated with the significant reserves of the essential nutrients from these ecosystems, explains the presence of such a large amounts of the aquatic macrophytes, Fig.1.

By the composition of the cells, the major component is carbon, because the proliferation of the bioavailability algae depends on it. As a result, the required algal mass can be satisfactory in water, where the chemical elements are present in different composition different from the cell concentrations (Seteanu 1998).

Table 6. Report of consumption/offer of substances in water

Element	Symbol	Consumption (vegetal) %	Water offer %	Consumption /offer (approx.)
Oxygen	O	80.5	89	1
Hydrogen	H	9.7	11	1
Carbon	C	6.5	0.0012	5.000
Silica	Si	1.3	0.00065	2.000
Azoth	N	0.7	0.000023	30.000
Calcium	Ca	0.4	0.0015	<1.000
Potassium	K	0.3	0.00023	1.300
Phosphor	P	0.08	0.000001	80.000
Magnesium	Mg	0.07	0.0004	<1.000
Sulfur	S	0.06	0.0004	<1.000
Chloride	Cl	0.06	0.0008	<1.000
Sodium	Na	0.04	0.0006	<1.000
Iron	Fe	0.02	0.00007	<1.000
Bore	B	0.001	0.00001	<1.000
Mangham	Mn	0.0007	0.0000015	<1.000
Zinc	Zn	0.0003	0.000001	<1.000
Copra	Cu	0.0001	0.000001	<1.000
Molybdenum	Mo	0.00005	0.0000003	<1.000
Cobalt	Co	0.000002	0.000000005	<1.000

Figure 1. Existent aquatic vegetation in analyzed lakes

If it is considered an average composition of the natural waters, is determined for each element the report required/offer, it appears that a ratio value 80,000. Phosphorus comes first ahead nitrogen (30,000) and carbon (5,000).

As shown in Table 6, the N/P ratio of the aquatic vegetation is 0.7/0.08 = 8.75, which means that the nutrient medium has a ratio N/P equal to this value, being thus in a perfect balance with the desired ratio of the vegetable medium (Walker 2006).

The lake Vadeni because it has features morphometric, hydraulic, and hydrological closer to a channel, the aquatic macrophytes are less developed. The tributary rivers Susita, Jiet bring additional amounts of nutrients used by these vegetable bodies.

Lake Vădeni records a value of pH of 7.7, slightly exceeding the limit of 7.5. Ammonia, nitrites, and nitrates do not exceed much the maximum permissible, but the heavy metals are often exceeded. The cadmium reaches values 11 times higher than the maximum permissible one, the lead almost twice, the zinc maximum is limited at 1000µg/l, and copper exceeds sporadically the limit of 100 mg/l. The lake is clogged in a proportion of 85%, meaning that there is a risk of the dam functioning. The hydroelectric power plant can operate only two hours per day. Nowadays a plan of rehabilitation intends to raise the dam and the lateral dikes to have a higher volume of water. The data resulting from the hydro-chemical analysis of samples taken in 2016, between August and November are presented in Table 7.

Table 7. Measurements in 2016

Parameter	Data	River Jiu	Vadeni	Tg. Jiu	Izbiceni
Temperature	06.08	12.0	14.0	15.5	15.0
^{0}C	01.11		9.3	6.8	6.2
pH (u.pH)	06.08	7.6	7.5	7.5	7.5
	01.11		7.3	7.3	7.2
Oxygen dissolved	06.08	8.28	9.04	8.74	8.44
mg O_2/l	01.11		9.20	10.53	7.93
Organic dissolved	06.08	9.10	9.10	12.40	12.09
mg $KMnO_4$/l	01.11		14.16	10.97	6.73
Nitrates	06.08	1.53	2.51	2.41	2.28
mg NO_3^-/l	01.11		1.15	1.90	3.03
Nitrites	06.08	0.040	0.014	0.026	0.013
mg NO_2^-/l	01.11		0.020	0.012	0.014
Ammonium	06.08	0.32	0.19	0.21	0.15
mg NH_4^+/l	01.11		0.28	0.31	0.24
Phosphates	06.08	0.012	0.014	0.012	0.010
mg PO_4^{3-}/l	01.11		0.016	0.010	0.030
Total Alkalinity	06.08	3.44	2.02	1.96	2.00
mval/l	01.11		2.40	2.20	5.52
Calcium	06.08	64.13	37.67	34.47	35.27
mg Ca^{2+}/l	01.11		49.70	40.88	70.54
Magnesium	06.08	9.73	6.81	8.07	7.78
mg Mg^{2+}/l	01.11		7.30	8.27	10.21
Bicarbonates	06.08	209.8	123.2	119.6	122.0
mg HCO_3^-/l	01.11		146.4	134.2	214.7

It was elected an interval between full ranges of developed vegetation until the period of regression. If this ratio is below the value of 8.75, there is a deficit of nitrogen relative to phosphorus. In this case, the nitrogen is the limiting factor. If the ratio is greater than the value of 8.75, the nitrogen induces a phosphorus deficiency. In this case, the limiting factor is the phosphorus. The chemical element phosphorus is the key to cellular metabolism compared to nitrogen and carbon.

Results and Discussion

The power supplies of the river Jiu and its tributaries and the cascade power plants (e.g. Vadeni, Tg. Jiu, Izbiceni) shows comparable values of pH, oxygenation, organic loading and phosphate concentrations. On the trophic level, the lakes are classified as mesotrophic to eutrophic lakes. This is primarily due to the large volume of wastewater discharged. Comparing the maximum values of some parameters, measured in 2010 and 2016, it was observed significant differences, such as:

- Permanganate consumption (KMnO4 mg/l)	7.9	14.85
- Dissolved oxygen (mg/1)	9.6	14.20
- Nitrates (mg/1)	1.5	5.20
- Phosphorus (mg/1)	<determination limit	0.038
- Chlorine (mg/1)	9.93	17.02

Due to the multiple utilization of water, a mismatch between resources and requirements, and due to the reuse of the watercourse, it requires the coordination of an activity of management of the water resources (Smith 1999). The setting sampling stations for the water analysis was performed taking into account the whole system approach, to identify the possible sources of nutrients that contribute to the proliferation of vegetation. It is important to know the chemical composition of water mainly from the accumulations upstream being the major source of water supply for the downstream HPPs (Hydro-Power Plants). Table 8 summarizes some measurements in 2015 which highlight how is affected the water structure.

Table 8. Measurements along the analyzed area

Station	pH	Ca^{+2} mg/1	NH_4^+ mg/1	NO_3- mg/1	$PO_4^{'3}$ mg/1	CCOMn $mgKMnO_4/l$
Downstream Vadeni	7.85	43.25	<0.001	1.20	0.003	10.23
Preparation Plant Coroieşti	7.60	55.18	0.060	2.60	0.250	68.00
Downstream discharge	7.03	40.28	0.013	1.20	0.032	15.80
Isalnita	7.98	99.39	0.056	3.70	0.210	20.85
Sugar Podari	7.85	46.69	0.009	4.65	0.067	18.40
Effluent Treatment Station	7.73	43.20	0.016	1.35	0.080	14.85

Downstream the dam Vaduri is an industrial effluent, row 2. The wastewater from the unit, although it passed through a water treatment plant, still inserts large amounts of ammonium nitrate, phosphorus, and organic substances. After the mixture with the water coming from the upstream, there is a certain reduction of the amounts of nutrients, as result of dilution, but the contribution from this industrial effluent remains substantially as a continuous process of additional nutrients for the downstream sector. Although there still are many places without sewage plants, after the rehabilitation of the treatment, plant in Tg. Jiu an improvement of the water composition appeared. There still is much sewage delivered directly into the watercourse. The water remains significant loaded with nitrogen, and phosphorus. In Fig.2 are presented the areas necessary to be protected as nature reserves, 2a) and areas needed to be protected from excessive intake of nutrients 2b).

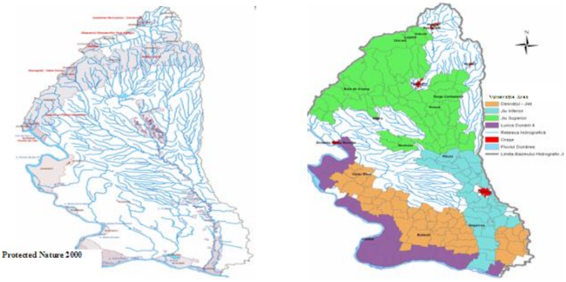

Figure. 2 Protected areas 2a) 2b)

High concentrations of nutrients in the water allow the development of populations of Cladophora in the downstream sector. During time have been evacuated significant amounts of toxic substances (phenols, cyanides etc.). The measures proved that they act as an inhibiting for the vegetation Cladophora, but with unexpected effects on human health.

Conclusions

Pollution by the emissions of organic matter and nutrients (nitrogen and phosphorus) is due to the wastewater from human agglomerations, industrial, and agricultural sources. Lack of or insufficient wastewater treatment leads to pollution of the surface waters that started to be degraded and consume oxygen. This causes a significant impact on the aquatic ecosystems by reducing the biodiversity, vegetation abundance, and lakes eutrophication (the nutrient enrichment and excessive algae growth). The fight against nitrates can solve the problem of lakes eutrophication. The nitrates are the target, but their presence contributes treating two undesirable pollution problems with phosphates:

- Nitrogen increases the report N/P; helps the appearance of nitrogen compounds
- Oxygen maintains the iron oxidation and at the interface, water-sediments is opposing to formation of the phosphorous associations.

Romania was identified as being a sensitive area to pollution with nutrients (total nitrogen and total phosphorus) based on Annex II to Directive 91/271/EEC.

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DETECTION OF CYTOSTATIC DRUGS IN MUNICIPAL WASTE WATER AND THEIR TRANSFER TO SURFACE WATER

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Abstract

A new sensitive and selective LC-MS/MS method with positive electrospray ionization was developed to detect seven cytostatic drugs and one metabolite from municipal waste water. The method separates the target analytes in only 16 minutes using a Hypersil Gold column (100 x 2.1 mm, 3.0 µm) kept at 20°C and a mobile phase made of aq. 0.2% HCOOH and ACN in the ratio 92/8 (v/v). A low mobile phase flow of 0.2 mL/min was used to increase MS ionization yield and hence method sensitivity. A complex two steps (10%/minute) and two plateau gradient elution program was applied for 12 minutes to achieve analyte separation from matrix and each other with highly efficient peaks. Collision energy, fragmentor and capillary voltages were optimized to increase MS sensitivity. Optimization of LC-MS parameters generated low instrumental LOQs situated in the range 0.1 ÷ 1.0 ng/mL. MS detector response was linear between 1 and 100 ng/mL with R^2 coefficients > 0.997 for all eight target analytes. SPE using Oasis HLB cartridges was employed to concentrate target analytes from water samples with MeOH as elution solvent. Intra-day and inter-day precision (RSD %) was situated between 5.4 ÷ 7.2% and 7.3 ÷ 10.8%, respectively. Cytostatics recovery after SPE was good due to internal standard correction with values between 70 ÷ 134%. Overall method LOQs were situated between 0.6 and 5.6 ng/L. The method was tested on four waste water samples from a WWTP plant in Bucharest, but none of the targeted cytostatic drugs were found above detection limit.

Keywords*: cytostatic drugs, LC-ESI-MS/MS, metabolites, municipal waste water*

Introduction

In the last decade, pharmaceuticals have attracted increasing attention from environmental scientists and are studied for their ecotoxicological effects in municipal wastewater treatment processes and occurrence in surface waters, sediments, along with ground and drinking water (Kovalova et al. 2009). From the various classes of pharmaceuticals, cytostatic drugs are amongst the most toxic ones, presenting serious adverse health effects for all living organisms (Johnson et al. 2008a). They are designed to interact with the genetic material and interrupt cell replication. Cytostatic drugs act unselectively on all growing cells and practically all eukaryotic organisms are vulnerable to damage, even at extremely low concentrations of ng/L as found in surface or waste water. Cytostatic compounds and their metabolites can have serious carcinogenic, mutagenic and teratogenic effects on living organisms, including humans. The most important effects, even at low concentrations, are found in foetuses, babies and children with a large number of rapidly growing cells (McKnight

2003). Many cytostatic compounds have very short half-lives and can be eliminated, as unchanged substances or as a mixture of metabolites, by urine and faeces and be directly discharged into the sewer system from hospitals and household discharge from outpatients (Lienert et al. 2007). It is well known that sewage treatment plants do not completely remove organic pollutants found in municipal waste water due to technological limitations and contamination of water with a growing number of new organic molecules, such as cytostatic (Buerge et al. 2006). Due to their low biodegradability, biodegradation of these compounds in municipal waste waters can be assumed to be low to moderate (Kosjek et al. 2011, Negreira et al. 2104). Significant increases in cancer cases over the past few years have led to an increased number of chemotherapy treatments with a related growing concern over the presence of cytostatic drugs in water systems putting humans and aquatic organisms at risk (Johnson et al. 2008b, Rowney et al. 2009). This is the main reason for which an ever-increasing number of studies focused on cytostatics occurrence in the waste water have been reported (Parrella et al. 2014, Busetti et al. 2009). The aim of the present study was to develop, optimize and validate a sensitive, selective, and accurate LC-ESI-MS/MS method able to determine seven cytostatic drugs (Methotrexate, Doxorubicin, Ifosfamide, Cyclofosfamide, Capecitabine, Docetaxel, Tamoxifen) and one metabolite (4-OH Tamoxifen) from municipal waste water at trace level concentration (ng/L).

Experimental

Reagents and chemicals

HPLC grade acetonitrile and methanol were acquired from Merck. HCOOH (p.a.) was obtained from Sigma-Aldrich. Ultra purified water was obtained in-house using a MilliQ instrument. High purity reference standards of cytostatic drugs: Methotrexate, Doxorubicin, Ifosfamide, Cyclophosphamide, Capecitabine, 4-hydroxytamoxifen, Docetaxel and Tamoxifen were acquired from Sigma-Aldrich. Isotopically labelled cytostatic compounds: Methotrexate-d_3, Cyclophosfamide-d_4, and EZ Tamoxifen-d_5 were obtained from Cambridge Isotope laboratories Inc. (Andover, MA, USA) and from Santa Cruz Biotechnologies. These compounds were used as surrogate/injection internal standards. Oasis HLB (500 mg/6 mL) cartridges used for SPE extraction were acquired from Waters (Milford, Massachusetts, USA).

LC-MS instrumentation and conditions

Experiments were performed using an Agilent 1260 series LC system (Agilent, Waldbronn, Germany) coupled with an Agilent 6410B triple-quadrupole mass spectrometer with electrospray ionization source (ESI). All chromatographic runs were carried out on a Hypersil Gold column (100 x 2.1 mm, 3.0 μm) from Thermo Scientific which was kept at 18°C. Initial mobile phase composition was a mixture of Aq. 0.2% HCOOH (A) and Acetonitrile (B) in the ratio 92/8. Separation was done in a complex gradient elution program at a flow-rate of 0.2 mL/min, as follows: time 0 ÷ 1 min (8%B - isocratic plateau); time 1 ÷ 5 min (8 ÷ 48%B); time 5 ÷ 7 min (48%B - isocratic plateau); time 7 ÷ 11 (48 ÷ 88%B); time 11 ÷ 12 min (88%B - isocratic plateau); time 12.1 ÷ 16 min (8%B isocratic plateau). Method injection volume was 20 μL using 0.2% HCOOH and Methanol 95/5 (v/v) as sample diluent. MS detection was achieved using Multiple Reaction Monitoring (MRM) acquisition mode.

Retention time, MRM transitions fragmentor voltages, collision energies and other MS parameters are given in Table 1. ESI ionization source was operated in positive mode with 300°C as the drying gas temperature, 10 L/min drying gas flow, 50 psi nebulizer pressure and 4000 V capillary voltage. Two MRM transitions were used, one for quantitation (quantifier) and another for analyte confirmation (qualifier).

Table 1. MS parameters for the detection of cytostatic drugs and labelled internal standards (MRM transitions, collision energy, fragmentor voltages)

Compound	Time segment (min)	MRM Transitions	Fragmentor voltage (V)	Collision energy (V)	Dwell time (msec)
Methotrexate-D_3	2.5 - 9.0	458.2→311.1 458.2→175.1	90 90	25 25	150 150
Methotrexate	2.5 - 9.0	455.2→308.2 455.2→175.1	90 90	25 25	150 150
Doxorubicin	9.0 - 11.6	544.3→361.0 544.3→397.1	90 90	15 15	80 80
Ifosfamide	9.0 - 11.6	261.1→92.0 261.1→154.0	85 85	25 25	80 80
Cyclophosphamide-D_4	9.0 - 11.6	265.1→140.0 265.1→106.0	90 90	30 30	80 80
Cyclophosphamide	9.0 - 11.6	261.1→140.0 261.1→106.0	90 90	30 30	80 80
Capecitabine	9.0 - 11.6	360.2→244.2 360.2→174.1	95 95	13 13	80 80
4-OH Tamoxifen	11.6 - 13.2	388.2→72.1 388.2→44.1	90 90	45 45	200 200
Docetaxel	13.2 - 15.9	830.3→549.4 830.3→304.1	95 95	25 25	120 120
EZ tamoxifen-D_5	13.2 - 15.9	377.3→72.1 377.3→44.1	90 90	45 45	120 120
Tamoxifen	13.2 - 15.9	372.3→72.1 372.3→44.1	90 90	45 45	120 120

Results and Discussion

LC separation optimization

Taking into account the different polarities of the studied cytostatics (log Kow = -1.85 ÷ 7.88), a gradient elution was chosen starting from a mobile phase with a high aqueous solvent concentration, allowing adequate retention and separation of the most polar compound (Methotrexate, log Kow = -1.85). Increasing the concentration of organic solvent will also allow elution in a reasonable time of higher hydrophobic compounds (Docetaxel, Tamoxifen, log Kow = 2.83, 7.88). Thus, the starting composition of the mobile phase was 92/8 aqueous solvent / organic solvent. The low flow rate of 0.20 mL/min favored analytes ionization in the electrospray source, as it is known that this type of ionization gives better yields at low flow-rate. The reduced column temperature (20°C) was chosen for a better separation between the pair of E and Z geometric isomers of the 4-hydroxy tamoxifen metabolite. The chromatographic column, with 2.1 mm internal diameter, allowed working at a reduced flow rate of 0.2 mL/min without loss of chromatographic peak efficiency, and the small particle size of the stationary phase (3 μm) led to narrow peaks with high chromatographic efficiency. Different additives in the aqueous component of the mobile phase were tested in order to improve MS Electrospray ionization (MS response) and also the peak shape of the compounds. Formic acid (0.1 ÷ 0.3%), Ammonium formate (5 ÷ 10 mM), and Ammonium acetate (5 ÷ 20 mM) were used as aqueous component of the mobile phase. The best ESI ionization was observed for the mobile phase with 0.2% formic acid and thus it was finally chosen for the optimized method. A representative chromatogram showing separation of the target analytes is given in Fig. 1.

MS detection optimization

MS detection parameters were optimized to obtain maximum sensitivity for the cytostatic compounds quantitation. The detection was performed using MS/MS mode Multiple Reaction Monitoring (MRM) to increase selectivity and sensitivity. All analytes responded best in MS detector when using positive polarity for the electrospray source ionization and thus it was chosen for the final method. All ESI ionization source parameters were optimized by modification in a wide range to obtain highest ionization efficiency for all compounds. The final chosen values, giving maximum peak area response, were: 4000V capillary voltage, 300°C drying gas temperature, 50 psi nebulizer pressure and 10 L/min drying gas flow. Collision energy (CE) applied in the collision cell (Q2) to the precursor ions to dissociate them and obtain product ions was varied between 5 and 60V. CE between 13 - 45V generated highest dissociation yield of the precursor ions for all cytostatic compounds. CE showing the highest S/N ratio values for each analyte was chosen for the MRM transitions (Table 1). After the entire procedure of MS optimization, the obtained instrumental quantitation limits (IQL) for all compounds were lower than 0.4 μg/L, except for Docetaxel with a value of 1 μg/L (see Table 2).

Automated SPE optimization

All parameters of the automated SPE extractor were varied to determine the most efficient procedure to concentrate target analytes from waste and surface water. The optimized extraction procedure is given in the following: SPE cartridge conditioning was done with 2 x 5 mL MeOH and then 2 x5 mL H_2O. Water samples (250 mL) were filtered (0.45 μm cellulose). Samples were loaded on the SPE cartridge (Oasis HLB - 500 mg/5 mL) at a constant flow-rate of 5.0 mL/min. Next, the cartridges were washed with 10 mL H_2O to remove endogenous polar matrix compounds and purify the extract.

After washing, the cartridges were air-dried for 40 min and then the analytes were desorbed with 2 portions of 5 mL MeOH. Extracts are then evaporated to dryness under a gentle N_2 stream (45°C) and re-dissolved in 1 mL with aq. 0.2% HCOOH / methanol 95/5 (v/v). The final samples were filtered through 0.45 μm cellulose filters and then injected into the LC-MS system.

Automated SPE provided a 250 fold increase in analyte concentration allowing a detection of target compounds down to few ng/L (LOQs between 0.6 – 5.6 ng/L).

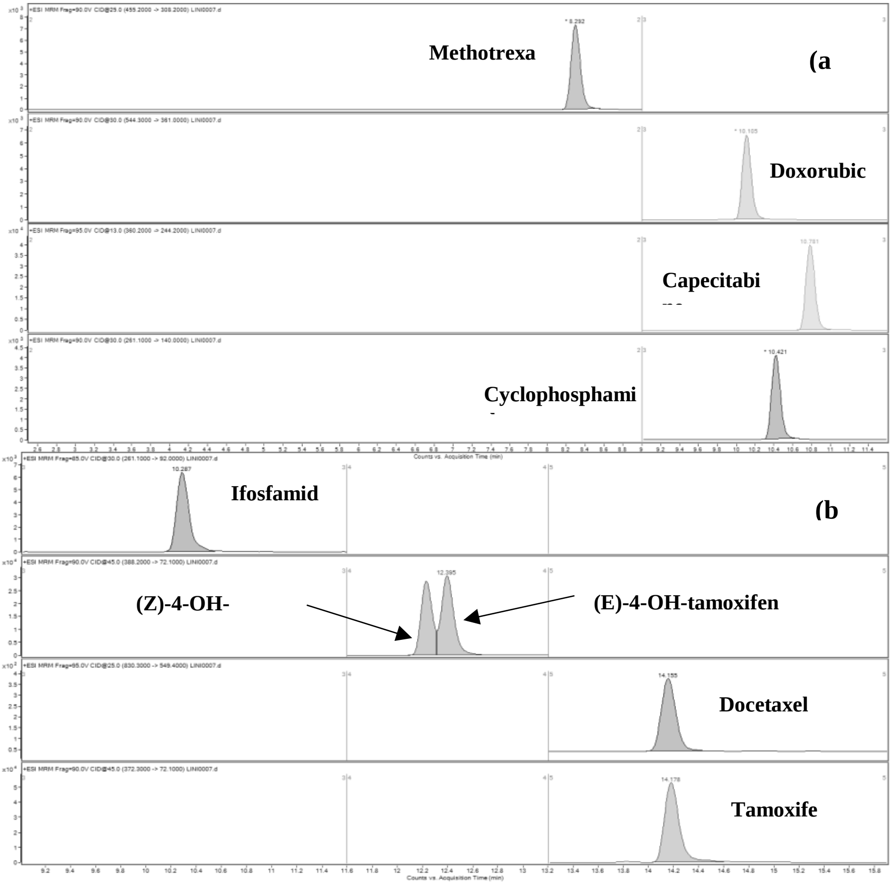

Figure 1. Representative MS/MS chromatograms (MRM) for the target analytes (7 cytostatics and 1 metabolite) obtained after injection of a 50 μg/L mixed solution: (a) Methotrexate, Doxorobicin, Capecitabine, Cyclophosphamide, (b) Ifosfamide, (Z) and (E) 4-OH-tamoxifen, Docetaxel, and Tamoxifen.
MRM transitions are given also in chromatograms legend.

SPE-LC-MS/MS method validation

The performance parameters of the developed method followed during the validation were: selectivity, linearity, precision, limit of quantitation, accuracy and recovery. MS detector response was linear in the range 1 ÷ 100 μg/L with high determination coefficients ($R^2 > 0.997$). Intra-day and inter-day method precision and accuracy were tested on 12 sample replicates. The procedure involved spiking a mixture of cytostatic drugs and internal standards (50 ng/L) in a waste water sample previously tested to be free from the all target analytes. Method precision was expressed as RSD% and it was situated between 5.4 - 7.2% (repeatability procedure or intra-day precision) and between 7.3 - 10.8% (reproducibility procedure or inter-day precision). The obtained analyte recovery (method accuracy) was situated between 70 and 134% due to surrogate internal standard addition which compensated for sample preparation losses (SPE extraction, evaporation, re-dissolution, etc.). Validation data are presented in detail in Table 2.

Table 2. Determination coefficients (R^2), intra-day and inter-day precision, analyte recovery, instrumental quantitation limit (IQL) and overall method quantitation limit (LOQ) obtained for the proposed method

Analyte	**R^2**	**Precision (RSD %)**		**Overall method recovery (% ± RSD %)**	**IQL (µg/L)**	**LOQ (ng/L)**
		Intra-day	Inter-day			
Methotrexate	0.9998	6.1	9.6	98 ± 9.6	0.21	1.3
Doxorubicin	0.9996	6.9	8.4	111 ± 8.4	0.22	1.4
Ifosfamide	0.9999	5.4	7.3	94 ± 7.3	0.30	1.8
Cyclophosphamide	0.9998	5.7	7.9	106 ± 7.9	0.38	2.4
Capecitabine	0.9992	7.2	10.8	93 ± 10.8	0.10	0.6
4-OH-Tamoxifen	0.9975	7.1	9.9	134 ± 9.9	0.40	2.5
Docetaxel	0.9972	6.6	8.0	70 ± 8.0	0.98	5.6
Tamoxifen	0.9999	6.0	8.5	96 ± 8.5	0.18	1.1

In order to test the ability of the method to detect the targeted cytostatics at ng/L level, it was further applied on four different waste water samples from Bucharest, Glina WWTP plant. None of the targeted cytostatics were detected (< LOD) and thus these samples were spiked with a known mixture solution of cytostatics (25 ng/L) and analysed. The obtained results were included in a recovery range between 62 and 118% which is in agreement with that obtained when method accuracy was evaluated. It was observed that no significant matrix effects were generated with respect to the target analytes except for Docetaxel which did not have an isotopically labelled compound as the surrogate internal standard. For this compound a matrix effect of 35-40% expressed as absolute MS signal decrease was established due to interfering compounds from the waste water.

Conclusions

A new sensitive, selective and accurate LC-ESI(+)MS/MS method coupled with automated SPE extraction was developed to detect seven cytostatic drugs (Methotrexate, Doxorubicin, Ifosfamide, Cyclophosphamide, Capecitabine, Docetaxel and Tamoxifen) and one metabolite (4-hydroxytamoxifen) from waste water samples. All chromatographic conditions (mobile phase nature and composition, column temperature, gradient intensity) and MS parameters were optimized to separate and detect the target analytes from a complex matrix like waste water. Samples were concentrated 250 times using SPE on Oasis HLB cartridges with methanol as desorption solvent. MS detector response was linear in the range 1 ÷ 100 ng/mL with determination coefficients higher than 0.997 for all eight cytostatics. Method accuracy was good with recovery values between 70 and 134% due to very good error compensation by using surrogate internal standard addition (previous to sample extraction). Method precision generated RSD values up to 10% (inter-day precision) indicating an adequate method from precision point of view taking into account that SPE, waste water matrix, MS analysis may generate all-together similar or even higher values. Optimization of LC-MS parameters generated very low instrumental LOQs situated in the range 0.1 ÷ 1 ng/mL. Coupled with the sample extraction and concentration procedure (SPE), the overall method quantitation limits (LOQ) for the targeted cytostatic drugs were determined to be below 6 ng/L - more precisely in the range of 0.6 ÷ 5.6 ng/L. The obtained values are comparable with results generated by other similar studies already reported for these compounds. The developed LC-ESI(+)MS/MS method coupled with automated SPE extraction allows for adequate detection and confirmation for the seven cytostatic drugs and one metabolite from waste water samples at trace level concentrations (ng/L). The optimized method was tested on four waste water samples from Glina WWTP plant in Bucharest, but none of the targeted cytostatics were found above detection limit.

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DETERMINATION OF ESTROGENIC STEROIDS IN SEWAGE SLUDGE SAMPLES FROM EIGHT DOMESTIC WASTEWATER TREATMENT PLANTS

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Abstract

Sludges from urban wastewater treatment plants (WWTPs) were tested for the presence of the following natural and synthetic estrogenic steroids: estrone, 17α-estradiol, 17β-estradiol, estriol, 17α-ethinylestradiol and equiline. The method involved ultrasonic extraction followed by solid phase extraction cleanup and liquid chromatography tandem mass spectrometry coupled with electrospray ionization in the negative mode. The steroids were identified and determined by internal standard method in selected multiple reaction monitoring mode. All target compounds were detected in the investigated sludge samples. The highest estrogen concentrations were determined for estrone, which reached 164.4 ng/g in one sample. Synthetic estrogen 17α-ethinylestradiol was detected in 50% of the analyzed samples, in concentrations ranging from 2.7 to 16.1 ng/g.

Keywords: *determination, estrogenic steroids, liquid chromatography, sludge*

Introduction

Estrogenic steroids are chemicals that have the ability to interfere with the normal function of the endocrine systems of humans and animals. Their pathway to the environment is mainly through wastewater effluents from municipal treatment plants, hospital effluents and from livestock activities. WWTPs wastewater effluents are discharged into the river while the sludges, resulted during biological and chemical processes, that contain a large variety of substances including estrogens are used as fertilizer (Aris et al. 2014). It is important to control the presence of estrogenic steroids in sewage sludge because these contaminants can penetrate into the food chain (Nieto et al. 2008).

The purpose of this study was the determination of six natural and synthetic estrogens estrone (E1), 17α-estradiol (αE2), 17β-estradiol (βE2), estriol (E3), 17α-ethinylestradiol (EE2) and equiline (Eq) in sewage sludges collected from eight selected wastewater treatment plants (WWTPs) which can be found in some cities in the south-east of Romania. To achieve this goal, a method consisting of ultrasonic extraction and silica gel cleanup followed by LC-MS/MS analysis was optimized.

Experimental part

Materials and Reagents

Reference standards of estrogens (E1, α E2, βE2, EE2, E3 and Eq) with purity between 98.4 % and 99.8 % were obtained from Sigma-Aldrich (Steinheim, Germany). Isotopically labelled estrogens, 17β-Estradiol-16,16,17-d3 (βE2-d3) used as surrogate internal standard was obtained from TRC Inc. (Toronto, Ontario, Canada) and $^{13}C2$-Ethinylestradiol ($^{13}C2$-EE2) in acetone (100 µg/mL) used as injection internal standard for the quantitation of the six targeted estrogens was acquired from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). HPLC grade acetonitrile and methanol were acquired from Merck. HCOOH (p.a.) and NH_4OH 25% (p.a.) were obtained from Sigma-Aldrich. HPLC grade water was obtained in-house using a MilliQ instrument. Oasis HLB (500 mg/6 mL) cartridges were acquired from Waters (Milford, Massachusetts, USA). Stock solution of individual standards were prepared by dissolving each compounds in methanol at a concentration of 1000 mg/L and stored at -18°C for later use. Working standard solutions were prepared daily by diluting this solution with binary mixture water: methanol (50:50, v/v). All glassware was hand-washed with detergent (Extran) and tap water and rinsed with HPLC grade water.

Sample collection

The sewage sludge samples were collected from eight domestic wastewater treatment plants in Brăila, Buzău and Calarași Counties. The collected samples were grab samples of sludge and were kept on ice during tranzit to the laboratory where they were stored at -20°C until treatment took place. Sludge samples were first lyophilized in a Christ Alpha 1-2 LD lyophilizer (Martin Christ GmbH, Germany) for 24 hours, crushed and homogenized by a mortar and pestle, sieved (particle size <100µm) and stored in glass bottles at -20 °C until they were analysed.

Chromatographic analysis

The chromatographic method was described elsewhere (Galaon et al. 2016). To sum it up, the target compounds were analyzed by HPLC-MS/MS with electrospray ionization. Liquid chromatography was performed on an Agilent 1260 series system (Agilent Technologies) equipped with a degasser, a binary pump, a column oven and an auto sampler. All the analyte were separated on an Zorbax Eclipse Plus C18 (150 x 2.1 mm, 3.5 µm) column Agilent Technologies that was kept at 20°C. All experiments were performed in gradient elution conditions with a flow rate at 0.25 mL/min. Mobile phase composition was a mixture of aq. 0.01% NH_4OH and MeOH. Mass spectrometry was performed using an Agilent 6410B Triple Quadrupole detector.

Results and Discussions

Sample extraction and cleanup optimization

Sludge sample extraction method was developed by optimizing different extraction solvents: methanol, ethyl acetate, acetonitrile, ethyl acetate/methanol, methanol/acetone. All the experiments were performed by spiking 100 ng/g of each target compounds and surrogate internal standard to 0.5 g freeze-dried sludge. It was found that binary mixture of methanol/acetone (5:2, v/v) as extraction solvent gives better recoveries. The final optimized method for simultaneous extraction and cleanup of 6 steroids in sludge using 0.5 g sludge and methanol/acetone (5:2, v/v) as extraction solvent is given as follows. Sludge samples were extracted successively twice with 5 mL of methanol and 2 ml acetone in an ultrasonic bath for 15 minutes (30 °C) and then centrifuged at 3000 rpm for 20 min. The supernatants obtained from each extraction step were combined and transfered by a glass pipette into extraction vials and evaporated to dryness under a gentle nitrogen stream (45 °C). The extracts were re-dissolved in 100 mL HPLC grade water. In order to reduce the matrix interferences, further cleanup of the obtained extracts is necessary (Liu et al, 2011). For this, the automated SPE system AutoTrace 280 Thermo Scientific Dionex was used. In the purification step, the elution solvent is the most important parameter. The best elution solvent should be able to elute the target compounds, have good recovery, and reduce the interference of other compounds and matrix substances. Taking into account that the polarities of the target compounds are of medium level (log K_{ow}: 2.527-4.146), the polar mixture of methanol and water was tested. The cartridges were conditioned with 10 mL of methanol and 10 mL of water at a flow rate of 1 mL/min, adjusted by vacuum pump with an air flow rate of 15 mL/min. After the entire sample was passed through the cartridge at a flow rate of 10 mL/min, the adsorbent phase was washed with 10 mL of ultrapure water at a flow rate of 20 mL/min. The adsorbent was then dried with a gentle stream of nitrogen for 5 minutes. The analytes were eluted in a concentration tube with 2 x 2 mL methanol at a flow rate of 5 mL/min.

The extracts were concentrated to near dryness with a gentle stream of nitrogen in a water bath (45 ± 5 °C), after which was added 0.1mL (100 ng/g) of $^{13}C_2$-EE2 injection internal standard, with the purpose of following the effect induced by the sample matrix, and then reconstituted to a volume of one milliliter with a binary methanol-water mixture (50:50, v/v) and transferred to an LC vial for chromatographic analysis. Solutions that showed visible particles in the extract or were turbid were filtered through a 0.45 μm Millipore filter before being introduced into the vial.

Method validation

The method was validated for this type of matrix of sludge sample in terms of recovery, precision, LODs and LOQs. Using the optimized extraction and instrumental methods, good recoveries were achieved for all targeted compounds (Table 1). The intra-day, inter-day method precision and recovery were tested on 3 replicates by spiking 100 ng/g of estrogens mixture into 0.5 g of sludge. Recovery was situated between 71 and 104 % with internal standard correction.

Application to real samples

The optimized method was applied to eight dehydrated sewage sludge samples collected in May 2016 from different municipal WWTPs. Fig. 1 shows the results of this study. In the samples analyzed, Estrone occurred in 90 % of samples in concentrations ranging from 18.3 to 164.4 ng/g d.w. 17β-Estradiol was quantified only in one sample at level of 5.9 ng/g d.w. For as far as Equline is concerned, it was found in three samples at levels below 121.7 ng/g d.w. Estriol was detected in 60% of sludge samples in concentrations that varied from 4.5 to 16.6 ng/g d.w, with a mediane of 9.1 ng/g d.w.

17α-ethynylestradiol, a synthetic hormone which is a derivative of the natural hormone estradiol, was found in 4 samples in concentrations ranging from 2.7 ng/g to 16.1 ng/g (d.w.). These results are in agreement with the reported values for some sewage sludges samples collected in France (Díaz-Cruz et al. 2009). It is well known that EE2 has the ability to alter the endocrine systems of exposed organisms, even in low concentrations. Consequently, the occurrence of this compound has become a widespread concern in the topic of environmental protection due to its high resistence to the process of degradation and among others, also due to its tendency to accumulate in organic matter (Aris et al. 2014).

Table 1. Intra-day and inter-day precision, recoveries and detection and quantification limits of estrogens in sludge samples by HPLC-MS/MS (100 ng/g)

Compound	**Precision**		**Overall method recovery**[a]	**LOD (ng/g)**[b]	**LOQ (ng/g)**[b]
	Intra-day (ng/g) [a]	**Inter-day (ng/g)** [a]			
E3	11.7± 0.8	10.6 ± 1.7	84.5 ± 10	1.18	3.95
Eq	122.9 ± 6.7	120.9 ± 14.5	84.1 ± 8	0.07	0.24
E1	49.6 ± 1.4	50.5 ± 4.6	86.6 ± 13	0.39	1.31
βE2	5,3 ± 0,5	5.7 ± 0.8	71.3 ± 7	0.73	2.43
EE2	3.9 ± 0.2	4.2 ± 1.0	91.0 ± 8	0.54	1.79
αE2	5.5 ± 0.6	6.5 ± 1.2	104.1 ± 14	1.05	3.49

[a] Mean (%) ± standard deviation (%) (n =3, replicate samples at the same time)
[b] LOD, method limit of detection; LOQ, method limit of quantification

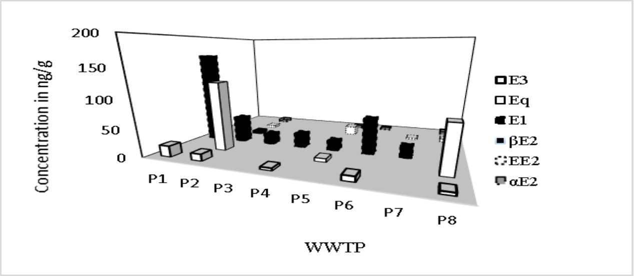

Figure 1. Results in ng/g (d.w.) of sewage sludge samples analyzed

As an example, Fig. 2 shows the MRM chromatograms of the P1 sample where the presence of Estriol (19.6 ng/g d.w.) and Estrone (164.4 ng/g d.w.) can be seen.

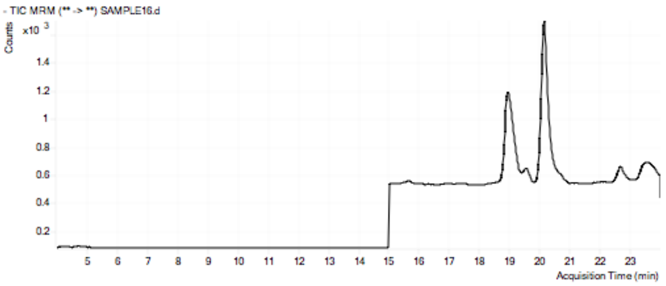

Figure 2. MRM chromatogram obtained by HPLC-MS/MS of sewage sludge collected from WWTP1

Conclusions

A sensitive method was applied to the analysis of eight sludge samples from different municipal WWTPs. The concentrations of detected residual estrogenic steroids in sludge samples varied greatly from 2.7 ng/g d.w. to 164.4 ng/g d.w. The most frequently detected compounds were Estrone and Estriol, with the latter having the highest concentrations.

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DETERMINATION OF SULFUR CONTENT IN WASTE MATERIALS BY ION CHROMATOGRAPHY

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Abstract

The aim of this work is to apply an ion - chromatography method which was initially developed for the determination of sulfur content in fuels, on other classes of samples as municipal waste and oil and sewage sludge.

With respect to their physical properties and texture, solid waste materials as municipal waste, are typically strongly heterogeneous and thus, sample preparation can be critical in obtaining reliable analysis results so that, particle size reduction and homogenizing of the municipal waste was an important step in conducting the experiments. The homogenization of the samples was performed by cutting and then grinding the material in two steps: first a reduction of the particles to diameters passing a 10-mm sieve and secondly to diameters passing a 2-mm sieve.

The sulfur extraction from the homogenized waste samples was carried out by the combustion method in the calorimetric bomb. Sulfur as sulfate anion was then analyzed by ion-chromatography and gravimetric techniques and the results were compared. Depending on the nature and sulfur content of the sample, the repeatability standard deviation s_r and the relative repeatability standard deviation RSD of the results were of the same order of magnitude for the both gravimetric and ion – chromatography methods and they were in the range of about 0.01- 0.05 % for s_r and in the range of about 3.23 – 6.25 % for RSD.

Keywords: *ion-chromatography, municipal waste, oil sludge, sewage sludge, sulfur*

Introduction

According to the European legislation, preventing the waste generation and performing an adequate management (recovery/disposal) is a strategy focusing on the prioritization of practical actions taking into account the sustainable development principles (Arama 2016). The term "waste" means any solid, liquid or contained gaseous material that is discharged by being disposed of, burned, incinerated or recycled (Puiu 2016). Conventional fuels (coal / petroleum coke, fuel oil or methane gas) or conventional raw materials (limestone, clay, marl, loess, bentonite) traditionally used in the cement manufacturing process, could be partially replaced by the waste with a composition corresponding to the requirements of the technological process, the quality requirements and the environmental protection.

There are also types of waste that have a relatively low calorific value, but with a mineralogical content similar to those of conventional raw materials, these wastes could be exploited by recovering both their energy and material value. The essential condition at the recovery of the wastes is to not lead to a significant increase of pollutants in air emissions and of harmful substances in the finished product. This is also achieved by quantitative limitations of the pollutants content in waste, which are intended to be introduced into co-incineration, depending on the specificity of each installation and the clinker production process. In order to characterize the waste composition, analytical investigations are necessary. One of the parameters required of our customers is the sulfur content in waste. To meet these requirements, an ion - chromatography method which was initially developed for the determination of sulfur content in fuels, was applied on other classes of samples as municipal waste and oil and sewage sludge. Three types of waste have been used for the experiments: RDF (resulting from municipal waste containing mainly plastics, textiles and paper), sewage sludge and oil sludge. The results obtained by ion-chromatography (sulfur content, standard deviation of repeatability and coefficient of variance) were compared with the values indicated of the relevant standards for determining the sulfur content of waste. Another comparison was made with the values obtained by the gravimetric method used in parallel.

Materials and Methods

Sample collection

The methods were tested on samples of: RDF (refuse-derived fuel) resulting from municipal waste containing mainly plastics, textiles and paper – 4 different samples; sewage-sludge (N) – 4 different samples; oil-sludge (OS) – 4 different samples. Until sample preparation, the samples are stored at 4 degrees maximum 7 days after their entry into the laboratory.

Apparatus

The analysis of sulfur as sulfate anion from wastes was carried out according to SR EN ISO 10304-1:2009 using a Dionex ICS-5000 + ion chromatography system (Thermo Scientific, Sunnyvale, CA, USA). The system is equipped with a conductivity detector, an IonPac® AS18 hydroxide selective anion-exchange column (2 mm), operating at a flow rate of 0.25 mL/min, sample volume 5 μL and incorporates an electrolytic eluent generator (for 30 mM NaOH production. All samples were prepared according to SR EN 15002:2015. Reduction of the particle size was performed by using a Rotor Beater Mill SR 300 Retsch for RDF samples and Vibratory Disc Mill RS 200 - Retsch for dried sewage sludge. Oil sludge sample was mixed using a Rotor Beater Mill SR 300. After the samples pre-treatment, the sulfur as sulfate anion was extracted by combustion in a calorimetric bomb Parr 6200.

Reagents and Calibration

All reagents used were prepared with ultrapure water (<0.1 μS/cm) from a purification system (Ultra Clear TWF UV Siemens SG Water, Germany), and all chemicals used were of analytical quality. 30 mM Sodium Hydroxide is the eluent solution for Ion chromatography method. Two 1000 mg/L certified solutions of sulfate (CertiPUR-Merck and Sulfate Standard for IC TraceCERT®, Sigma-Aldrich) were used for preparing and verifying the calibration curve. To assess the linearity, calibration curve was prepared in the range 1-100 mgSO_4^{2-}/L. The linear range of the curve was assessed by the value of correlation coefficient of the linear regression and the residuals. The intercept, slope, correlation coefficient and performance parameters obtained are given in Table 1 and Fig. 1.

Table 1. Performance parameters of the method for sulfate anion determination by ion-chromatography method

Performance parameters	Value
Measuring range	1 – 100 mg/L
Linear regression *equation*	$Y = 0.4293x + 0.1971$
R correlation coefficient	0.9998
Detection limit, LOD	0.07 $mgSO_4$/L
Quantitation limit, LOQ	0.7 $mgSO_4$/L
Residual standard deviation, Sy	0.2176
Standard deviation, S_{x0}	0.507
Coefficient of Variation, RSD	0.92 %

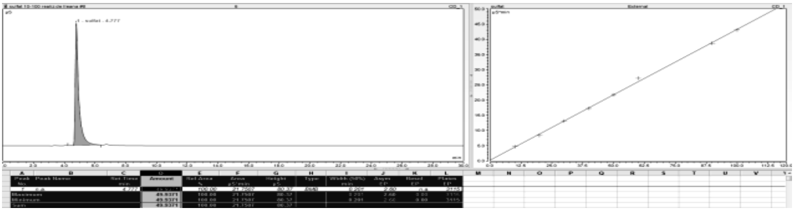

Figure 1. Calibration curve and retention time for sulfate anion determination

Sample pre-treatment

Drying, milling and sieving of the solid samples

European Standard 14582:2016 and SR EN 15002:2015 specifies the pre-treatment required for solid, pasty and liquid samples. As sulfur is an inorganic analyte, sample preparation was performed by the procedure recommended for inorganic chemicals. The samples were dried in air or in oven at 40°C until constant mass. Dry sewage sludge samples were milled and sieved to 200 µm, sealed in plastic containers and stored at 20 °C. In Fig. 2 are shown the samples of sewage sludge before and after pre-treatment.

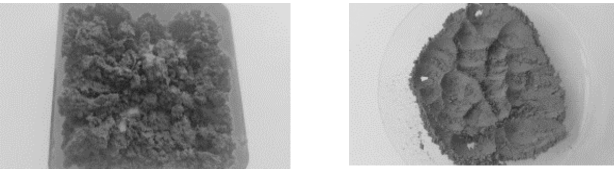

Figure 2. Sewage sludge sample before and after pretreatment

Dry samples of RDF were milled and sieved three consecutive times using a series of 3 sieves with the mesh size of 10, 2 and 0.5 mm. In Fig. 3 are shown the samples of RDF after each stage of milling and sieving.

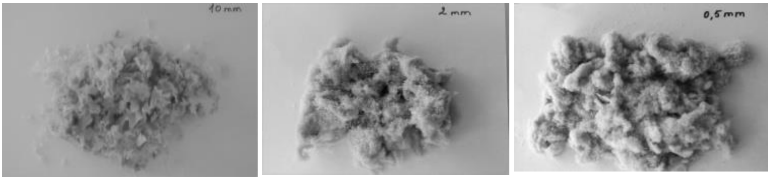

Figure 3. Samples of RDF after each stage of milling

Oil sludge contains volatile organic compounds so, this sample is not dried. In this case, the sample is mechanically mixed as recommended by the European Standard EN 15002:2015.

Combustion of the samples in calorimetric bomb

Sample combustion is commonly used to prepare solid matrices for analysis by IC. This involves total combustion of the sample in oxygen, which converts nonmetallic elements to volatile gaseous compounds. These gases can be collected into a suitable absorbing solution which can then be analyzed using IC (Jackson 2000). In our experiments, RDF, sewage sludge, and oil sludge samples were oxidized by combustion in a calorimetric bomb containing oxygen under pressure. Sulfur containing compounds were converted to sulfate anion which was absorbed in ultrapure water present in the bomb. The aqueous samples with sulfate content and the washing waters resulting from a rigorously rinsing of the bomb using ultrapure water were transferred and diluted in 250 ml volumetric flask of. Aqueous solutions with anion sulfate content were analyzed in parallel by ion-chromatography and gravimetric methods, after a proper filtration through a 0.45 mm membrane based filter.

Results and Discussion

Results for sulfur content in samples of waste (RDF, sewage sludge and oil sludge) and standard deviation and relative standard deviation of the results are centralized in the Tables 2, 3 and 4. According to Fig. 4 one can observe the difference between the RSD results obtained by the ion-chromatography and the gravimetric method. The experimental data showed that the relative standard deviations for the determination of sulfur content in waste by ion-chromatography technique are situated in the range: 3.23% - 6.25% and they are in accordance with the relevant standards. Also, the results are comparable and slightly more homogeneous than those obtained by the gravimetric method used as routine in our laboratory.

Table 2. Results obtained for sulfur content in samples of RDF

Ion-chromatography				**Gravimetry**			**Standard requirements**
Sample	x_{mean}	s_r	**RSD**	x_{mean}	s_r	**RSD**	
	[%]						**SR EN 15408:2011**
RDF1	0.17	0.01	5.88	0.15	0.02	13.33	$[SO_4] = 0.13\%$ $s_r = 0.02\%$ RSD = 15.38 %
RDF2	0.16	0.01	6.25	0.14	0.02	14.28	

Table 3. Results obtained for sulfur content in samples of oil sludge

	Ion-chromatography			**Gravimetry**			
Sample	**x_{mean}**	**s_r**	**RSD**	**x_{mean}**	**s_r**	**RSD**	**Standard requirements**
	[%]						
OS.1	0.73	0.03	4.11	0.71	0.04	5.63	**SR EN 14582:2017** [SO_4] = 0.65% s_r = 0.14% RSD = 21.3% **ASTM D129-13** [SO_4] = 0.5-1% s_r = 0.06% RSD = 6.45 -14.63 %
OS.2	0.84	0.04	4.76	0.84	0.05	5.95	
OS.3	0.93	0.03	3.23	0.92	0.05	5.43	
OS.4	0.41	0.02	4.87	0.39	0.03	7.69	

Table 4. Results obtained for sulfur content in samples of sewage sludge

	Ion-chromatography			**Gravimetry**			
Sample	**x_{mean}**	**s_r**	**RSD**	**x_{mean}**	**s_r**	**RSD**	**Standard requirements**
	[%]						
N1	0.98	0.05	5.10	0.98	0.07	7.14	**SR EN 15408:2011** [SO_4] = 1.06 % s_r = 0.06 % RSD = 5.66 %
N2	0.76	0.04	5.26	0.74	0.05	6.76	
N3	0.68	0.03	4.41	0.64	0.04	6.25	
N4	0.62	0.03	4.83	0.58	0.04	6.89	
N5	0.19	0.01	5.26	0.18	0.014	7.77	

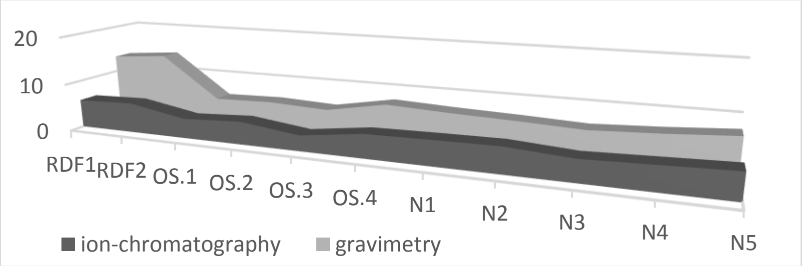

Figure 4. RSD values obtained for ion-chromatography and gravimetric methods

Conclusions

In this paper, an ion - chromatography method was applied for sulfur content determination in waste. Experiments were carried out with samples of RDF (refused derived fuel resulting from municipal waste containing mainly plastics, textiles and paper), sewage sludge and oil sludge. Due to the homogeneity of the results obtained and the analysis time which is much lower than in the case of the gravimetric determinations, ion-chromatography method is appropriate to be used for sulfur determination in studied waste.

Acknowledgements

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ENVIRONMENTAL FACTORS – POTENTIAL RESERVOIRS OF NOSOCOMIAL INFECTIONS

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Abstract

All infections follow the basic epidemiological pattern that if recognized early helps to apply the measures to prevent and control pathologies. The epidemiological process cannot be triggered in the absence of the microorganism's reservoir and therefore it is very important to control the potential reservoirs involved in nosocomial infections. The etiological structure of nosocomial infections varies and includes a wide variety of potentially or strictly pathogenic bacteria that have native or acquired proprieties of virulence and antibiotic resistance. The aim of this project was to monitor the potential role of the environmental risk factors involved in outbreak nosocomial infections. The microbiological studies from an emergency hospital from Bucharest have been started in January 2016 and samples were quarterly collected from drilling and tap water, waste water, air and surfaces. There were performed quantitative analyzes of microbiological contamination level and qualitative analyzes for pathogenic and resistant bacteria detection. Some pathogenic bacteria have been identified in the waste water and drilling water, indicating their interference. The antibiotic resistance properties were observed especially in bacteria from waste waters. Bacteria from vegetables from food preparation were detected in air samples and surfaces tests from kitchen. The results indicated that environmental factors from a medical unit could constitute a reservoir of microorganisms that can trigger nosocomial infections.

Keywords: *antibiotic resistance, infection pathogenic bacteria*

Introduction

Nosocomial infections, also called "hospital acquired infections" are infections acquired during hospitalization which are not present or incubating at administration. Studies throughout the World Health Organization (WHO) documents showed that nosocomial infections have been a major cause of morbidity and mortality.

Contact between patients and a microorganism during hospitalization does not necessarily result in the development of clinical disease. Other factors influence the nature of nosocomial infections such as antibiotic resistance of microorganisms, intrinsic virulence, infected materials and hospital environmental conditions. Water, air and surfaces from hospital must meet aseptic conditions. Drinking water should be safe for ingestion. Fecal contamination most likely is sufficient to cause infections during food preparation, washing or in aerosols, unless adequate treatment is provided (WHO 2002).

Nosocomial waterborne pathogens may reach patients through several modes of transmission. Colonization of healthcare waterworks facility could occur in the proximal infrastructure, in the distal water outlets, or both. Hospital should have prospective water safety plants that include preventive measures, as prevention is preferable to remediation of the contamination from hospital water distribution systems (Decker et al. 2014).

Biofilms develop on all surfaces in contact with non-sterile water. Pathogens, even present below detection limit in water, could attach to biofilms generating a pathogenic environmental reservoir, a potential source of water contamination. Particularly critical are the water systems of hospital where biofilm borne pathogens can considerably contribute to water-associated nosocomial infections. Biofilm can represent the source of pathogens at continuous exposure of patients, care-givers and all surfaces which may come into contact with contaminated water (Wingender et al. 2011). Many outbreaks of waterborne nosocomial infections have been reported and an estimated 1400 deaths occur each year in the United States as a result of waterborne nosocomial pneumonias caused by *Pseudomonas aeruginosa* (Anaissie et al. 2002). In addition, other hygienically relevant bacteria such as *Escherichia coli, Klebsiella oxytoca* were detected in drinking water from hospitals

Inanimate surfaces have often been described as a source for outbreaks of nosocomial infections. The most common nosocomial pathogens may well survive or persist on surfaces for months and can thereby be a continuous source of transmission if no regular preventive surface disinfection is performed (Kramer et al. 2006).

Health centers constantly generate wastewater and a consequent discharge of effluents that require appropriate treatment and disinfection. Hospital wastewater releases a variety of substances such as pharmaceuticals, disinfectants, antimicrobial drugs and multiresistant bacteria (Emmanuel et al. 2005; (Emmanuel et al. 2009). Beta-lactam antibiotics are commonly used to treat hospitalized patients infected by Gram negative bacteria. The production of beta-lactamases is the principal mechanism involved in the inactivation of these antibiotics and the ESBLs (extended-spectrum beta-lactamases) confer resistance to the penicillin, third-generation of cephalosporins and aztreonam. These resistant microorganisms get into the hospital wastewater, for instance the pathogenic and antibiotic resistant bacteria detected in the wastewater treatment plant of hospital from Rio de Janeiro, Brazil, indicated a potential risk for the microbiological pollution of water resources and a way of transmitting resistant bacteria (Chagas et al. 2011).

Over all, studies conducted during 2012 on more than 1000 hospitals in more than 30 countries allowed European Center for Disease Prevention and Control to estimate that every day in European hospitals around 8000 patients suffer from at least one nosocomial infection. Acquired pathology is an important public health issue since in 2013, 366 cases of nosocomial infection were recorded in Romania (ECDC 2013).

As regards the control of nosocomial infections, the knowledge of the degree of water, air, objects and surfaces contamination with potential pathogenic microorganisms, constitutes an important criterion for the assessment by hygiene conditions.

The aim of this project was to monitor the environmental risk factors potentially involved in outbreak nosocomial infections in an emergency unit from Bucharest, Romania.

Materials and Methods

The experimental study has been started in the first quarter of 2016 then quarterly were collected samples from the hospital drillings, dispensers and municipal water supply, wastewater plant, air and surfaces (ISO 19458 2006).

The quantitative analyses of drinking water indicators (L 458 2002) based on colony count technique on yeast extract agar (Oxoid, UK) for heterotrophyc bacteria (ISO 6222 1999) and membrane filtration method for coliform bacteria and *Enterococcus spp.* The Chromogenic coliform agar (Biolife, It.) was used to isolate and count coliform bacteria and *E. coli* (ISO 9308-1 2014) Slanetz & Bartley agar (Biolife, It.) and Bile aesculine agar (Biolife, It.) were used for detection of *Enterococcus* (ISO 7899-2 2000)

The most probable number technique on Colilert-18 (IDEXX, UK) was performed for detect coliform bacteria from wastewater samples (ISO 9308-2 2012). *Enterococcus spp* was detected through the same membrane filtration method as for the drinking water samples.

Aeromicroflora samples were taken by the Koch method and the surfaces samples were taken with sterile strips. The sampling points have been established according to risk activities such as kitchen and pediatrics.

The qualitative analyses identified the bacterial strains based on metabolic reactions by the Omnilog system (Biolog, USA) and detected the antibiotic resistance profile (CLSI 2015).

Results and Discussion

There were performed quantitative analyses for the microbiological indicators of water samples and quantitative analyses for identification of potentially pathogenic and resistant bacteria from the collected samples.

The results of microbiological analyses of drinking water from 2016 sampling campaign indicated a high degree of contamination with potentially pathogenic bacteria in drillings water and dispenser's water from pediatrics (Banciu et al. 2016). Based on these previously reported results the medical unit decided to renounce of the use of own drillings water and dispensers. The microbiological analyses for drinking water were performed during 2017 only from the municipal water supply. The values of microbiological indicators analyzed in the first two quarters of 2017 for drinking water were within the limits imposed by the present legislation.

The quantitative results of microbiological indicators of wastewater indicated a significantly increased values of Gram negative bacteria (Figure 1) among them we identified *Raoutella ornitholityca, Proteus mirabilis, Klebsiella oxytoca, Serratia liquefaciens*. These microorganisms presented resistance to beta-lactams, the most commonly used substances in treatment procedures from the studied hospital.

The air and sanitation tests of the kitchen tables resulted in the identification of bacteria with food origin, *Brevibacterium linens*, *Rhizobium vitis* and *Paenibacillus provencensis*.

The sanitation test of the water tap from the hospital kitchen detected *Rahnella aquatillis*, resistant to the majority of beta-lactam antibiotics (Figure 2) and *Klebsiella oxytoca* resistant to Gentamicin and Chloramphenicol (Figure 3).

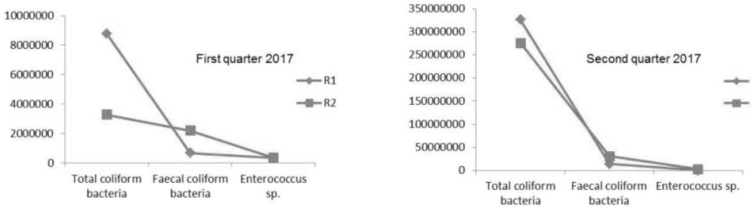
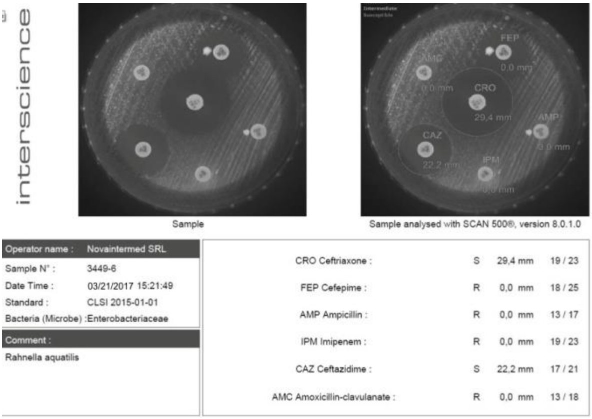


Figure 1. Density of microbiological indicators in wastewater samples for an emergency hospital (Bucharest, Romania) in the first two quarters of 2017



Sample

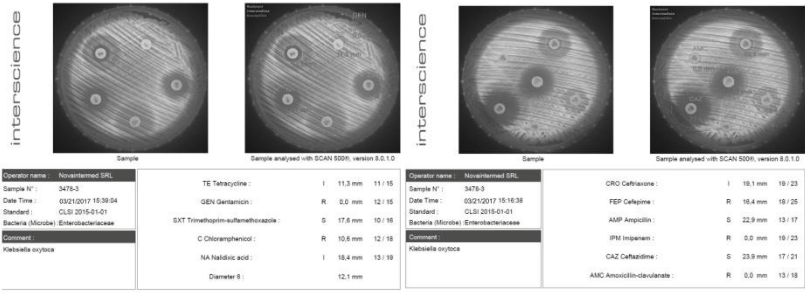
Sample analysed with SCAN 500®, version 8.0.1.0

Operator name : Novaintermed SRL
Sample N° : 3449-6
Date Time : 03/21/2017 15:21:49
Standard : CLSI 2015-01-01
Bacteria (Microbe) : Enterobacteriaceae

Comment :
Rahnella aquatilis

CRO Ceftriaxone :	S	29,4 mm	19 / 23
FEP Cefepime :	R	0,0 mm	18 / 25
AMP Ampicillin :	R	0,0 mm	13 / 17
IPM Imipenem :	R	0,0 mm	19 / 23
CAZ Ceftazidime :	S	22,2 mm	17 / 21
AMC Amoxicillin-clavulanate :	R	0,0 mm	13 / 18

Figure 2. Antibiotic susceptibility testing for *Rahnella aquatilis* isolated from sanitation test of water tap from kitchen – emergency hospital from Bucharest, Romania.



Sample

Sample analysed with SCAN 500®, version 8.0.1.0

Operator name : Novaintermed SRL
Sample N° : 3478-3
Date Time : 03/21/2017 15:39:04
Standard : CLSI 2015-01-01
Bacteria (Microbe) : Enterobacteriaceae

Comment :
Klebsiella oxytoca

TE Tetracycline :	I	11,3 mm	11 / 15
GEN Gentamicin :	R	0,0 mm	12 / 15
SXT Trimethoprim-sulfamethoxazole :	S	17,6 mm	10 / 16
C Chloramphenicol :	R	10,6 mm	12 / 18
NA Nalidixic acid :	I	18,4 mm	13 / 19
Diameter 6 :		12,1 mm	

Sample

Sample analysed with SCAN 500®, version 8.0.1.0

Operator name : Novaintermed SRL
Sample N° : 3478-3
Date Time : 03/21/2017 15:16:38
Standard : CLSI 2015-01-01
Bacteria (Microbe) : Enterobacteriaceae

Comment :
Klebsiella oxytoca

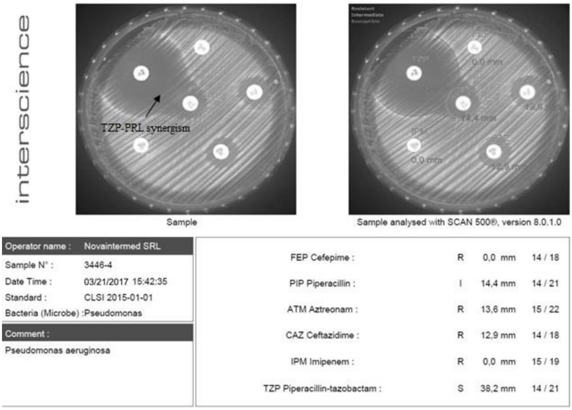
CRO Ceftriaxone :	I	19,1 mm	19 / 23
FEP Cefepime :	R	16,4 mm	18 / 25
AMP Ampicillin :	S	22,9 mm	13 / 17
IPM Imipenem :	R	0,0 mm	19 / 23
CAZ Ceftazidime :	S	23,9 mm	17 / 21
AMC Amoxicillin-clavulanate :	R	0,0 mm	13 / 18

(a) (b)

Figure 3. a. Beta-lactams susceptibility testing for *Klebsiella oxytoca* isolated from sanitation test of water tap from the kitchen – emergency hospital from Bucharest, Romania; **b.** General antibiotic susceptibility testing for *Klebsiella oxytoca* isolated from sanitation test of water tap from kitchen – emergency hospital from Bucharest, Romania.

The water on this tap was provided by the city network and it was assumed that the water met the highest microbiological quality and the quantitative results of this study demonstrated it. It could be speculated that the contamination with antibiotic resistant bacteria came entirely from the hospital environment.

The results of surfaces analyses in the pediatric unit indicated the presence of *Pseudomonas aeruginosa* resistant to Cefepime, Aztreonam and Ceftazidime (Figure 4).



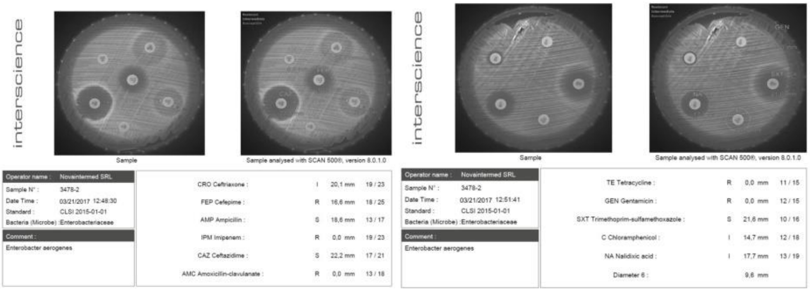
Operator name : Novaintermed SRL
Sample N° : 3446-4
Date Time : 03/21/2017 15:42:35
Standard : CLSI 2015-01-01
Bacteria (Microbe) :Pseudomonas
Comment :
Pseudomonas aeruginosa

FEP Cefepime :	R	0,0 mm	14 / 18
PIP Piperacillin :	I	14,4 mm	14 / 21
ATM Aztreonam :	R	13,6 mm	15 / 22
CAZ Ceftazidime :	R	12,9 mm	14 / 18
IPM Imipenem :	R	0,0 mm	15 / 19
TZP Piperacillin-tazobactam :	S	38,2 mm	14 / 21

Figure 4. Antibiotic susceptibility testing for *Pseudomonas aeruginosa* isolated from sanitation test of pediatric unit – emergency hospital from Bucharest, Romania

The expression of beta-lactam activity and the piperacillin-tazobactam susceptibility of the *Pseudomonas aeruginosa* showed antibiotic resistance profile (Figure 4).

The aeromicroflora from the pediatric room showed the presence of *Enterobacter aerogenes* resistant to beta-lactams and other some antibiotics (Figure 5).



Operator name : Novaintermed SRL
Sample N° : 3478-2
Date Time : 03/21/2017 12:48:30
Standard : CLSI 2015-01-01
Bacteria (Microbe) :Enterobacteriaceae
Comment :
Enterobacter aerogenes

CRO Ceftriaxone :	I	20,1 mm	19 / 23
FEP Cefepime :	R	16,6 mm	18 / 25
AMP Ampicillin :	S	18,6 mm	13 / 17
IPM Imipenem :	R	0,0 mm	19 / 23
CAZ Ceftazidime :	S	22,2 mm	17 / 21
AMC Amoxicilin-clavulanate :	R	0,0 mm	13 / 18

(a)

Operator name : Novaintermed SRL
Sample N° : 3478-2
Date Time : 03/21/2017 12:51:41
Standard : CLSI 2015-01-01
Bacteria (Microbe) :Enterobacteriaceae
Comment :
Enterobacter aerogenes

TE Tetracycline :	R	0,0 mm	11 / 15
GEN Gentamicin :	R	0,0 mm	12 / 15
SXT Trimethoprim-sulfamethoxazole :	S	21,6 mm	10 / 16
C Chloramphenicol :	I	14,7 mm	12 / 18
NA Nalidixic acid :	I	17,7 mm	13 / 19
Diameter 6 :		9,6 mm	

(b)

Figure 5. a. Beta-lactams susceptibility testing for *Enterobacter aerogenes* provided from aeromicroflora of pediatric room – emergency hospital from Bucharest, Romania; **b.** General antibiotic susceptibility testing for *Enterobacter aerogenes* provided from aeromicroflora of pediatric room – emergency hospital from Bucharest, Romania.

Resistance mechanisms associated with modification of membrane permeability such as porin alteration and active efflux are released of *Enterobacter aerogenes* environmental matrices of hospital.

Conclusions

The results of the microbiological indicators for municipal water supply showed that this water was fine for drinking purposes.

The wastewater analyses indicated a high density of fermentative bacteria and the necessity of a more efficient treatment plant could be taken into consideration.

The microbiological experiment for hygiene conditions highlighted that bacteria might be involved in the outbreak nosocomial infections. Some of these bacteria had a food preparation origin and could trigger pathologies at immunocompromised patients due to its antibiotic resistance properties. *Pseudomonas aeruginosa* and *Enterobacter aerogenes* were two species of considerable medical importance due to their multidrug resistant properties.

The experimental study from 2016 to the present has led to the decommissioning of water from own drillings and automatic dispensers. Correlation between beta-lactams commonly used in hospital and antibiotics those for which microorganisms showed resistance may suggest more attention to controlling the antimicrobials administration.

The data obtained demonstrated that environmental factors of hospitals, especially disinfection conditions and presence of antibiotic resistant microorganisms, may represent reservoirs for nosocomial infections.

The adoption of increased prevention and control measures is required to eliminate the occurrence of risk factors. The monitoring of the sterilization and disinfection conditions in the various sections of hospital is part of the international program of surveillance and control of nosocomial infections.

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IMPACT OF ANTIBIOTICS OF ANTHROPOGENIC ORIGIN ON BACTERIAL SOIL COMMUNITIES IN AGRICULTURAL ECOSYSTEMS. REVIEW

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Abstract

Soil is considered to be the most diverse microbiological ecosystem on Earth. Microbial soil biodiversity is substantially influenced by animal husbandry, intensive agricultural practices and soil cultivation (tillage, crop rotation, irrigation, organic and inorganic fertilization, application of pesticides etc.). Soil mismanagement represents a worldwide topic that impairs natural ecosystem sustainability as a first consequence. In order to understand and correctly apply soil management practices a deep insight in ecological processes is necessary.

Soil microbiota have a great impact on both natural processes (biogeochemical cycles) as well as various other aspects that could influence human health and the quality of life (micro- or macro-contaminants, pharmaceuticals, fertilizers, phytosanitary products). Pharmaceuticals, especially antibiotics are intensively used in animal husbandry either as therapeutic agents or for prophylactic measures. Antibiotics of microbial, semi-synthetic or synthetic origin impact the metabolism of bacteria: at subinhibitory concentrations they act as hormetic intercellular messengers stimulating gene expression. Higher amounts have bacteriostatic or bactericidal effects according to their mode of action. Both result in a profound modulation of bacterial community structure and biodiversity by boosting genotypic and phenotypic variability and induction of antibiotic resistance. They also pose an indirect effect on the communities (generating different genotypic and phenotypic variability such as antibiotic resistance). Agricultural management practices like application of organic fertilizers (e.g. manure) expose soil microbiota to a variety of hazardous agents of anthropogenic origin including antibiotics, antibiotic resistant bacteria and antibiotic resistance genes which interact with the indigenous soil resistome.

This paper describes the impact of human land-use, especially the ecological effects of antibiotics on natural ecosystems and the increase of antibiotic resistance in soil communities.

Keywords: *antibiotics, antibiotic resistance genes, natural ecosystems, soil microbiota, soil management practices*

Introduction

Soil is considered to be the most diverse microbiological ecosystem on Earth. Soil microbiota plays a key role in the ecosystem sustainability and stability. Soil microorganisms take part in different biogeochemical processes such as nitrogen and carbon cycling and they act also as mediator in several ecological processes such as bioremediation, pollution control, soil health and fertility (Paul 2007). Soil microcosms present a broad microbial biodiversity closely related with abiotic factors (soil types, agriculture practices, temperature, pH, moisture, selective pressure factors – metals, biocides, antibiotics) and biotic factors (plant types, soil microbial communities, other relationships between soil inhabitants) (O'Brien 2002; Aminov 2011; Pal et al. 2015).

Approximatively 65% of total soil microorganisms are found in the top 25 cm of soil, with an abundance of Gram negative bacteria at the soil surface and Gram-positive bacteria residing in deeper layers (Paul 2007). Microbial biodiversity and activity is higher on top of the soil due to the pores which influence the availability of water and energy sources. Usually, soil communities are attached to different soil constituents such as humic acids, clays, soil organic matter, due to their negative charge and also for protection (Paul 2007).

Understanding the multifunctionality of ecosystems represents a difficult task due to multiple and complex interactions between soil microbiota and environmental factors such as land use, different soil/crops types and climate changes (Singer et al. 2016), but also due to competitive, pathogenic or mutualistic relationships between the involved organisms. Agricultural management practices have a great impact on soil microbiota due to the release of antibiotics, metals and other compounds like pesticides/biocides which act as selective pressure factors and contribute to the emergence, maintenance and spread of antimicrobial resistance in the environment (Hölzel et al. 2012; Bender et al. 2016). Land use intensification, such as application of different pesticides/biocides, low plant diversity and intensive soil tillage, have been shown to have a negative impact on soil microorganisms. Soil mismanagement represents a worldwide topic that impairs natural ecosystem sustainability as a first consequence (Singer et al. 2016).

Ecological effects of antibiotics on natural ecosystems

Animal husbandry and intensive agriculture practices influence particularly the microbial soil biodiversity and also contribute to different environmental problems related with human health and the quality of life. Pharmaceuticals, especially antibiotics are intensively used in animal husbandry either as therapeutic agents or for prophylactic measures (Kummerer 2009a; Tasho & Cho 2016). Land spreading of animal manure releases in the environment a large variety of antibiotics (A), antibiotic resistant bacteria (ARB) and a vast variety of antibiotic resistance genes (ARGs) into the environment (Bender et al. 2016).

Antibiotics of microbial, semi-synthetic or synthetic origin impact the metabolism of bacteria: at subinhibitory concentrations they act as hermetic intercellular messengers stimulating gene expression (Davies et al. 2006). Higher amounts have bacteriostatic or bactericidal effects according to their mode of action. Both result in a profound modulation of bacterial community structure and biodiversity by boosting genotypic and phenotypic variability and induction of antibiotic resistance (Gothwal & Sashidhar 2014).

The origin of antibiotics in natural environments such as soil or water is related especially with their fate: firstly, urban wastewater treatment plants (UWWTPs) are considered to be one of the most important hot-spots of the dissemination of A, ARB and ARGs (Rizzo et al. 2013) – a large part of antibiotics that are consumed by humans are excreted in urine and faeces and thus enter UWWTPs. Reclaimed water (WWTP effluent) is used in many countries for irrigation purposes and thus A, ARB and ARGs present in this matrix are introduced into soil habitants because wastewater treatment processes only inefficiently remove these substances (Durso & Cook 2014). Also, ground and surface waters (which could receive drainage water from contaminated soils) used for animals or for irrigation are important sources of ARB and ARGs. Another way is represented by land application of sludge/biosolids that originate from UWWTPs. It is estimated that in Europe, 37% of biosolids are land applied (Kinney et al. 2008). Secondly, another important source of antibiotics is animal husbandry. Antibiotics which are used either as therapeutic agents or for prophylactic measures are excreted in urine and faeces and subsequently used as natural fertilizers and are deposited in agricultural soils. Manure management plays a key role in assessing the risks of soil contamination with ARB and ARGs and thus the faeces that come from swine farms are continuously monitored (Haley et al. 2012). Also, grazing animals could contribute to the spread of antibiotic resistance in soil. From soil the A, ARB and ARGs get into the fresh water (groundwater, surface water, like streams, rivers, sea) or in different crops/vegetables and thus could adversely impact human health (Singer et al. 2016).

Antibiotics persistence and antibiotics resistance in agricultural ecosystems

The negative effects of antibiotics in natural environments such as soil could be divided in two important directions: on the one hand, they act on the development of antimicrobial resistance and/or on the other hand they alter the natural ecological functions of soil.

The most frequent antibiotics found in animal faces are represented by oxytetracycline, doxycyclin and sulfadiazine, followed by tetracycline, tylosin and lincomycin (Berendsen et al. 2015). In contrast, the antibiotics found in sludge are norfloxacin, ofloxacin, ciprofloxacin, trimethoprim, sulfamethoxazole and doxycycline (McClellan & Halden 2010; Clarke & Smith 2011). Studies have shown that different residual antibiotics are frequently detected in activated sludge, urban biosolids (Zhang & Li 2011), animal manure, sewage sludge, sediments (Kemper 2008; Yang et al. 2010b), wastewater, reclaimed water, surface water or groundwater (Renew & Huang 2004; Gulkowska et al. 2007).

The persistence of antibiotics in soil microcosms is influenced mainly by temperature (Gavalchin & Katz 1994; Winckler & Grafe 2001), soil type (Marengo et al. 1997), pH (Gilbertson et al. 1990), adsorption affinity (Tolls 2001; Boxall et al. 2004), photodegradation (Kummerer 2009a, Knapp et al. 2005), biodegradation (Li & Zhang 2010), oxidation (Adams et al. 2002). Also, the excretion rate (Jjemba 2002; Zuccato et al. 2001) and the half-life of the antibiotics (Gavalchin & Katz 1994; Weerasinghe & Towner 1997) play a key role in the persistence of these antimicrobials in agricultural ecosystems. The adsorption of the antibiotics in soil environments is influenced by soil pH (Basakcilardan-Kabakci et al. 2007) and soil clay content (Cermak et al. 2008). Different antibiotic classes have different adsorption properties in soil environments (Wang & Wang 2015).

The evolution of antimicrobial resistance is related to both long term exposure to low doses as well as short term exposure to high doses of antibiotics, genetic variation and horizontal transfer of antibiotic resistance genes (HGT) (Martinez 2009; Tasho & Cho

2016). The dissemination of ARGs in the natural environments is related with horizontal gene transfer (Williams-Nguyen et al. 2016; von Wintersdorff et al. 2016). Antimicrobial resistance acquired due to horizontal gene transfer can occur through different mechanisms such as conjugation (cell-to-cell contact), transduction (HGT mediated by phages), and transformation (uptake of extracellular DNA) (Williams-Nguyen et al. 2016). Soil microcosms offer good conditions for HGT due to the great microbial diversity, high cell densities, the persistence of extracellular DNA and also by the presence of different ARGs located on mobile genetic elements (Levy-Booth et al. 2007; Pietramellara et al. 2009).

The pesticides/biocides that are used in agriculture purposes act as selective pressure factors for the selection of antibiotic resistance (European Commission 2009; Webber et al. 2015; Buffet-Bataillon et al. 2016). In Europe, the use of biocides in veterinary settings has intensely increased between 1992 and 2007 by 40% (Sattar et al. 2007). Nowadays, both the use of antimicrobials as well as biocides in veterinary purposes is strictly regulated by different guidelines (Guidelines 2015/C 299/04; Regulation 528/2012). Different antibiotic resistance mechanisms are common for pesticides/biocides and antibiotics; thus, they allow the acquisition of antibiotics resistance genes which enable higher tolerance for different bacteria strains (Russell 2003).

The fate and the development of antibiotic resistance in agricultural soils due to the intensive use of the veterinary antibiotics as therapy, disease prevention and control, and growth promotion (National Committee for Clinically Laboratory Standards 2002) have been reviewed previously by different researchers (Jechalke et al. 2014, 2015; Kummerer 2009a, 2009b; Landers et al. 2012; Du & Liu 2012; Ashbolt et al. 2013). The researchers highlight the importance of antibiotic usage in subinhibitory concentrations (veterinary purposes) and how the applied manure affects the signaling and maintenance of regulatory networks of soil bacteria communities. Also, it is important to take into account the selective pressure which could act on the environment resistome and also to identify and describe the rates of HGT in environmental hot-spots. In order to minimize antibiotic resistance, the European Union has banned the use of antibiotics as growth promoters since January 1st 2006 (Kemper 2008; Grenni 2017; Regulation 1831/2003/EC).

The effects of antibiotics present in soil on human health

World Health Organization (WHO) classified the drugs for animal use (antibiotics) in three important categories: critical drugs, highly important drugs and important drugs (WHO Critically important antimicrobials for human medicine. 5th revision 2016). Most of the critical drugs are used frequently in cattle, swine and poultry farms. Not only is the type of the antibiotic important in human health risk assessment, but also the spectrum, mode of action and concentration. For each antibiotic, there could be not only one gene that encode it, but several genes that code for resistance, so it is also important to know how many genes are involved in resistance and monitor all of them (Ibekwe et al. 2011; Durso et al. 2011; Frye et al. 2011).

WHO presents the implications of antibiotic resistance for human health as being a serious problem – "associated with more frequent and longer hospitalisation, longer illness, a higher risk of invasive infection and a twofold increase in the risk of death ..." (WHO, Tackling antibiotic resistance from a food safety perspective in Europe, 2011). In order to diminish the usage of antibiotics, it is necessary to implement specific conditions such as publish clear policies for the use of antibiotics (especially for prophylactic measures), actively measure usage levels of antibiotics (especially for critical drugs) and report different situations of antimicrobial resistance (data bases).

In order to evaluate the benefits and risks of the presence of antibiotics in agroecosystems, especially because the dissemination of antimicrobial resistance in soil could affect human health through the food chain, soil, water, insects, dust and animals (Phillips et al. 2004; Landers et al. 2012), it is necessary to improve our understanding of the ecology and evolution of antibiotic resistance and its relationship with indigenous environmental bacteria, ARG and HGT (Święciło & Zych-Wężyk 2013; D`Costa et al. 2007).

Conclusions and future perspectives

This paper describes the complexity and diversity of the antibiotic resistance in natural ecosystems (influenced by biotic and abiotic factors) and how soil mismanagement practices could act as mediators in the increase of environmental levels of antimicrobials.

The available data on the dynamics of ARB and ARGs in soil environments in response to the misuse of antibiotics from anthropogenic resources and to the increasing application of certain pesticides which affect bacterial population structure highlight how little we know regarding the impact of these compounds on soil microbial communities. Additional research focusing on the ecological impact of pharmaceuticals and pesticides used in agriculture or animal husbandry on natural environments like soil and water is necessary and will provide new insights for a better understanding of agricultural management practices and the interactions between antimicrobials and resistance towards them.

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Abbreviations: A – antibiotics; ARB – antibiotic resistant bacteria; ARGs – antibiotic resistance genes; HGT – horizontal gene transfer; WHO – World Health Organization; UWWTP - urban wastewater treatment plants; DNA – deoxyribonucleic acid.

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INFLUENCES OF ORGANIC AMMONIUM DERIVATIVES ON THE CHANGE OF CONCENTRATIONS OF NH_4^+, NO_2^-, NO_3^- IN RIVER WATER

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Abstract

One of the logical reasons for the study of nitrogen is the toxicity of its various forms. Their effect on the natural aquatic environment is very different and depends on the amount and structure of organic radicals associated with amine nitrogen. The difference of the effect of amines of natural origin (diethylamine - DEA) and synthetic origin (1-naphtylamine - 1-NA, diphenylamine - DPA and cetyltrimethylammonium - CTMA) on the processes of ammonia oxidation has been investigated. The maximum allowable concentration (MAC) for synthetic amines and for natural origin amines differs by almost two orders of magnitude. Both natural and synthetic amines affect oxidation-reduction processes caused by the activity of bacterial enzymes, even within MAC values. In the case of 1-NA, the inhibitory effect is associated with a toxic effect, whereas for DEA this effect is doubled (due to a toxic effect, as well as from the amine-bound carbon). CTMA also has an impact on the inhibition of processes. But in the presence of anionic surfactants (egg, lauryl sulfate-LS) in an aqueous medium, the effect of CTMA is clearly reduced. Conversely, the presence of $CaCO_3$ particles reduces the ability of anionic organic substances to decrease the effect of cationic ones. Typically, the amines, arising from the decomposition of organic materials of natural origin, have less toxicity and lower MAC than those of synthetic origin. It is important to note here that laboratory models are sensitive even at concentrations below the MAC. Because of this, MAC can not be perceived as absolute values and only meaning within certain limits.

Keywords: *ammonium, amine, calcium carbonate, nitrite, surfactants*

Introduction

Concerns the behavior of cationic organic substances with different structure and toxicity in surface water, which combine with other types of organic substances, as well as the changes in their combinations in this environment. The amines, which are homologues of the ammonium in which the hydrogen is replaced by various organic radicals and which inhibit the oxidation of ammonium, decompose into the aquatic environment, which complicates the process (Spataru 2011; Britto 2001; Britto & Konzucker 2002; Tanaka 2009). In this situation, the dynamics of the stable, soluble forms (NH_4^+, NO_2^-, NO_3^-) give us new research opportunities (Spataru 2015; Spataru 2017).

In the present study, both amines used in the chemical industry and those that can be the result of natural processes of protein and amino acid decomposition have been investigated. Due to various toxicity, they have maximum admissible concentrations (CMA) ranging for about two orders of magnitude. The study was performed at concentrations below the permissible limit and in case of overdose.

Materials and methods

The model included water samples from the Nistru River, where different amounts of the ammoniacal nitrogen were added. To river water samples, the NH_4Cl solution has been added, in order to achieve concentrations of ~ 3 mg/L and ~ 6 mg/L of ammonium. In parallel with the reference sample, to which only ammonium was added, both amines of chemical industry waste (1-NA, DPA, CTMA) and those resulting from the decomposition of proteins (DEA). Laboratory models have been initiated, respecting the minimum recommended sample of water in glass vessels. The model was produced under natural lighting conditions, away from direct sunlight. Natural water research was conducted according to ISO, the methods published in the literature. Sample testing was performed using the HACH DR/2500 Spectrophotometer.

Results and Discussion

Considering that ammoniacal nitrogen is a physiological product of living organisms eliminated, we can understand its oxidation process in which it participates through its catalytic systems a wide range of bacteria (Müller 2006; Spataru 2011) as one of the reference. Thus, the dynamics of ammonium oxidation can serve as an indicator of the state and potential of self- purifying of the aquatic environment. Laboratory simulations comprised five concentrations (0.025, 0.05, 0.1, 0.25, 0.5) of 1-NA corresponding to 0.5; one; 2; 5; 10 MAC for this one substance.

Dynamics of $[NH_4^+]$; $[NO_2^-]$ in Fig. 1 and Fig. 3 demonstrates the influence of 1-NA on the river water purification process. In previous experiments, the concentration of ammoniacal nitrogen concentration increased by more than 50% of the initial NH_4^+ concentration in the sample with 1-NA after three days of experiment. This increase took about ten days the spring period (Spataru 2015). In the sample containing the same amount (1 MAC) of 1-naphthylamine in the present simulations, we also notice a significant increase in ammonium concentration.

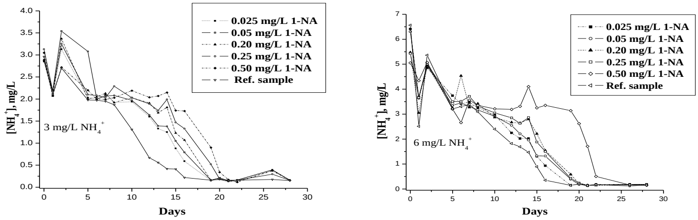


Figure 1. Dynamics of ammonium ions concentration in the Nistru River water containing 3 and 6 mg/L NH_4^+ in the presence of 0.025 mg/L (0.5 MAC); 0.05 mg/L (1.0 MAC;) 0.1 mg/L (2.0 MAC); 0.25 mg/L (5 MAC); 0.5 mg/L (10 MAC) 1-naphtylamine (1-NA)

If microbial populations that have nitrogen fixation properties are well represented, then the selection through the additions introduced into the river water model is possible. This phenomenon is the clearest for 0.05 mg/L of 1-NA and decreasing for 0.25, 0.1 and 0.025 mg/L 1-NA in the presented simulations. The total nitrogen of soluble mineral forms is increasing during the period of nitrogen fixation (on 5 day).

For its 0.5 mg/L, the nitrogen fixation does not take place. Probably, the toxic effect is also dominant for the nitrogen fixation biota. Even at lower and equal concentrations of MAC, ammonium oxidation occurs more difficult than in the reference sample. In the case of concentrations exceeding MAC values of 1-NA, the ammonium oxidation brake is more pronounced. Oxidation braking takes place gradually as the concentration of 1-NA increases.

The changes in the first three days after the initiation of laboratory simulations, in the 6 mg/L NH_4^+ range, the 1-naphthylamine concentration has a well-defined impact. In Figure 2, the trend curves of 1) concentration differences (C_0-C_1) of initiation day and a day after this; 2) the difference between the first and second concentrations (C_1-C_2); 3) that between day of the initiation and after two days (C_0-C_2). By extrapolating the curves of these dependences of 1- NA, we obtain a concentration to which these changes will no longer be. The value of 1-NA, which is supposed to stop these changes completely, is 0.659 mg/L. The synchronization of the increase of the difference value (C_0-C_2) with that of the concentration of total mineral nitrogen in water demonstrates of the possible azotfixation. Denitrification process also brings increasing [NH_4^+]. We have to note that the natural aquatic environment demonstrates obvious sensitivity to the presence of 1-naphthylamine even at concentrations equal to and lower than its MAC. And at the equal and lower concentration than the MAC of the 1-naphthalene, the dynamics of the NH_4^+ and NO_2^- indices describe a similar pathway.

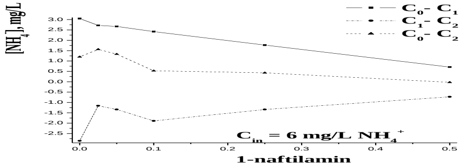


Figure 2. Dynamics of the initial ammonium ion concentration difference on the second and third day in dependence of 1-naphthylamine increase in the laboratory simulations with 6 mg / L NH_4^+

Deviations of the stable soluble mineral form (NH_4^+, NO_2^- și NO_3^-) in water demonstrate a change in the ammonium, nitrite and nitrate ion concentrations due to the oxidation of various forms of organic carbon in the context of nitrate and nitrite oxygen consumption. A decrease in the concentration of nitrite ion at the 20th day is evident in both the 1-NA laboratory simulations of 3 mg/L and of 6 mg/L. Even in the case of the reference sample (with 3 mg/L NH_4^+ , without 1-NA), this redox effect is highlighted, which in the ammonium dynamics synchronizes with a small peak. There is an increase in the duration of the intermediate process such as NO_2^- and its concentration. The increase in nitrite takes place simultaneous with developing of heterotrophic and autotrophic bacteria (Spataru 2011).

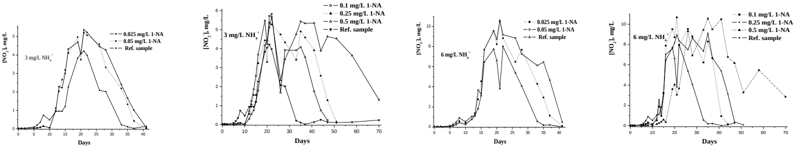


Figure 3. Dynamics of nitrite ions concentration in the Nistru River water with 3 and 6mg/L NH_4^+ and 0.025 mg/L - 0.5 mg/L 1-NA initially

Diethylamine, an amine which is assimilated by aquatic microorganisms, has a more selective toxicity. Even at the MAC value it has the same effect as 1-naphthylamine on redox processes generated by bacterial enzyme activity. The difference between samples of diethylamine simulations compared to 1-NA is manifested by MAC values (almost two orders) for these amines. In the case of 1-NA, only ammonium oxidation is delayed in the model samples containing this amine. And, in the case of diethylamine, there is a delay of both NH_4^+ and nitrite formation exceeds this index compared to the reference sample, braking oxidation and NO_2^- formation and oxidation compared to the reference sample.

The presence of diethylamine (2.0 mg/L) increases the peak value of the ion nitrit formation and oxidation dynamics curve, and in the presence of 20 mg/L DEA, this index decreases in both 3 and 6 mg / L simulations. In the first case, DEA causes an enzymatic activation in which the organic carbon in the river water sample is preferentially involved, but also the organic radicals of the DEA. Decomposition, oxidation, assimilation of DEA occurs naturally much easier than 1-NA. 20 mg/L of DEA in the water sample increases the amount of organic carbon available for reduction. In this case, the dynamics of the redox processes is influenced by both the increased organic carbon (upon addition of 20 mg/L DEA) and the amine nitrogen, which can be converted into the ammonia form. We mention that two steps of increasing ammonium ions are evident. The first period is up to day 5, already described, and the second - only for the sample with 20 mg/L DEA, where the initially massively grows of the ammoniacal nitrogen commensurable with the sum of the added and the one that accumulated on the complete decomposition of this amine.

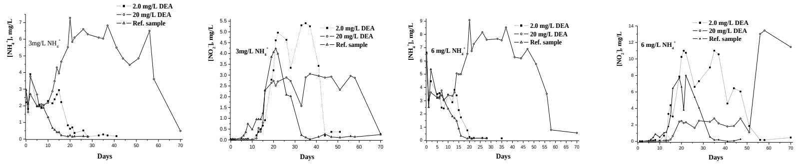


Figure 4. Dynamics of ammonium ions concentration and nitrite in Nistru River water with 3 mg/L and 6 mg/L NH_4^+ and containing 2.0 mg/L (MAC) and 20.0 mg/L (10 MAC) diethylamine (DEA)

The maximum amount of NH_4^+ obtained at the decomposition of 2 mg of DEA is 5.14 mg. For the sample with 20.0 mg/L, the difference between the values of concentrations in days 12-15 and days 20-40 is about 5 mg/L and somewhat longer. In samples with 3 mg/L NH_4^+, there is also a syncronization of the ammonium concentration maximum with the NO_2^- concentration lows. This aspect denotes a process in which the nitrite nitrogen passes into the ammoniacal one.

Fig. 5 demonstrates the braking of NH_4^+, NO_2^- oxidation in water in both the 1 MAC and even more in those with 10 MAC for DPA samples. Curves of DPA samples are mostly similar to those of 1-NA and will deserve the same comments.

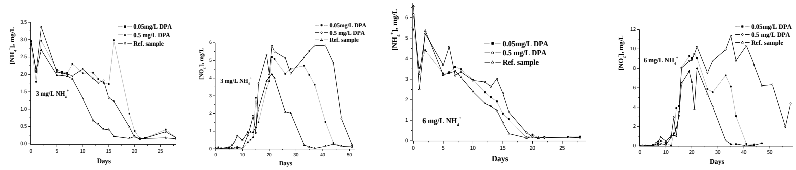


Figure 5. The dynamics of ammonium and nitrite ions (3 mg/L and 6 mg/L NH_4^+ initially) in water Nistru River in the presence of diphenylamine 0.05 mg/L (MAC) and 0.5 mg/L (10 MAC)

In spring samples from the Nistru River, in the presence of $CaCO_3$ the ammonium ion oxidation and formation of nitrite ion is stopped practically. The oxidation of ammonia in the rivulet water of the Cunicea village (Figure 6) is similar in both (in the presence and absence of $CaCO_3$) samples (Spataru 2015). The toxicity of cationic surfactants (SAS) amplifies with the water hardness increasing. The phenomenon of the nitrification braking in the presence of $CaCO_3$ is characteristic for the water of downstream WWTP of cities from where are flows cationic and anionic surfactants in river. In the presence of mixtures of cationic and anionic SAS, the preferential binding of anionic SAS to calcium carbonate particles is found.

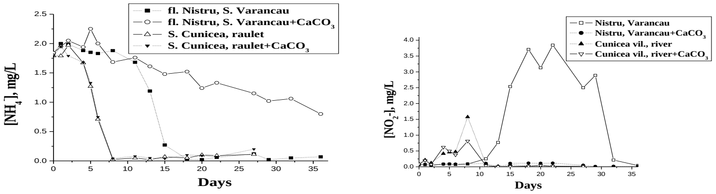
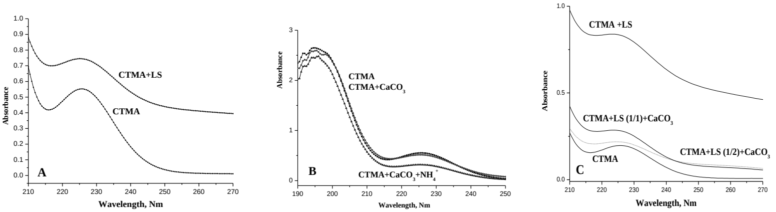


Fig. 6. Dynamics of ammonium (a) and nitrite (b) ion concentration in the waters of the Nistru River, Varancau and in the rivulet of the Cunicea village collected on May 2012

The assessment of these changes was performed using the ability of [Ct SAS*An SAS] complexes to take the form of UV VIS spectrum similar to that of Ct SAS. Thus, the combination [CTMA*LS] has similar spectral line configuration of CTMA (see Fig. 7-a) in the segment of 210-250 nm, but higher values. Using this difference, we can determine the change in concentration of this complex. The study spectra solutions only CTMA (10^{-5} M) and together with LS in the presence of $CaCO_3$ particles, demonstrates considerable changes in aqueous solutions (Fig. 7-c). Thus, the difference spectra movement of complex [CTMA*LS] solution in the absence of $CaCO_3$ particles and in presence of substrate of coincidence with that of only CTMA solution demonstrates almost complete breakdown of the combination CTMA*LS caused by the presence of $CaCO_3$ nanoparticles. It is necessary to note that in the solution remains SAS Ct. The UV VIS spectra (Fig. 7-c) solution of the CTMA in combination with LS taken in different proportions 1/1 and 1/2 without $CaCO_3$ particles and in their presence, proves the impact of LS of the changes taking place (Spataru 2017). The amount of Ct SAS decreases in solution with increasing An SAS. Thus, the formation of the SAS Kt * SAS An and changes occurring under the impact of calcium carbonate particles is due to geometry, but mostly of hydrophobic chain length of quaternary ammonium species.

In the simulation laboratory research activity, a surface change CaCO3 particles were highlighted difference on UV VIS spectra of aqueous solution of CTMA, with and without NH_4^+. UV VIS spectra of aqueous solutions of cationic SAS do not show the change in concentration to the addition of fine calcium carbonate particles in the absence of NH_4^+ (Fig. 7B). But in the solutions of the CTMA with adding ammonium ion (10^2 mg / L) the change of concentration SAS is evident. Thus, the surface of the calcium carbonate in the absence of ammonium ion is selective of anion SAS only, and adding an aqueous solution of NH_4^+ in the surface of the particles $CaCO_3$ may have the properties of the adsorbent of both the anionic and the cationic SAS. This effect does not depend on the structure of cationic SAS.



(a) (b) (c)

Figure 7. UV VIS spectra (a) of cetiltrimetilamoniului (CTMA) and his combination with lauryl sulfate (LS); (b) of CTMA together with $NH_4{}^+$ (10^2 mg/L) and calcium carbonate particle; (c) CTMA solutions in the ratio 1:1 and 1:2 with LS, and the addition of $CaCO_3$

Conclusions

Ammonium derivatives (amines) have a brake impact of redox processes of stable soluble nitrogen forms at concentrations below MAC. With increasing their concentration in river water, the effect is in progress. Calcium carbonate causes no braking nitrification in clean water; Organic cationic pollutants caused in the presence of calcium carbonate produce a clear braking impact on the dynamics of oxidation of NH_4^+, NO_2^- in natural waters. Experience has shown the changes in the SAS interaction with $CaCO_3$ particles, depending on the proportions of these substances in water. So, the transfer and the reorientation of CTMA to carbonate particles takes place depending on the amount of LS. So, decomposition occurs combination CTMA*LS and depositing them on nanoparticles, wherein the first bonding layer is formed with LS, and the rest are oriented based on the hydrophobic chains and groups electrostatic interaction. The UV-VIS method demonstrated the loss of selectivity of calcium carbonate particles is obvious in the presence of higher concentrations (about

10^2 mg/L) of ammonium. Simulations and laboratory tests water samples from the Nistru River demonstrate the Ct SAS negative influence on treatment and self-purification processes.

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INTERDEPENDENCE BETWEEN TOTAL ORGANIC CARBON CONTENT AND HEATING VALUE OF SEWAGE SLUDGE SAMPLES

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Abstract

Sewage sludge from urban wastewater treatment plants come from different stages of wastewater treatment and are considered as waste, falling under the waste regulations. In order to reduce the negative environmental impacts, the removal of sewage sludge on landfill is considered as the last waste management option.

One of the sludge management alternatives is to recover energy from the sewage sludge by incineration in waste incinerators or co-combustion in cement or thermal power plants.

The use of sewage sludge as a source of renewable energy is an ecologically and economically efficient option, both in the EU and Romania sludge management strategy.

Total organic carbon is a key environmental indicator for soil, sludge and sediment and a parameter for characterizing sludge for energy recovery.

The paper presents the methodology for total organic carbon determination from acidified sludge samples by dry combustion, in an oxygen atmosphere using FlashEA 1112 Series Analyser.

From the experimental laboratory researches the following aspects were highlighted: the interdependence between the total organic carbon content and the heating value of sludge samples, an important factor for energy recovery/elimination by incineration, co-combustion and utilization as secondary raw materials in cement plants.

Keywords: *co-combustion, heating value, incineration, sewage sludge, total organic carbon*

Introduction

The modernization of existing municipal wastewater treatment plants or the construction of new ones leads to a substantial increase in the amount of sewage sludge to be managed. Sludges from urban waste water treatment plants come from different stages of sewage treatment and are considered as waste falling under the waste legislation. Removal of sludge in a landfill is considered as the last sludge management option to reduce adverse environmental impacts (Arama & Kim 2016).

One of the sludge management alternatives is energy recovery from sludge. The use of sludge from sewage treatment plants as a source of renewable energy is an option indicated to be both ecologically and economically efficient, both in the EU and Romania sludge management strategy.

A greater emphasis was put on energy recovery from sludge incineration, so at the EU 15 level, the amount of sludge incinerated increased from 1.5 Mt D.S./year in

1995 to 3.1 Mt in 2010 (an increase of 106.7 %) with an estimated increase in 2020, to 3.6 Mt D.S./year (Neamt & Ionel 2013).

Through the research-development activity and implementation of high technology in recovery renewable energy resources in Germany, energy recovery through incineration of sewage sludge increased significantly, from 9 % in 1991 to 53.2 % in 2010 (an increase of 491 %) of the total sludge produced, with a humidity of 60 % D.S. (Federal Institute of Ecology UBA 2011).

Sludge mono-incineration plants, in combined cycles, have been tested and developed in Germany beginning with 2005 at the Technical University of Braunschweig (Vockrodt 2004), as well as in the "HUBER - sludge2energy" technology (HUBER TECHNOLOGY).

The sewage sludge is mainly composed of wastewater, organic and inorganic suspensions. The factors influencing the characteristics of the sewage sludges are: the source and characteristics of wastewater (municipal and / or industrial); sludge removing as primary, secondary and tertiary sludge; aerobic or anaerobic stabilization; whether or not there are dehydration installations; addition or not of dehydrating additives (lime, polyelectrolytes) (Vockrodt 2004).

Sewage dehydrated sludge (25% - 40% dry substance) or dried (over 85% dry substance) can be incinerated in municipal waste incinerators, in municipal sewage sludge incineration plants or coincinerated in cement kilns, or co-incinerated in thermal power plants with lignite (Vockrodt 2004).

In order to estimate the available heat in sewage sludge is necessary to know the net calorific value of the sewage sludge, which is given by the organic substances contained therein. For the characterization of sludge for energy recovery purpose, an important parameter is also the total organic carbon content.

The paper presents the methodology for total organic carbon content determination from acidified sludge samples by dry combustion, in an oxygen atmosphere using FlashEA 1112 Series Analyser, and the interdependence between the total organic carbon content and the net calorific value of sludge samples.

Materials and Methods

Materials

Between 2014-2016, a sample of dehydrated sludge from a municipal wastewater treatment plant, was monthly characterized.

In the lab the sludge samples were air-dried at ambient temperature to remove the moisture content. The dried samples were milled using the Retsch Vibratory Disc Mill RS 200 in order to obtain a laboratory sample with a grain size of less than 200 μm.

Methods

The characterization of the sewage sludge samples was done by laboratory determination of the most relevant parameters, using standardized methods.

Determination of moisture and ash content was performed by gravimetric methods according to SR EN 12880:2002 and SR EN 15169:2007.

To predict the potential use of municipal sludge as a fuel, the most relevant parameters to consider are the net calorific value and the total organic carbon content.

The gross calorific value was determined by a calorimetric method according to SR EN 15170: 2009, using the PARR 6200 calorimetric bomb.

The net calorific value was calculated according to SR EN 15170:2009 standard, using the gross calorific value and the hydrogen content. The net calorific value represents the available energy to be converted to thermal and / or electrical energy from the sludge.

Total Organic Carbon content determination

Total organic carbon is a key indicator for the characterization of sludge for energy recovery. Organic carbon in sludge is found in different forms. Due to the diversity of organic carbon compounds, the global total organic carbon (TOC) indicator is used. Total organic carbon content in sewage sludge was determined by a chromatographic method using the Thermo Scientific FlashEA 1112 Elemental Analyser according to SR EN 15936: 2013 standard.

The FlashEA 1112 is based on the well-known Flash Dynamic Combustion method, which produces complete combustion of the sample within a high temperature reactor, followed by an accurate and precise determination of the elemental gases produced using a TCD thermal conductivity detector. The sample combustion temperature was 950^0C. Total carbon dioxide released during combustion is expressed as carbon percent.

For total organic carbon content determination in sewage sludge samples the analytical process starts with the elimination of all inorganic carbons in the form of carbon dioxide by the effect of acidification of the sample with a small volume of phosphoric acid in special container.

The liquid phase produced was dried at a temperature lower than 40 °C, and the special container was then closed and loaded into the autosampler carousel, and analyzed.

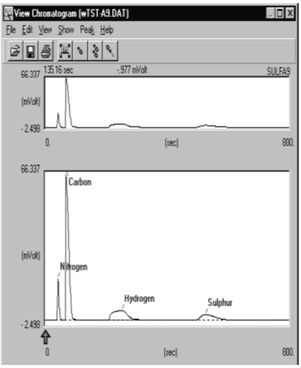

Figure 1. Chromatogram model for Thermo Scientific FlashEA 1112 Elemental Analyzer

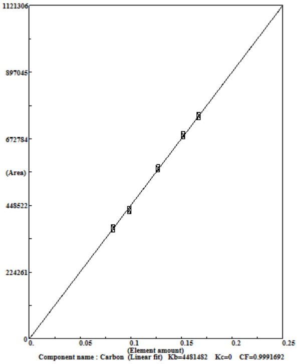

Figure 2. Calibration curve for carbon content

The sample quantity was chosen in such a way that the carbon dioxide released during combustion was in the analyzer working range.

For Thermo Scientific FlashEA 1112 elemental analyzer calibration, calcium carbonate reference material was used. In Fig. 1 it is presented a chromatogram, and in Fig. 2 a calibration curve for carbon. The regression coefficients for the calibration curves were about 0.999.

In Table 1 presents the characteristics of the dehydrated sewage sludge samples analyzed during the period 2014-2016, in the form of minimum, average and maximum results and the used methods.

Table 1. Main chemical characteristics of the dehydrated sewage sludge sample analyzed during the period 2014-2016

Parameters	U.M.	Minimum values	Maximum values	Average values	Standardized Methods
Proximate analysis					
Moisture content	%	61.29	75.20	69.06	SR EN 12880:2002
Dry substance	%	24.8	38.71	30.94	SR EN 12880:2002
Ash (550^0C), ar	%	11.19	26.08	16.21	SR EN 15169:2007
Ash (550^0C), db	%	45.02	70.59	51.94	SR EN 15169:2007
Ultimate analysis					
Carbon, ar	%	7.80	10.30	8.45	SR EN 15407:2011
Carbon, db	%	23.70	34.05	27.55	SR EN 15407:2011
Hydrogen, ar	%	0.56	1.54	1.05	SR EN 15407:2011
Hydrogen, db	%	1.88	4.48	3.43	SR EN 15407:2011
Nitrogen, ar	%	0.90	1.67	1.20	SR EN 15407:2011
Nitrogen, db	%	2.45	5.30	3.91	SR EN 15407:2011
Sulfur, ar	%	0.06	0.41	0.24	SR EN 14582:2017
Sulfur, db	%	0.17	1.42	0.78	SR EN 14582:2017
TOC, ar	%	6.57	10.19	7.73	SR EN 15936:2013
TOC, db	%	19.95	31.87	25.19	SR EN 15936:2013
LHV, ar	kcal/kg	217	633	375	SR EN 15170:2009
	MJ/kg	0.91	2.65	1.57	SR EN 15170:2009
LHV, db	kcal/kg	1700	3107	2458	SR EN 15170:2009
	MJ/kg	7.12	13.01	10.29	SR EN 15170:2009

ar-as received; db-dry basis; TOC-total organic carbon; LHV-low heating value

Results and Discussion

The characteristics of the dehydrated sewage sludge samples analyzed (Table 1), are compared with the characteristics of a low grade coal (lignite) used in many combustion power plants in Romania. The results were compared at dry state.

The analyzed sludge samples showed a dry matter content between 24.8% and 38.7%, compared to lignit. The carbon content of sludge samples, as well as the net calorific value, is about 75% and 70% respectively of the lignite value. The hydrogen content of sludge samples is about 120% higher than in lignite.

The nitrogen content of sludge samples, an important indicator due to the formation of nitrogen oxides, is approx. 4 times higher than for lignite. Despite of the great content of sewage sludge in nitrogen, the conversion ratio of fuel N to NO_x is less than 5%, and the total net emissions of NO_x are in very low levels (Fytili 2008 after Zhao 1994). The sulfur content of sludge samples is up to 50% lower than for lignite.

From the data presented in Table 1, a close correlation is observed between the total organic carbon content and the low heating value of the analyzed sludge samples. In Table 2, the monthly results obtained for the total organic carbon content and the low heating value for the sewage sludge samples analyzed are presented. Fig. 3 shows the interdependence between the total organic carbon content and the low heating value of the analyzed sludge samples.

Table 2. Variation of total organic carbon content and low heating value for dehydrated sewage sludge samples

Crt. No	TOC db %	LHV db kcal/kg	LHV db J/g	Crt. No	TOC db %	LHV db kcal/kg	LHV db J/g
1	20.13	1849	7.74	15	25.99	2630	11.01
2	20.36	2098	8.78	16	26.51	2530	10.59
3	20.40	1964	8.22	17	26.68	2686	11.25
4	21.00	1991	8.34	18	26.79	2550	10.68
5	21.40	2145	8.98	19	27.04	2629	11.01
6	21.84	2236	9.36	20	27.10	2709	11.34
7	21.94	2194	9.19	21	27.21	2775	11.62
8	22.03	2293	9.60	22	27.21	2666	11.16
9	23.71	2291	9.59	23	28.50	2690	11.26
10	23.94	2253	9.43	24	28.98	2919	12.22
11	24.49	2416	10.12	25	29.80	2869	12.01
12	25.12	2544	10.65	26	30.34	2966	12.42
13	25.22	2401	10.05	27	31.87	3107	13.01
14	25.60	2581	10.81				

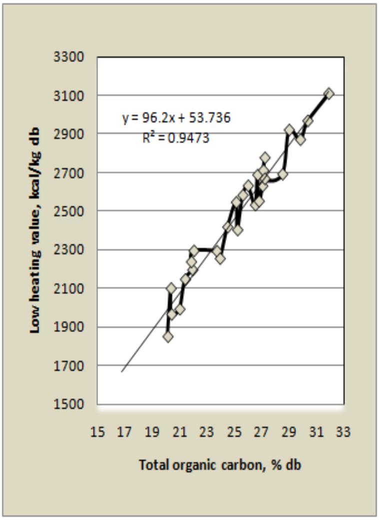

Figure 3. Interdependence between the total organic carbon content and the low heating value of the analyzed sludge samples

Between the total organic carbon content and the low heating value of the characterized sludge samples there is a linearity relation, described by the equation: $y = 96.2 * x + 53.736$.

The degree of interdependence between the two variables, the total organic carbon and the low heating value, was evaluated using the Pearson (r) linear correlation coefficient. It is the ratio between the series covariance and the product of their standard deviations and presents values between -1 and 1 (ecuation no.1). The sign of the correlation coefficient indicates the direction of the association (inversely proportional to the sign - and directly proportional to the + sign) of the investigated variables (Facultatea de Medicina si Farmacie Iuliu Hategan Cluj Napoca 2017).

$$r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}} \qquad (1)$$

The value of the correlation coefficient r for the presented curve is 0.973. According to Colton's empirical rules (1974), a correlation coefficient greater than 0.75 (or less than -0.75) indicates a very good association or correlation of values.

The coefficient of determination R^2 is the square of the correlation coefficient r.

The value of the determination coefficient expresses an intensity of the linear relation between the two variables (total organic carbon and low heating value) or answers the question: how much of the variation of Y can be explained by the linear relationship with X.

The value of the determination coefficient is 0.9473. This value suggests a very good performance. In general, R2 value greater than 0.9 indicates a very satisfactory model performance.

Conclusions

Laboratory experimental researches were highlighted the interdependence between the total organic carbon content values of analysed sewage sludge samples and the low heating values, an important factor for energy recovery / final disposal through incineration / co-incineration processes and, last but not least, the use as secondary raw materials in cement factories from Romania.

The main advantages of the combustion or energy utilization of the sewage sludge are: electricity from sewage sludge saves fossil fuels and reduces fossil originated CO2 emissions, the amount of solid waste can be reduced, bacteriological load with pathogen agents does not present any more risks.

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MATERIAL COMPOSITION AND PROPERTIES OF RED MUD COMING FROM DOMESTIC ALUMINA PROCESSING PLANT

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Abstract

Red Mud from domestic alumina plant contains high excess alkaline components and traces of many toxic heavy metals. The results showed that Red Mud contains as main components hematite, goethite, residual aluminium oxide-hydroxides, desilication products (DSP), TiO_2 and does not contain radioactive elements such as Uranium (U), Thorium (Th). U and Th in Red Mud are less than the average concentration values of Uranium (4ppm) and Thorium (12 ppm) in the earth´s crust. Physical structural composition of domestic Red mud can be classified by an equilateral triangle iron oxide/hydroxide-sandy components-clays (23.2÷53.7% iron oxide/hydroxide; 34.1÷63.8% sandy components; 7.3÷34.1% clays). Chemical composition of red mud is, by weight (%w/w): Fe_2O_{3Tot} in the range 31.02 to 47.04; Na_2O: 2.45÷5.39; CaO: 3.01÷20.86; K_2O: 0.02÷0.07; MgO: 0.05÷ 0.73; Al_2O_3: 10.97÷22.78; SiO_2: 1.09÷8.28; TiO_2: 2.59÷ 5.76; Loss of Ignition (LOI): 13.03÷ 38.75. Red Mud also contains traces of some heavy metals and valuable metals (Cr, Mn, Zn, V, Ga, Gd, Sc, etc.) and has the pH in the range 13.0 ÷ 11.9 (when it is fresh) and 9÷10 (when it is aged) respectively. The search results are an important basis to select the proper treatment and recovery this waste as secondary resources for ceramic materials production (ceramic foams).

Keywords: *alumina plant, chemical analysis, material properties, red mud, wastes*

Introduction

The red mud is the solid waste generated in the Bayer process alumina production (Al_2O_3) from high bauxite grade ore, which has fine, micronized to colloidal texture and a chemical composition that varies due to the many types of bauxite processed over the time in Romania. The red mud contains mainly elements such as Fe, Al, Si, Ti, Na, Ca, traces components (V, Ga, Sc, Mg, Ba, K, Cu, Pb, Zn, Cr, Ce, Gd etc.) and has an excessively alkaline pH. The high alkalinity level is due to the residual non-recoverable soda content; however it is acceptable for storage as non-hazardous waste (01 03 09), (Council Directive 91/689/EEC 1991). The US Environmental Protection Agency has rated red mud as a residue based on 4 risk characteristics: corrosively, reactivity, ignition capacity and extraction procedure toxicity but does not classify it as hazardous waste. However, large quantities generated globally at world level (between 0.8 and 2.0 Mt/Mt Al_2O_3) could be a problem for the environment due to deposits and possible leaching under severe environmental conditions. At the same time, red mud pits can lead to impacts and risk perceived by the population in the areas surrounding these deposits by: landscape changes and visual discomfort, air pollution, surface water pollution, soil fertility changes and biocenosis composition on the land of adjacent landfills. Removal from the natural or economic circuit of land for red mud deposits is a process that can be considered temporary but which, in terms of the concept of "sustainable development", extends over at least two generations if the planning periods are summed up (1-3 years), exploitation period (about 15-30 years), ecological recovery and post-monitoring (15-20 years). In terms of biodiversity, such a deposit means removing about 30-300 species / ha from the affected area, without considering the microbiological population of the soil. In addition, the biocenosis in the vicinity of the landfill are changing in the sense that vegetal associations become dominate by the ruderal species specific to the polluted areas, and some mammals, birds or insects leave the area. These features require precautionary storage and intense concerns for finding alternative solutions (a pre-treatment to reduce the level of alkalinity might be beneficial) and recovery (for example, as a secondary resource for production of building materials, special cements, adsorbents and catalysts for wastewater treatment, recovery of useful elements, and more recently the obtaining of ceramic oxide materials), (Çengeloğlu 2003; Paramguru 2005; Sglavo 2000; Yalcin 2000; Patent RO131328 (A2) 2016). The composition and properties of Red Mud in the world were presented by many researchers in their publications (Snars 2009). The results from this work showed that: Red Mud generated from domestic alumina plants contains a high content of oxides, such as: Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O, CaO, K_2O, MgO, and sometimes a high concentration of valuable metal elements (V, Ga, Sc, Gd, etc.) and does not contain radioactive elements such as U, Th, are less than the average concentration values of Uranium (4 ppm) and Thorium (12 ppm) in the earth´s crust (Galateanu 1976; Hodgman 1960). The physical-structural composition of the domestic Red Mud is based on three classes of components: iron-oxide/hydroxides-sandy components-clays. However, due to the bauxite origin and the technology utilized by the alumina processing plant, the composition and properties of Red Mud are very different. Currently, the alumina processing plant, from Romania, is a big and modern plant with a capacity 600,000 Mt of alumina annually (Vitmeco Alum 2017). The Romanian processing plant uses bauxite from the Sierra-Leone mine and other types of bauxite and Bayer technology for alumina production. A second alumina processing plant, which mainly used boehmite-diaspore and boehmite-gibbsite bauxite ore, was closed several years ago, but there are still red mud deposits in its vicinity. Investigation of the composition and properties of Red Mud from domestic alumina processing plant in order to turn its use towards the obtaining of ceramic oxide materials (foams) is a main objective of the project "WATOPREM" PN-II-PT-PCCA-2013-4-177, Ctr. 78/2014.

Materials and Methods

Fresh Red Mud (RM2, RM7, RM8, RM9 red mud samples) were collected from red mud deposits located in vicinity of alumina processing plant from east of Romania, in April, 2015;

Older Red Mud (up to 1 year aged), RM10, RM11, RM12, RM13, RM14 red mud samples, were collected from a red mud deposit near the closed alumina processing plant from west of Romania, in February 2013.

Determination of basic physical and chemical characteristics of Red Mud

Physical texture of Red Mud was determined using dry sieving-classified particles method according to the methods SR EN 244971994; SR EN 12192-1 2003.

Red mud samples dissolved by hot acid HCl 1:1, norm up 250mL, or through dissolution in HNO_3 + HCl acids while the solid residues were digested by fusing Na_2CO_3 and K_2CO_3 in a platinum dish at $1{,}000^0$C. The solutions were used to determine the percent concentration (%w/w) of the oxides and heavy metals.

Fe_2O_3, Al_2O_3, SiO_2, TiO_2, MgO, trace elements: Cu, Cr, Ni, Zn, Zr, Ba, Ce, Gd, Sc, U, Th were determined by the spectrometric methods SR EN 14242 2005; ASTM E1479 2016, using an ICP-OES AGILENT 725 equipment;

Na_2O, CaO, K_2O, trace elements Ga, Cd and Pb were analysed by atomic absorption spectrometry using AAS ZEEnit 700 Analytic Jena AG firm, Germany equipment according to STAS 3223/2- 1980; STAS 3223/1 1992; STAS 1269/17 1982; STAS 1269/7 1983; STAS 1269/3 1987, IEC 61010-2-061, 2015.

Loss on Ignition (LOI) was determined by chemical analysis method according to SR 9934-2 1998 standard.

pH of Red Mud sludge (in water and saline suspensions – mass/volume) was determined according to the methods SR 7184-13 2001; SR EN 60746-1 2004; SR EN 60746-2 2004.

Mineral composition analysis

The mineral composition of red mud has been determined by X-rays diffraction method Bragg-Bretano Θ-2*Θ on BRUKER diffractometer XRD D8 Advance with CuKα radiation and software DIFFRAC^{PLUS} XRD Commender – BRUKER AXS, EVA12, 2006. X-ray diffraction angle varied from 4^0 to 74^0, U=40kV, I=40mA.

Determination of radioactive level

The radioactive level have been analysed by dose rate measuring method covering the range of the environmental back-ground up to the dose rate range of $200\mu Sv\cdot h^{-1}$ - $50\mu Sv\cdot h^{-1}$ on SCINTO dose rate meter instrument with Scintillation Detector (NaI) 1.5x1" for the measurement of Gamma-radiation and X-rays, Germany according to EN 55 011 (Class B); EN 61326-A1; EN 61326-1(Class B). By means of the scintillation detector it is possible to perform measurements in the energy range from approx. 25keV up.

Results and Discussion

Physical texture of Red Mud

Analysing results of physical texture of Red Mud was shown in Table 1, Box plots from Fig. 1 and Fig. 2.

The results presented in Table 1 and Fig. 1 and 2 showed that, the physical texture of Red Mud classified by an equilateral triangle iron oxide/hydroxide-sandy components-clays are: 23,2÷53,7% iron oxide/hydroxide; 34,1÷63,8% sandy components and 7,3÷34,1% clays for fresh and aged Red Mud.

Table 1. Physical texture of red mud

Mean aperture of passing/ retaining sieves x_i, (mm)	**Fresh red mud**				**Aged red mud**			
	Cumulate distribution $Q_3(x_i)$	**Density distribution $q_3(x_i)$, [1/mm]**	**Cumulate weight (%) passing**	**Average particle size P80 (mm)**	**Cumulate distribution $Q_3(x_i)$**	**Density distribution $q_3(x_i)$, [1/mm]**	**Cumulate weight (%) passing**	**Average particle size P80 (mm)**
0.2	0.0238	0.0031	97.76	0.038	0.1161	0.0155	93.26	0.049
0.125	0.0347	0.0056	93.80		0.1158	0.0187	85.64	
0.063	0.6316	0.2746	54.43		0.7478	0.3251	25.46	
0.040	0.3099	0.0775	39.99		0.0201	0.0050	10.03	

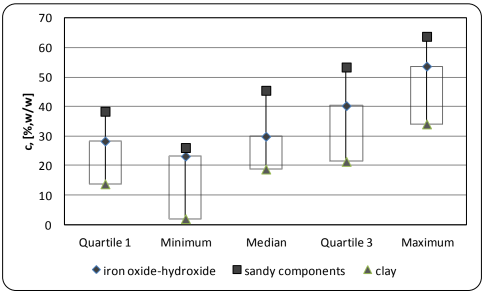

Figure 1. Box plots, physical texture of Red Mud

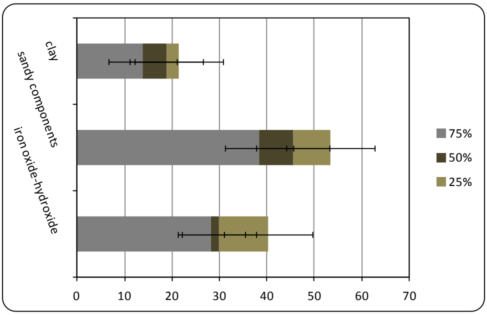

Figure 2. Box plots, physical texture of Red Mud

Particle size distribution in Red Mud showed a fine physical texture of solid sludge: > 93.80 % particles smaller than 0.125 mm size in fresh Red Mud and respectively, higher 85.64 percent of particles with lower size of 0.125 mm in aged Red Mud.

The chemical composition of the red mud samples expressed as distribution of oxides
The chemical composition of the fresh and aged red mud samples expressed as distribution of oxides is presented in Table 2. In high-grade bauxite ore, iron is commonly found as minerals such as: Hematite (α-Fe_2O_3), Goethite (α-$FeOOH$), Magnetite ($FeO.Fe_2O_3$), clay minerals, (Patterson 1986; Borra 2016).

Table 2. Concentration of oxides in Red Mud, fresh and aged samples, (%w/w)

Sample		Fe_2O_3	Al_2O_3	SiO_2	TiO_2	Na_2O	K_2O	CaO	MgO	L.O.I.
Fresh mud	RM2	37.97	16.79	5.56	3.56	2.97	0.06	4.15	0.10	28.75
	RM7	47.04	14.92	7.48	3.07	4.08	0.03	3.36	0.05	17.67
	RM8	42.89	18.19	8.28	2.77	5.39	0.02	3.30	0.05	17.47
	RM9	44.46	19.83	7.51	3.27	4.81	0.02	3.01	0.07	16.46
Aged mud	RM10	43.18	11.50	2.34	5.76	2.45	0.02	16.94	0.73	18.30
	RM11	31.02	11.26	0.84	2.80	2.84	0.04	23.10	0.41	26.52
	RM12	35.31	10.97	1.09	2.85	2.98	0.04	20.86	0.38	24.98
	RM13	35.03	22.78	1.56	5.04	4.93	0.02	9.97	0.35	17.51
	RM14	33.60	21.57	2.01	2.59	4.87	0.07	5.35	0.28	26.76

The results in Table 2 showed that in fresh Red Mud the iron content as Fe_2O_3 was 37.97÷44.46% which is 1.2 times higher than in the aged Red Mud. A similar trend is noticed for Al_2O_3 content, which in fresh red mud was in average 17.43%, slightly higher than in aged red mud. Silicon, which is the second element as percentage after oxygen in the earth crust, is commonly found in soil as Quartz (SiO_2). In Red Mud, Silicon can be found also as Quartz and clay minerals (desillication products – DSP, Cancrinite $3Na_2O\cdot 3Al_2O_3\cdot 5SiO_2\cdot 5H_2O\cdot Na_2CO_3$, Cancrisillite/Sodalite $Na_4Al_3Si_3O_{12}\cdot Cl$; Katoite $Ca_3Al_2(SiO_4)(OH)_8$)). The results in Table 2 showed that SiO_2 concentration in fresh red mud was in average 7.21%, higher than in aged red mud (0.84÷2.34%). Meanwhile the concentration of TiO_2 concentration was higher in the aged red mud (average concentration 3.81%), than in fresh red mud (average concentration 3.17%). These differences in the chemical compositions are related to the bauxite ore sources for the two types of technologies and corresponding emerging deposits. Analysing the results in Table 2 showed that the residual non-recoverable soda content Na_2O in fresh red mud is comparable to the values obtained at the analysis of the aged red mud. Potassium element, both present in fresh and aged Red Mud (0.02÷0.07%) was lower than K content in the Earth´s crust. The estimated average Potassium (K) concentration in the Earth´s crust is in the order of 1.84% to 2.3%, (O´Brien 2008). Most of this K is bound in primary minerals or is present in the secondary clay minerals, which largely make up the clay fraction of the soil of particle size less than 2 micrometre (O´Brien 2008). Exchangeable K^+ is electrostatically bound to the surface of clay minerals and humus substances present in Red Mud. CaO concentration in fresh red mud was 3.1÷4.15% which was much lower than the CaO content in the aged red mud (which has suffered during depositing a subsequent treatment with lime). The same behaviour was noticed for MgO content in fresh mud which was 0.5÷1% lower than MgO content in aged red mud (0.28÷0.73%).

The distribution of trace elements (heavy metals and rare elements) in indigenous Red Mud

The results of the trace analysis for heavy metals and rare elements concentration in fresh and aged Red Mud are given in Table 3.

Table 3. Concentration of heavy and rare metals in Red Mud from domestic alumina processing plants, (ppm)

Metal	Fresh Red Mud				Aged Red Mud				
	RM2	**RM7**	**RM8**	**RM9**	**RM10**	**RM11**	**RM12**	**RM13**	**RM14**
V	28	150	22	240	300	23	200	190	300
Ga	50	61	61	67	56	50	46	64	77
Cd	15	22	17	15	43	31	32	35	33
Cu	34	90	100	94	96	81	86	82	100
Cr	73	665	845	912	900	2,400	3,400	1,000	700
Ni	45	90	85	88	28	350	33	46	50
Pb	56	20	15	21	270	7,900	1,240	180	70
Zn	32	37	34	65	96	660	1,000	59	62
Ba	10	13	20	110	260	1,600	1,500	480	330
Zr	40	18	120	130	1,100	570	590	250	750
Ce	10	10	13	21	628	282	204	250	520
Gd	15	19	25	32	65	44	43	53	32
Sc	20	38	43	38	120	62	64	70	52
U	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Th	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0

According to the results in Table 3, both fresh and aged Red Mud contain trace concentrations of many heavy metals and rare elements (V, Ga, Cd, Cu, Cr, Ni, Gd, Sc). Heavy metals may become hazardous for environment (soil, water, air) by successive accumulation. The content of Uranium and Thorium in the investigated Red Mud was lower than the average content of Uranium (4 ppm) and Thorium (12 ppm) in the Earth´s crust (Table 3). From the broad composition of red mud, some of the heavy metals and rare elements such as: Fe, Ti, V, Ga, Sc, and Gd can be extracted as valuable economic resources.

pH of Red Mud sludge

The pH values of the investigated Red Mud samples in aqueous suspension (w/w= liquid: solid ratio =10:1) are displayed in Table 4.

Table 4. pH value of Red Mud sludge

No.	**fresh Red mud**	**pH_{H2O}**	**pH_{KCl}**	**No.**	**aged Red Mud**	**pH_{H2O}**	**pH_{KCl}**	**No.**	**aged Red Mud**	**pH_{H2O}**	**pH_{KCl}**
1	RM2	11.30	10.87	5	RM10	9.10	8.74	9	RM14	9.96	9.97
2	RM7	11.60	10.97	6	RM11	9.35	9.13	-	-	-	
3	RM8	11.90	10.20	7	RM12	9.48	9.02	-	-	-	
4	RM9	11.98	10.25	8	RM13	9.92	10.18	-	-	-	

The results in Table 4 showed that the pH of fresh Red Mud was 1.22% higher than for the aged Red Mud, and it decreased with the increase of the storage time. Na dominated among the soluble cations, but the concentration of soluble Na, decreased with increasing duration of storage time as a result of leaching (natural weathering). Ca was the predominant exchangeable cation in fresh Red Mud but the concentration of exchangeable Ca markedly decreased in aged Red Mud, which was dominated by exchangeable Na. This fact suggests that in the fresh red mud a higher amount of Ca is found as soluble species, while in the aged red mud which has also suffered a subsequent treatment with lime Ca was mainly converted to non-soluble species. Therefore, cation exchange capacity also decreased with increasing period of storage time. It could also be assumed that this fact could be due to a decrease in pH causing a reduction in negatively charged sites on the red mud particle. A high pH of Red Mud suspension may have a strong environmental impact on soil and surface waters.

Mineral composition of Red Mud

Mineral composition of research Red Mud (fresh and aged mud) generated from domestic alumina processing plant has been determinate by X-ray diffraction method is showed in Table 5.

Table 5. Mineral composition of Red Mud determined by X-ray diffraction method

Compound		Hematite	Titano-Hematite	Goethite	Gibbsite	Boehmite	Diaspore	Calcite	Katoite Silicatian	Amesite	Cancrinite	Cancrisilite	Hidroan-	Quartz	Anatase/	Ilmenite
Formula		Fe_2O_3	$Fe_{1.696}Ti_{0.228}O_3$	$FeO(OH)$	$Al(OH)_3$	$AlO(OH)$	$AlO(OH)$	$CaCO_3$	$Ca_3Al_2(SiO_4)(OH)_8$	$(Mg_{4.15}Al_{1.85})(Si_{2.15}Al_{1.85}O_{10})$	$Na_{0.262}(CO_3)_{0.932}Al_6Si_6O_{24}$	$Na_7(Al_5Si_7O_{24})CO_{3.3}H_2O$	$Ca_3Fe_2Si_{1.15}O_{4.6}(OH)_{7.4}$	SiO_2	TiO_2	$Fe^{+2}TiO_3$
Red Mud (fresh)	RM2	10.0	-	34.0	29.0	-	-	5.0	-	-	14.0	-	7.0	-	1.0	-
	RM7	14.8	-	25.5	8.0	3.1	-	4.8	12.2	-	-	9.2	-	7.3	1.5	13.7
	RM8	9.1	-	17.6	25.4	1.9	-	7.5	7.0	-	-	6.8	-	17.5	1.1	-
	RM9	12.1	-	16.8	35.0	2.4	-	13.1	-	-	-	7.3	-	4.7	1.5	7.1
Red Mud (aged)	RM10	-	46.8	-	5.5	-	5.2	23.4	7.0	-	12.0	-	-	-	-	-
	RM11	-	26.5	1.8	5.5	-	8.2	39.2	5.2	3.2	10.4	-	-	-	-	-
	RM12	-	27.8	3.4	2.2	-	5.7	37.6	5.7	4.9	12.7	-	-	-	-	-
	RM13	-	19.0	4.2	12.3	2.8	8.1	15.1	10.1	4.0	20.0	-	-	-	4.3	-
	RM14	-	10.0	19.9	20.4	2.2	4.8	17.2	5.9	-	9.6	-	-	7.2	2.8	-

According to Table 5, almost all the components in the investigated Red Mud component are found as microcrystal states which can be determined by X-ray diffraction patterns. The degree of crystallization of the red mud increased with increasing duration of storage. Main mineral components determined by X-ray diffraction patterns were Hematite (α-Fe_2O_3), Goethite [α-$FeO(OH)$], Gibbsite [γ-$Al(OH)_3$], Boehmite [γ-$AlO(OH)$], Calcite ($CaCO_3$), Quartz (SiO_2) and new synthetic minerals with chemical formula Cancrinite ($Na_{0.262}(CO_3)_{0.932}Al_6Si_6O_{24}$), Cancrisilite ($Na_7(Al_5Si_7O_{24})CO_{3.3}H_2O$), Katoite Sillicatian [$Ca_3Al_2(SiO_4)(OH)_8$]. Hematite can occur partially from the dehydration of the Goethite, as a phase called "proto-Hematite" in literature date, which has although the structure of the hematite but is deficient in iron and still retains hydroxyl groups ($Fe_{2-x/3}O_3H_x$). Goethite has diffraction lines slightly offset to values of smaller interplanar spacing suggesting the formation of solid solutions with Diaspore, Goethite aluminian [$(Fe,AlO(OH)$]. Boehmite $AlO(OH)$, Gibbsite $Al(OH)_3$, Calcite $CaCO_3$ and Rutile/Anatase TiO_2 do not appear to form solid solutions. Cancrinite with the ideal formula $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$ knows the great variations due to possible substitutions:

$$CaCO_3 \leftrightarrow NaHCO_3, \tag{1}$$
$$CaCO_3 \leftrightarrow Na_2CO_3 + \text{vacancies}, \tag{2}$$
$$Ca^{2+} \leftrightarrow Mg^{2+}, \text{ in a small proportion}, \tag{3}$$
$$Si^{4+} \leftrightarrow Ti^{4+}, \text{ in a small proportion}, \tag{4}$$
$$Na^{+} \leftrightarrow K^{+}, \text{ in a small proportion}, \tag{5}$$
$$Al^{3+} \leftrightarrow Fe^{3+}, \text{ in a small proportion}, \tag{6}$$

Cancrisilite with ideal formula $Na_7Al_5Si_7O_{24}(CO_3)\cdot 3H_2O$, has the same structure as Cancrinite and shows variations due to similar substitutions.

Amesite with the ideal composition $(Mg_2Al)(AlSiO_5)(OH)_4$ belongs to the kaolinite group and also accepts a series of isomorphic substitutions:

$$Mg^{2+} \leftrightarrow Fe^{2+}, \text{ in large proportions}, \tag{7}$$
$$Mg^{2+} \leftrightarrow Ca^{2+} \leftrightarrow Mn^{2+}, \text{ in small proportion}, \tag{8}$$

Measurements of radioactive level of Red Mud

Table 6 shows the radioactive level of the investigated Red Mud samples generated from domestic alumina processing plants were determined by Gamma radiation measurement method. The resulting range of annual average effective absorbed doses in air and received by adults were estimated in according to United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR 2000).

According to the standard for residents, the limit of the total annual effective dose of gamma radiation is 1mSv. Annual effective dose due to natural gamma fond, according to United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly, is 0.48 mSv (UNSCEAR 2000). The results in Table 6 showed that the effective dose of gamma radiation of the fresh and aged Red Mud from domestic alumina processing plants varied in a small range from 72 $nSv\cdot h^{-1}$ to 79 $nSv\cdot h^{-1}$ and, subsequently the annual effective dose of gamma radiation was estimated in the range 0.505 - 0.554 mSv, which is fairly close to the average effective annual dose due to gamma radiation natural fond (0.48 mSv).

Table 6. Effective gamma radiation dose of Red Mud samples, comparative values with natural fond

Sample	Effective dose, [nSv·h^{-1}]	Effective annual dose(estimated), [mSv·a^{-1}]
RM2	72	0.505
RM7	78	0.547
RM8	73	0.512
RM9	72	0.505
RM10	75	0.526
RM11	76	0.533
RM12	78	0.547
RM13	79	0.554
RM14	75	0.526
Natural fond	75	0.526
Standard limit/year, [mSv·a^{-1}]	-	<1.0

Conclusions

Considering the three main categories of compounds (iron oxides-hydroxides, sands and clays) generating the textural properties of the red mud generated from both Romanian alumina processing plants, it may be inferred that these materials could be utilized to generate ceramic foams.

However, due to the fact that these residues have a high free alkalinity, a pre-treatment process for lowering the Na soluble content level is imperiously necessary before their utilization in ceramic foams synthesis.

Taking into account that both types of red mud contain insignificant amounts of radioactive elements their further processing does not present environmental risks.

Another direction of red mud valorisation could be the recovery of Fe, Ti, V, Ga, Sc, Gd by extraction. This method would be important especially in the case of Ga, Sc, Gd, which are critical metals with specific properties and rarely encountered in natural ores.

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SENSITIVITY OF FUNGAL AND STREPTOMYCETE STRAINS TO TRIFLURALIN AND MAGNETITE NANOPARTICLES

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Abstract

The aim of this study was to estimate the sensitivity of microorganisms, isolated from soil long-term polluted with obsolete pesticides, to magnetite (Fe_3O_4) nanoparticles and fluorinated dinitroaniline herbicide trifluralin, and to evaluate the inhibition activity of these substances. The response of fungi and streptomycete strains to the presence of magnetite nanoparticles in culture media is individual to each microorganism. For the most of studied microorganisms, the addition of trifluralin to culture media had a growth inhibition effect. An exception was the strain *Streptomyces sp.* 0412, which growth was stimulated in the presence of xenobiotic. The negative effect of pesticide was reduced, when before the addition to the culture medium the trifluralin was mixed and incubated with magnetite nanoparticles for 1 hour.

Keywords: *fungi, growth inhibition, magnetite nanoparticles, streptomycetes, trifluralin*

Introduction

Pesticides are extensively used in agriculture as a part of pest control strategies. The applied pesticides may harm the indigenous microorganisms, disturb soil ecosystem, and thus, may affect human health by entering in the food chain. Some pesticides stimulate the growth of microorganisms, but other pesticides have depressive effects or no effects on microorganisms. Pesticides interact with soil organisms and their metabolic activities and may alter the physiological and biochemical behavior of soil microbes (Nazarco 2008; Hussain et al. 2009; Lo et al. 2010; Ivantsova et al. 2015; Chowdhury et al. 2008).

Trifluralin is the synthetic fluorinated dinitroaniline herbicide. Trifluralin has been used in agriculture since 1963 for control of a variety of weeds in agronomic and horticultural crops. Adverse impacts of trifluralin on soil microbial diversity and activities have been described by many researchers (Hang et al. 2001; Fernandez et al. 2003; Nowak et al. 2008; Hussain et al. 2009).

Iron-containing systems are an effective remediation technology for contaminated environments with halogenated organic compounds (Moor et al. 2010; Tor et al. 2000; Klupinski & Chin 2003). The recent rapid development of the nanotechnology has generated a considerable number of studies dedicated to the usage of iron-based nanoparticles, which due to unique properties and high surface area, enhances many of the advantages of traditional iron remediation (Thompson & Bezbaruah 2008; Bai & Wang 2009).

Many recent studies reveal positive impact of nanoparticles on growth and production of secondary products by different microorganisms (Xiu et al. 2010; Kirschling et al. 2010; Chatterjee et al. 2011; Barzan et al. 2014; Darwish et al. 2015). However, information regarding the impacts of engineered nanoparticles on soil microbial communities is currently limited (Dinesh & Hamza 2012; Pawlet et al. 2013; Simonin & Richaume 2015) and appears conflicting.

The aim of our study was to estimate the sensitivity of microorganisms to magnetite (Fe_3O_4) nanoparticles and trifluralin, and to evaluate the inhibition activity of these substances.

Materials and methods

5 strains of micromycetes (1LD, 4D, 5D, 8D, *Penicillium viride*) and 5 strains of streptomycetes (*Streptomyces sp.* 0112, *Streptomyces sp.* 0312, *Streptomyces sp.* 0412, *Streptomyces sp.* 0512, *Streptomyces sp.* 0612) isolated from soil for long-term polluted by obsolete pesticides were used as test-microorganisms.

In our experiment, we used the solution of trifluralin in concentration of 100 mg/L (Variant 1), the solution of magnetite (Fe_3O_4) nanoparticles (diameter of nanoparticles was 20-25 nm) in concentration of 100 mg/L (Variant 2) and the mixture of these solutions in concentration of 100 mg/L each (Variant 3). The mixture of solutions of Fe_3O_4 nanoparticles and trifluralin was incubated for 1 hour before using. As a control, the solid Czapek medium (pH 5.5-5.7 for micromycetes and pH 7.0-7.2 for actinomycetes) have been used.

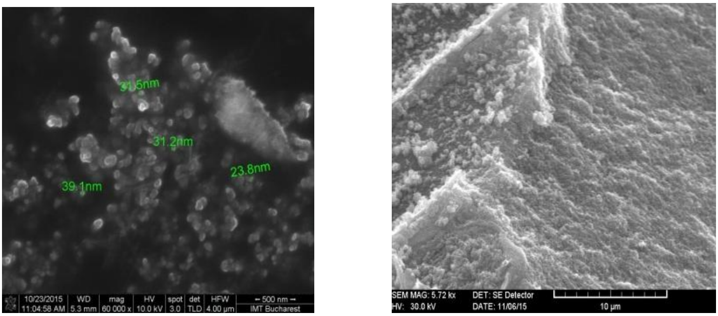

Figure 1. The scanning electron microscope photos of magnetite nanoparticles

For assessing the inhibition activity of the magnetite and trifluralin the agar diffusion method was used. Initially the strains were inseminated in lawn, after that agar disks of micromycetes / streptomycetes colony mass was prepared by using sterile borers. Disks were then aseptically transferred to Czapek plates having magnetite or trifluralin or the mixture of trifluraline and magnetite solutions.

Diameter of growth zones of the strains of fungi / streptomycetes was measured at the 8th day. Inhibition activity (IA, %) of trifluralin and Fe_3O_4 nanoparticles was calculated in percent of inhibition of growth, compared to the control, according to the method proposed by Pandey et al. 1982.

Results and discussions

The inhibition activity values (%) and sensitivity of fungal strains to the magnetite nanoparticles and trifluralin were represented in Table 1. The obtained results showed that the strain 1LD did not react to the presence of iron oxide nanoparticles in the culture medium, i.e. the diameter of growth zones was at the control level. On 4D and 5D fungal strains magnetite nanoparticles had a weak inhibitory action – their growth was inhibited only on 0.47 and 2.55% respectively, and the growth of micromycetes 8D and *P.viride* was even stimulated by nanoparticles of iron oxide.

Table 1. The sensibility of fungal strains to magnetite nanoparticles, trifluralin, and mixture of trifluralin and magnetite nanoparticles, on the 8th day of growth

Fungal strain	Inhibition activity (%)		
	Medium Czapek + Fe_3O_4 nanoparticles	Medium Czapek + trifluralin	Medium Czapek + trifluralin + Fe_3O_4 nanoparticles
1LD	0.00 ± 0.02	5.29 ± 0.25	1.18 ± 0.04
4D	0.47 ± 0.02	16.36 ± 0.21	10.28 ± 0.23
5D	2.55 ± 0.05	7.08 ± 0.68	-0.47 ± 0.01
8D	-0.39 ± 0.02	6.61 ± 0.15	5.06 ± 0.11
P. viride	-2.86 ± 0.52	10.48 ± 1.45	-2.86 ± 0.37

Experimental variant, where micromycetes were grown on the medium with addition of trifluralin, showed that all strains were sensitive, in particular the micromycetes 4D and *P.viride*, where the growth inhibition percent was 16.36 and 10.48% respectively.

Experimental variant, when the mixture of trifluralin and nanoparticles solutions was used, showed that inhibitory action of trifluralin was reduced by iron oxide nanoparticles, as in the case of 1LD, 4D, and 8D fungi strain, or even it was removed completely, as in the case micromycetes 5D and *P.viride,* where the diameter of growth zones exceeded the control.

Also, it should be mentioned that the solution of iron oxide nanoparticles had a stimulating effect on the formation and maturation of the fungal spores (Figure 2).

In Table 2 there were presented the values of IA, obtained by measuring the diameter of streptomycete colonies in the control and experimental variants at the 8th day of growth. The streptomycete strains had an individual reaction to the solution of magnetite nanoparticles added to the culture medium. The strain *Streptomyces sp.* 0412 has reacted by an active increase in the presence of iron oxide nanoparticles, the diameter of growth zones exceeded the control by 18% (Table 2).

The streptomycetes proved to be more resistant to trifluralin than fungi, and in the case of the strain *Streptomyces sp.* 0412 we obtained even a growth stimulation in the presence of trifluralin. When the streptomycetes were cultivated in the presence of the mixture of trifluralin and magnetite nanoparticles, in general, it was observed the same pattern – that iron oxide nanoparticles diminishes the negative effect of the xenobiotic.

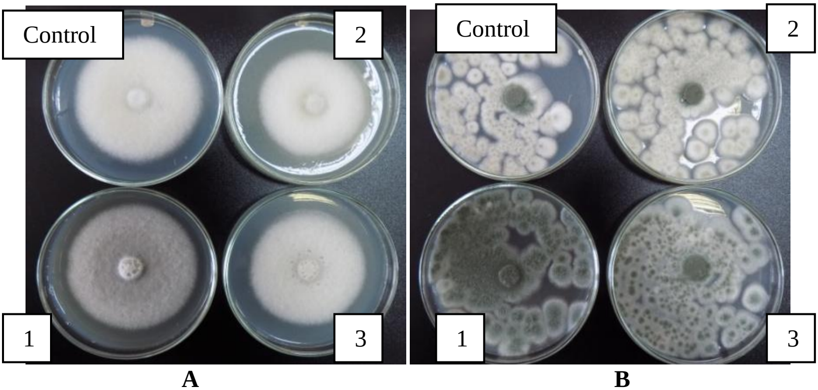

Figure 2. The growth of micromycetes *P.viride* (**A**) and 4D (**B**) on Czapek medium with addition of Fe_3O_4 nanoparticles (1), trifluralin (2) and the mixture of trifluralin and Fe_3O_4 nanoparticles (3)

Table 2. The sensibility of streptomycete strains to magnetite nanoparticles, trifluralin, and mixture of trifluralin and magnetite nanoparticles, on the 8th day of growth

Streptomycetes strain	Inhibition activity (%)		
	Medium Czapek + Fe_3O_4 nanoparticles	Medium Czapek + trifluralin	Medium Czapek + trifluralin + Fe_3O_4 nanoparticles
Streptomyces sp. 0112	-5.56 ± 0.21	0.00 ± 0.06	-4.17 ± 0.28
Streptomyces sp. 0312	0.00 ± 0.14	1.52 ± 0.06	0.00 ± 0.05
Streptomyces sp. 0412	-18.57 ± 2.63	-5.71 ± 0.45	-8.57 ± 0.67
Streptomyces sp. 0512	3.70 ± 0.17	3.70 ± 0.13	3.70 ± 0.17
Streptomyces sp. 0612	1.28 ± 0.05	7.69 ± 0.28	1.28 ± 0.06

Conclusions

Each fungal and streptomycetes strain had an individual reaction to the solution of magnetite nanoparticles added to the culture media. Most of the studied microorganisms were found to be sensitive to the trifluralin. The presence of xenobiotic in the medium had a growth inhibition effect, with the exception of strain *Streptomyces sp*. 0412, for which the stimulation was determined. In all cases, when the mixture of trifluralin and magnetite nanoparticles was added, the same phenomenon was repeated – namely, the negative effect of trifluralin was reduced.

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STUDY OF BACTERIA RESISTANCE MECHANISMS IN RESPONSE TO A STRESS INDUCED BY PHARMACEUTICALS COMPOUNDS

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Abstract

Three pharmaceutical compounds (Trimethoprim, Carbamazepine and Benzethonium chloride) were investigated to unveil possible toxic effects on two bacterial strains (*Citrobacter freundii* and *Comamonas testosteroni*). The pharmaceutical compounds stress triggered a bacterial defence mechanism which was evaluated at transcriptional and translational levels. In this study, potential bacterial biomarkers induced by the pharmaceutical stress were unraveled.

Keywords: *biological adaptive markers, pharmaceutical compounds, gram-negative bacteria, defense mechanisms.*

Introduction

Human welfare has been always based on their direct interest, so the economy was built on the expenses of the environment protection. The compounds resulting from anthropogenic activities, including the wastes generated through industrial and domestic activities could be very harmful to the environment, threatening the existence of entire populations and species.

In spite of this fact, all living organisms have developed particular adapting mechanisms to fight the effect of these contaminants / pollutants by spontaneous mutations (genetic variability) and activation of various defense mechanisms. Moreover, organisms react differently to pollutants according to their species, but their defense mechanisms could be very similar from prokaryotes to eukaryotes. Biological models, especially the bacterial ones, are very useful tools to observe the toxic effect of different pollutants by quantifying the EC50 based on the bacterial growth curve (Nita-Lazar et al. 2016). Bacteria react to various environmental condition (including pharmaceutical compounds-PhCs) by appointing different paths of regulation such as metabolic, translational and transcriptional regulation (van Hijum et al 2009).

Bacteria, as a biological model, was also selected due to ethical point of view, its biological simplicity as well as their handling. Bacteria grown in presence of toxic compounds could resist by different defense mechanisms, or die if the contaminant could reach vital biological pathways (Adams et al. 2015). In most cases, these microorganisms can develop a resistant strain via possible genetic mutations. Bacteria have several mechanisms of resistance such as horizontal gene transfer, elevated mutation rates, adaptive resistance, changes in cell permeability and efflux pumps

(Schroeder et al. 2017). The efflux pump is a physical channel to expelling the toxin from inside the cell to outside it.

This study focused on two gram-negative bacteria, *Citrobacter freundii*, a long rod-shaped bacterium and usually motile and *Comamonas testosteroni* an aerobic, motile, non-spore-forming, medium-to-long gram-negative bacillus (Banciu et al. 2016) chosen as a result of our previous ecotoxicological studies (Nita-Lazar et al. 2016).

The complexity of this study was due to the interdisciplinary approach going from gene expression to protein.

In this context, the present paper aims to detect the possible mechanisms responsible of this resistance to pharmaceutical compound induced both at transcriptional level by the overexpression or inhibition of some genes linked to these defence mechanisms and translational level.

Materials and Methods

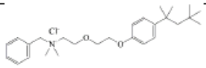
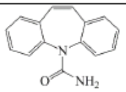
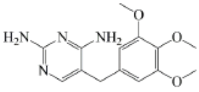
Bacterial strains

Citrobacter freundii (ATCC 8090) and *Comamonas testosteroni* (ATCC 11996) were purchased from ATCC.

Reagents

Growth medium was composed of tryptone soya agar (Oxoid, UK) and Lauryl Sulphate Broth (Himedia Laboratories Pvt. Ltd.). Pharmaceutical compounds Trimethoprim (TMP), Carbamazepine (CBZ) and Benzethonium chloride (BC) were purchased from Sigma-Aldrich (Sigma Corp. St. Louis, MO, USA) (Table 1).

Table 1. Description of the pharmaceutical compounds (according to Nita-Lazar et al. 2016)

Name	Formula/ M* (Da)	Structure/ Chemical Classification	mp**(C)/ ρ*** (g/mL) (20°C)	Water Solubility
Benzethonium chloride	$C_{27}H_{42}NO_2$ Cl 448.1		162-164 0.998	1-5 g/100 mL at 18 °C
Carbamazepine	$C_{15}H_{12}N_2O$ 236.09	 **Iminostilbene**	189-192 1.296	insoluble in water
Trimethoprim	$C_{14}H_{18}N_4O$ 3 290.32	 **Pyrimidine**	238 – 240 1.3	slightly soluble

* M - molar mass ;** mp - melting point ;*** ρ - density

The PhCs and the concentrations (Table 2) were selected according to EC50 obtained by Nita-Lazar et al. (2016) so as to increase the chances to induce biomarkers of the resistance phenomenon.

Table 2. The chemicals concentration selected for the bacterial assay

Bacterial strains	TMP	CBZ	BC
C. freundii (#3)	80 mg/L	80 mg/L	3 mg/L
C. testosteroni (#4)	7,5 mg/L	80 mg/L	3,5 mg/L

Bacterial assay

Each bacterial strain was grown on tryptone soya agar and it was incubated over night (O/N) at 37° C. A single colony from each bacterial strain was then incubated O/N in 10 ml Lauryl Sulphate Broth at 37° C at 130 rpm (New Brunswick Scientific, Innova 44). Optical density (OD) was measured at 600 nm using UV-VIS Spectrometer (VWR International, USA). The $OD_{600\ nm}$ was measured and a bacterial density of 0.3 $OD_{600\ nm}$ was incubated for 4 h in absence (control) or presence of TMP, CBZ and BC.

mRNA assay

RNA extraction was preformed according the protocol described into the PureLink RNA Mini kit (Invitrogen, Life Technologies, USA). RNA extracted concentration was detected by nanodrop (ClarioStar microplate reader, BMG Labtech, Germany) and it was used to quantify the purity and concentration of each extracted sample. The absorbance was measured at two different wavelengths: 260nm, to measure the concentration of the RNA (its absorbance wavelength) and at 280nm, to measure its purity (the absorbance wavelength of proteins). Four set of primers i) 27f/1492f (universal primers, 1500bP PCR product size); ii) NIRk1f/NIRk5 (specific to denitrifying bacteria, 514bp mRNA strand); iii) NOSz-f/NOSz1622r (specific to denitrifying bacteria, 453bp mRNA strand); iv) pao462f/pao651r (specific to phosphate accumulating bacteria, 429bp strand) (Braker et al 1998) were used to amplify the mRNA by SuperScript™ III One-Step RT-PCR System with Platinum™ Taq DNA Polymerase protocol. The RT-PCR kit has a Reverse transcriptase enzyme which synthetize cDNA strands from each mRNA strands: this reaction constitutes the first step. Then, by heating at a specific temperature, the cDNA could be amplified by a classic PCR reaction where the primers are attached and amplified on their specifics sites by the Taq DNA polymerase enzyme. The addition of the nucleotides on the single DNA strand from the sense primer to the reverse primer formed a new double strand DNA used as a template in a new cycle.

A program of 40 cycles was divided in three steps: i) denaturing DNA at 95°C; ii) annealing at 55°C and iii) amplifying at 68°C and it was set at PCR system (Applied Biosystems).

The PCR products were separated by electrophoresis on a 1% agarose gel mixed with the ethidium bromide tagging substance. The ethidium bromide tagged in a blue color each strand between its base pairs for identification. The smallest strands migrated further than the biggest ones; in order to know their length a reference to 1kbp and 100bp ladders was done.

Protein assays

Bacteria were lysed in the extraction buffer containing phenylmethylsulphonyl fluoride (PMSF) by sonication. After sonication and vortexing the samples, the protein concentration was measured at 280 nm.

The electrophoresis on acrylamide gel was done to separate the proteins depending on their size by referring to a ladder. The gel was stained with Coomassie blue and the bands made by different proteins were observed. The staining process consisted in four steps: 1) the gel was fixed with a 40% ethanol 10% acetic acid solution for 15 minutes, 2) the gel was rinsed with distilled water, 3) the gel was placed into Coomassie blue for 24 hours to have a better recovery of the bands and 4) the gel was rinsed again 3 times with tap water. The blue colored bands (corresponding of the proteins) and their size by comparing with the ladder were observed.

Results and Discussion

Bacterial assay

An antibiotic for bladder infections (TMP), an antiepileptic drug (CBZ) and an antimicrobial agent (BC) (American Society of Health 2015) were used as a stress factors for gram-negative bacteria. Bacterial was grown in presence of PhCs for 4-5 at 37°C (Table 2) then pelleted for mRNA and protein extractions.

mRNA extraction

The results of mRNA extraction showed a robust extraction with the exception of bacteria #3 grown in presence of BC (Table 3). This could be explained by the limited growth in presence of this particular PhCs.

Table 3. mRNA concentrations and mass in the RT PCR mix

Samples		RNA concentration (ng/ µL)	Dilution factor	RNA template concentration (ng)	Water volume (µL)
#3	Ctrl	2622,77	5	524,4	14
	TMP	2490,79	5	498,2	14
	CBZ	1442,54	3	480,9	14
	BC	41,02	-	410,2	5
#4	Ctrl	251,96	-	503,9	13
	TMP	180,78	-	542,4	12
	CBZ	372,87	2	559,3	12
	BC	171,38	-	514,1	12

#3 – *C. freundii* strain; #4 – *C. testosteroni* strain; Ctrl-control; TMP – Trimethoprim; CBZ – Carbamazepine; BC – Benzenthonium chloride.

The protein concentrations (mg/mL) was obtained by reading at 280 nm absorbance (Table 4).

After RT-PCR an electrophoresis on a 1% agarose gel mixed with the ethidium bromide tagging substance was proceed. Several differences between the samples were revealed (Figure 1). No particular bands were observed for *C. freundii* strain, but a very intense band of 1300bp molecular weight was detected in case of *C. testosteroni* (Ctrl) and *C. testosteroni* stressed with BC.

Table 4. Bacteria proteins concentration

Samples		**Proteins concentration (mg/ml)**
#3	Ctrl	4,42232
	TMP	4,3778
	CBZ	4,457512
	BC	4,094992
#4	Ctrl	4,142904
	TMP	4,347272
	CBZ	4,340912
	BC	4,111952

#3 – *C. freundii* strain; #4 – *C. testosteroni* strain; Ctrl-control; TMP – Trimethoprim; CBZ – Carbamazepine; BC – Benzenthonium chloride.

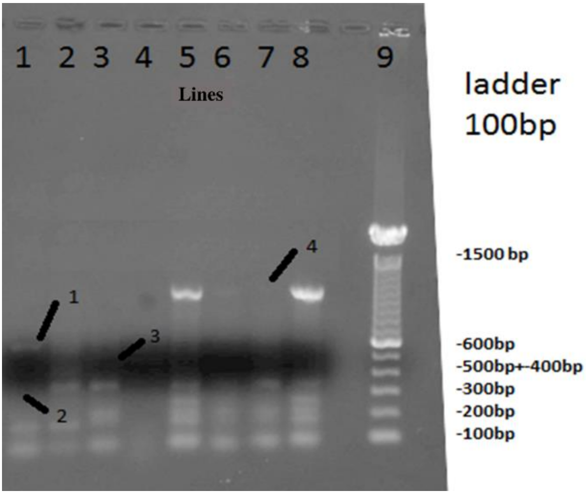


Figure 1. RT-PCR Gene Extract (mRNA) from *C. freundii*, lines: 1 (control), 2 (TMP), 3 (CBZ), 4 (BC) and *C. testosteroni*, lines: 5 (control), 6 (TMP), 7 (CBZ), 8 (BC). *Amplification of the universal bacterial gene (U), around 1500 bp PCR product; amplification of gene involved in nitrite reduction (NO_2) processes, around 520 bp PCR product; amplification of gene involved in nitrogen oxide (N_2O) reduction processes, around 450 bp PCR product; amplification of the gene involved in phosphorylation (P) processes around 300 bp PCR product. Potential biomarkers, bands 1,2,3,4.*

The results showed that the band 1 biomarker present in *C. freundii* (line 1) was not found as intensity and presence in *C. freundii* incubated in the presence of the three PhCs (line 2-3-4), which implies a specific inhibition of metabolic pathways in which this gene was functional. Band 2 biomarker was missing from the control (line 1), but was induced by the toxic activity of TMP and CBZ, but not of BC. The band 3 biomarker was induced only by CBZ compared to the control (line 1). The band 4 biomarker was completely inhibited by the CBZ, and it was induced at a same level with the control (line 5) by BC (line 8).

Protein extraction

The SDS-PAGE electrophoresis showed very smaller bands than the two other samples #3 TMP and #3CBZ (Figure 2).

It was also detected that #3 TMP and #3CBZ had a really thick band between 50 and 75kD, according to the Dual Color Prestained Protein Standard scale (BioRad, USA), which means that *C. freundii* strain stressed with TMP and CBZ expressed much more the proteins than #3 BC.

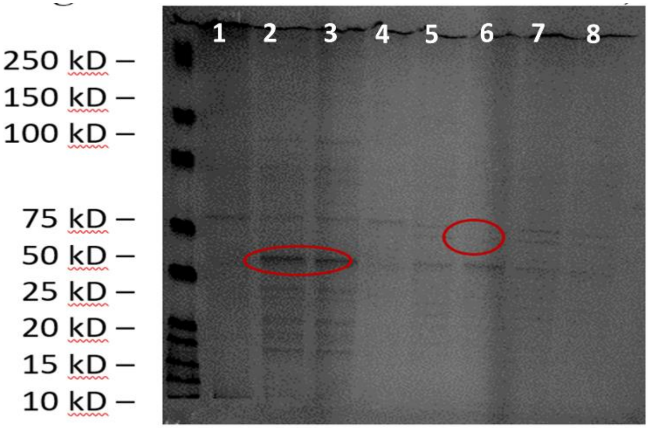


Figure 2. Bacteria proteins gel from *C. freundii*, lines: 1 (control), 2 (TMP), 3 (CBZ), 4 (BC) and *C. testosteroni*, lines: 5 (control), 6 (TMP), 7 (CBZ), 8 (BC).

This may be due to their resistance mechanisms involved especially since bacteria usually combine many proteins to metabolize or to expel the contaminant outside the cell (efflux pump). The thickest band it was observed for #3 TMP and #3 CBZ samples around 50kD corresponds to a big amount of the same protein due to an overexpressed gene. The same band was observed in the #4 TMP lane, which is also thicker than the other samples such as #4 Ctrl, #4 CBZ and #4 BC which were not inhibited by the chemicals. This protein might be a biomarker of the resistance mechanism. The presence of the bands in these samples lanes than in the #3 ctrl one was correlated with the mRNA profile, so that more genes and proteins were expressed. The results of protein extraction were very good corroborated with the mRNA ones (Figure 1), since three bands (marked in red) corresponding with the 2, 3 and 6 lines appeared as an overexpression of proteins due to toxic activity induced by TMP and CBZ in case of *C. freundii* strain as well as TMP, respectively in case of *C. testosteroni.*

Conclusions

The aim of this study was to determine the biomarkers of a biological resistance mechanism in response to chemical stress. One biological model (bacteria) was subjected to certain concentrations of chemicals in their growth medium. Toxicity tests were made to ascertain some differences between the bacteria strains in presence or absence of the PhCs. In terms of the bacteria mRNA and proteins, several marking differences on the protein bands between the stressed and unstressed strains which corresponds to the mRNA profile were observed. It can be considered a very interesting result because a trace of the bacterial resistance mechanisms through these proteins was revealed. Moreover, some biomarkers were identified such as the ones induced by TMP pressure on both *C. freundii* and *C. testosteroni* strains and CBZ pressure on *C. freundii*.

Future studies will be required to identify the proteins involved in these resistance mechanisms in order to know precisely which proteins were involved and in which resistance process, thus the mechanisms at a molecular level would be disclosed.

Acknowledgements

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VARIATION OF ANIONIC AND NONIONIC SURFACTANTS PRESENCE IN WASTEWATERS

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Abstract

It has been known the surfactants have been used to remove stains from leather, clothes and household items, particularly from kitchens and bathrooms.

Our studies were carried out during eight months in order to include all the seasons (July, August 2016 – Summer; September, October 2016 – Autumn; January, February 2017 – Winter and March, April 2017 – Spring) to detect the variation of anionic and nonionic surfactants concentration from industrial wastewaters. The wastewater samples were taken from three sampling points belonging to a subway maintenance company: Berceni, Militari and Pantelimon.

The total concentration of anionic surfactants in wastewaters was analyzed by Methylene Blue Active Substances Method (MBAS), and the total concentration of nonionic surfactants was detected by the method with Dragendorff reagent.

The results showed that anionic and nonionic surfactants concentrations detected in wastewater samples were less than 0.1 mg/L (under the quantification limit) up to 2.03 mg/L for anionic surfactants and the nonionic surfactants had less than 0.15mg/L (under the quantification limit) up to 1.72 mg/L. According to the national legislation (HG 352/2005, NTPA 002, Annex 2/2005), the accepted value of surfactants (as sum of anionic and nonionic) is less than 25 mg/L.

The results of the study revealed the highest concentration of both anionic and nonionic surfactants during March, one of the possibilities of this variations could be the lower level of maintenance in February than the other months. Furthermore, this change of concentration may be the result of switching the type of organic compound (detergent) using for the subways cleaning.

Keywords: *anionic surfactants, Dragendorff reagent, MBAS, nonionic surfactants, subways, wastewater*

Introduction

A detergent is an effective cleaning product because it contains one or more surfactants (American Cleaning Institute, 2017) that could be engineered to perform well under a variety of conditions (Figure 1). Sodium stearate is the most common component of most soap, which comprises about 50% of commercial surfactants and B, 4-(5-Dodecyl) benzenesulfonate is a linear dodecyl benzenesulfonate, one of the most common surfactants (Rosen & Kunjappu 2012).

The application of surfactants is various such as industrial use (oil recovery), domestic use (laundry detergent), food processing and pharmaceutics synthesis (Schramm, Stasiukb & Marangonic 2003).

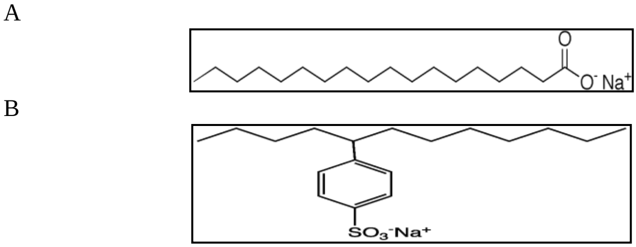
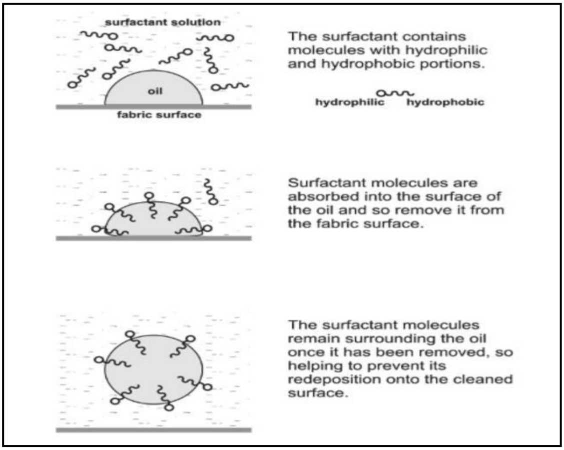


Figure 1. Structures of surfactants. A: Sodium stearate; B: 4-(5-Dodecyl) benzenesulfonate

The most wide-spread usage of surfactants was related to the domestic area. They have been used to remove stains from clothes, leather and household items, but also to clean kitchens and bathrooms.

Surfactants operate by breaking down the interface between water and oils and/or stains. They are able to act in this way, because they contain both a hydrophilic group, such as an acid anion, ($-CO_2^-$ or SO_3^-) and a group, such as an alkyl chain. As we can see in Fig. 2, the head is hydrophilic and the tail is hydrophobic. After the action of cleaning, the surfactant surrounds the stain in order to prevent its redepositing (Figure 2).



The surfactant contains molecules with hydrophilic and hydrophobic portions.

Surfactant molecules are absorbed into the surface of the oil and so remove it from the fabric surface.

The surfactant molecules remain surrounding the oil once it has been removed, so helping to prevent its redeposition onto the cleaned surface.

Figure 2. Action of a surfactant (The Essential chemical industry 2013)

Depending on the nature of the hydrophilic group, surfactants are classified as:

i) Anionic surfactants, a surfactant in which the hydrophilic part carries a negative charge such as soaps, $RCOO^-$, alkyl sulphates, $ROSO_3^-$;

ii) Nonionic surfactants, a surfactant in which the hydrophilic part carries a uncharged, such as acyl diethanolamides, $RCON(C_2H_4OH)_2$, ethoxylated fatty alcohols R(OC2H4)nOH;

iii) Cationic surfactants, a surfactant in which the hydrophilic part carries a positive charge, such as alkyltrimethilammonium salts $RN^+(CH_3)_3$, alkildimethilbenzylammonium salts $RN^+(CH_3)_2CH_2C_5H_6$;
iv) Amphoteric surfactants, a surfactant in which the hydrophilic part contains both positive and negative charges such asalkylaminopropionates $RNH_2^+(CH_2)_2COO^-$alkyl betaines, $RN^+(CH_3)_2CH_2COO^-$. It is possible for amphoteric surfactants to have more than one charge of either sign, or to lose one charge by addition or removal of a proton (Cullum 1994).
A large number of surfactants from wastewaters have been discharged into the environment, harming aquatic life, polluting the water and endangering human health. All these environmental issues could be address starting by the control of surfactants dispersion in wastewater (Yuan et al. 2014).
This study aimed to monitor the variation of anionic and nonionic surfactants of industrial wastewaters from a subway maintenance company, during July to October 2016 and February to April 2017. Anionic and non-ionic surfactants were chosen taking into account the frequency with which they are used as raw materials in the detergent composition and also, they are the most widely used type of surfactants because of their excellent cleaning and high foaming potential.

Experimental

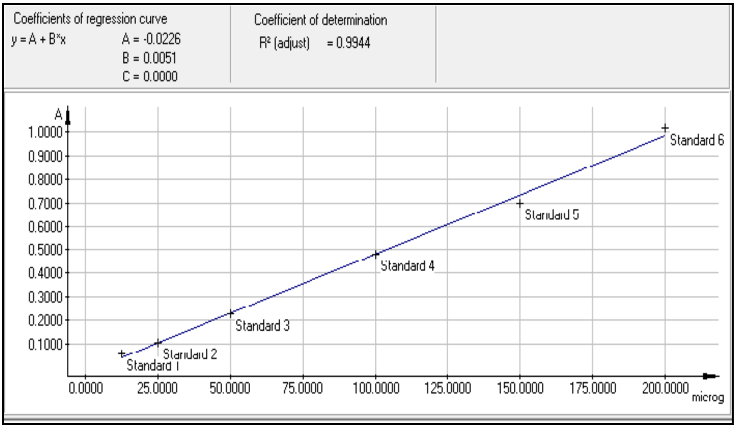
Reagents
The Methyl ester of dodecyl benzene sulfonic acid ($C_{19}H_{32}O_3S$, MDS, 99% purity, M= 340.53g/mole) purchased from Merck was used a reference for methylene blue active substances (MBAS).
Phenolphthalein indicator solution was prepared according to the standard method (SR EN 903). Moreover, 0.1 mole/L NaOH and 0.5 mole/L H_2SO_4 solutions were prepared for pH controlling. Chloroform (99% purity) was purchased from Chimreactiv (Bucharest, Romania) and was used in the separation process between water matrix and organic matrix. Methylene Blue reagent was prepared according to the standard method (SR EN 903). Glass wool was pre-washed with $CHCl_3$ to remove impurities. De-ionized water was used. Tampon solution used to sustain a constant pH (pH=10) was obtained by dissolving the sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3).
Nonylphenol polyethylene glycol ether ($C_9H_{19}C_6H_4(OCH_2CH_2)_9OH$, 99% purity, M= 616.82 g/mole) (Sigma Aldrich, USA) was used as a control reference for nonionic surfactants determination. For the precipitation agent, two solutions were used. Solution A was a mixture between bismuth oxynitrate and potassium. Solution B as barium chloride dissolved in water. Precipitation agent was based on two-thirds of solution A and one-thirds of solution B.

Equipment
Specord BU 205 spectrophotometer (Analytic Jena, Germany) was used for both anionic and nonionic detection by absorbance reading. The wavelength for detection of anionic surfactants was at 650 nm and the optical cell length path was of 10 mm. Detection of nonionic surfactants was carried out at 263.5 nm and an optical cell length path of 20 mm (Analytik Jena AG 2005).

Detection of anionic surfactants was performed by using a calibration curve based on reference material (RM) solutions of six different concentrations.

The RM was methyl ester of dodecylbenzene sulfonic acid ($C_{19}H_{32}O_3S$) and the calibration curve was constructed according to the standard method (SR EN 903) using 6 standards with concentrations between 15 µg to 200 µg,

The linearity range of the calibration curve was between 17.5 µg - 200µg (Figure 3).



Coefficients of regression curve
y = A + B*x   A = -0.0226
B = 0.0051
C = 0.0000

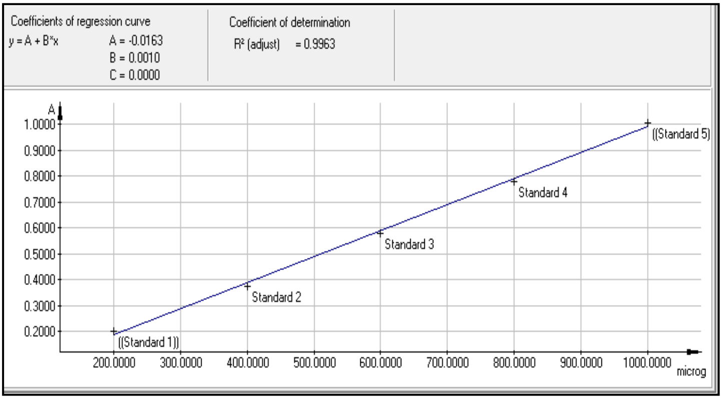
Coefficient of determination
R² (adjust) = 0.9944

Figure 3. Calibration curve of anionic surfactants

A calibration curve with five standards was used for determination of nonionic surfactants concentration.

The standards were prepared by adding 200 µg, 400 µg, 600 µg, 800 µg and 1000µg of Nonylphenol polyethylene glycol ether and then dissolved in 5 mL methanol and 400 mL of water according to the standard ISO 7875-2:1984.

The linearity range of the calibration curve was between 200 µg and 1000 µg (Figure 4).



Coefficients of regression curve
y = A + B*x   A = -0.0163
B = 0.0010
C = 0.0000

Coefficient of determination
R² (adjust) = 0.9963

Figure 4. Calibration curve of nonionic surfactants

As is presented below (Table 1), for both spectrometric methods, the following method performance criteria were investigated: linearity domain, detection limit, quantification limit, precision evaluated by repeatability (n = 10) and interim precision/reproducibility (6 replicates measured in 3 different days) (ISO 8466-1:1990). Sources of uncertainties were identified and extended standard uncertainty was estimated for each spectrometric method using measurements on wastewater samples.

Table 1. Performance parameters

Type of parameter	MBAS method	Nonionic determination
Detection limit	0.05 mg/L	0.05 mg/L
Quantification limit	0.10 mg/L	0.15mg/L
Repeatability (RSDr)	2.48%	4.75%
Reproducibility(RSDr)	4.18 %	6%
Measurement uncertainty	8%	11%

Formulas and calculation

The concentration of MBAS was detected by the formula:

$$p_{\mathrm{y}}=\frac{(A_1-A_0)f_2}{V_0} \tag{1}$$

where, p_y is masic concentration of MBAS;

A_1 is the absorption of sample;

A_0 is the absorption of control sample;

f_2 is the calibration factor which was the amount of anionic surfactant represented in milligrams (it was calculated as sodium salt of dodecyl benzenesulfonate acid);

V_0 is the volume was represented in milliliters.

The concentration of nonionic surfactant was detected by the formula:

$$p_{\mathrm{y}}=\frac{(C_1-C_0)*100}{V_0} \tag{2}$$

where, p_y is masic concentration of nonionic surfactant (µg/mL);

C_1 is the concentration of sample red with calibration curve (µg/mL);

C_0 is the concentration of control sample red with calibration curve (µg/mL);

V_0 is the volume was represented in milliliters.

Results and Discussion

An increase of anionic surfactants was recorded in August, 2016 and March 2017 in all the places (Berceni, Pantelimon and Militari). Thus, the highest concentration of anionic surfactants (2.03 mg/L) was observed in Pantelimon Station. The concentrations of surfactants were below the detection limit in all stations during the month of February 2017 (Figure 5).

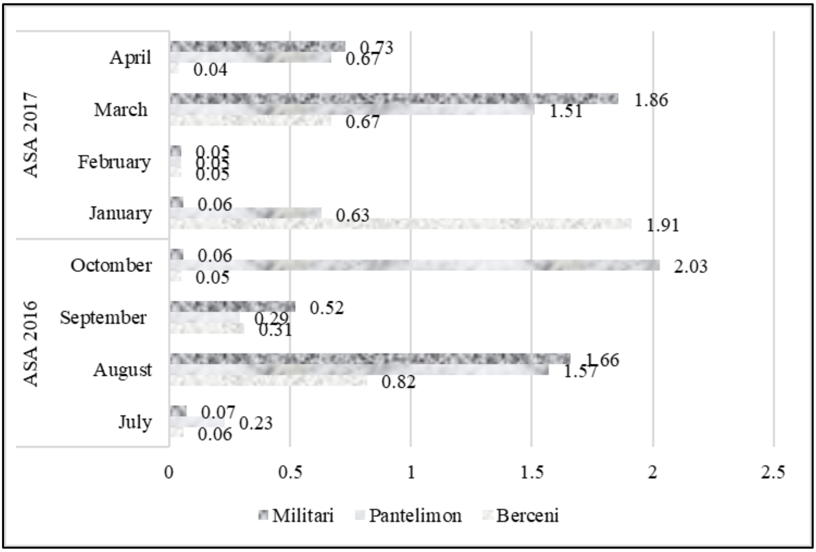


Figure 5. Concentration of anionic surfactants during eight months

The same situation was in case of nonionic surfactants, so in August 2016 and March 2017 it was recorded an increase of nonionic surfactants at the same places). Moreover, the highest concentration of nonionic surfactants was observed in Pantelimon Station (1.72 mg/L) and also, the lowest concentration was in February (below the detection limit) for all the Stations (Figure 6). Thus, the limit of concentration according to the national legislation was 25 mg/L (HG 352/2005, NTPA 002, and Annex 2/2005). It means that the results for the combined concentration of anionic surfactants and nonionic surfactants have to be less than 25 mg/L.

Low concentrations of surfactants recorded in February may be explained by a lower level of subway maintenance compared to the other months of investigation, was due to the fact that the cross between winter and spring, the possibilities of maintenance were lower than other periods of the year. Starting from March, more activities were performed (washing, oil changing, cleaning) so more surfactants were used.

The other possibility could be the snow retention of the especially since February (month with the snow time) and it could lead to a small amount of surfactant in sewage. Moreover, another explanation could be the change of detergent type (it supposed that was used a different class of surfactant (cationic/amphoteric) and that it meant different concentration of surfactants).

Overall, it was observed that the sampling location could play a role in surfactants variation. This fact was confirmed during February 2017 in all the places the concentration of surfactants where under the limit of detection, but in January 2017 we had an increase of concentration only in Berceni Station. That could be meaning that in every season a station is doing maintenance for all the others stations.

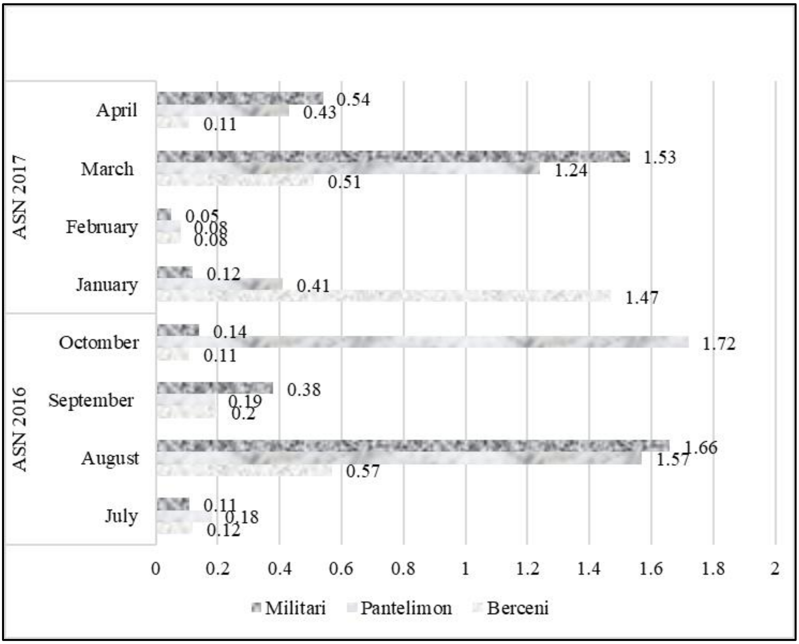


Figure 6. Concentration of nonionic surfactants during eight months

Conclusions

According to the legislation for wastewaters the concentration of surfactants detected were not so high.

The activity of the subway maintenance company was depending on the time of the year and the place (winter – less, except January 2017 – Berceni station; spring, summer, autumn – more).

The surfactants concentration has varied between sampling points. The results could be more comprehensive if the monitoring period would be more extensive (at least one year or above).

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OTHER ENVIRONMENTAL TOPICS

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ECOLIB, LIBRARY OF NATIONAL R&D INSTITUTE FOR INDUSTRIAL ECOLOGY, AN ON-LINE TOOL FOR ENVIRONMENTAL TOPICS AREA

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Abstract

Digital Repository of National Research and Development Institute for Industrial Ecology ECOIND, library was launched on the end of April 2017. ECOLIB Repository is structered in six communities, as follows: *Ecology and Pollution Control; Environmental Assessment; Environmental Technologies; Environmental Management; Other Topics*; *SIMI Proceedings* (International Symposium „The Environment and The Industry": editions 2011, 2013, 2015, 2016).

First four communities, representing the main research areas of ECOIND, contains articles authored by ECOIND researchers published in national and international journals, doctoral theses (abstract), conference papers, short description of the projects developed from 2006 till present, patents. The repository contains more than 800 documents, 850 author names, 1750 keywords.

The research results presented within repository documents are related to development / implementation of the analytical control methods used to assess environmental pollution level (water, soil, sediments, air, waste products); ecotoxicological assessment studies for chemicals / polluted environmental samples regarding their biodegradability, acute and chronic toxicity on different aquatic organisms (fish, green algae, planktonic and benthic crustacean, rotifers, ciliates, plants and bacteria); modern procedures applied for advanced removal of dangerous compounds from water; technologies / biotechnologies applied for water treatment, clean technologies with low energy inputs, innovative biotechnologies presenting unconventional treatment processes; evaluation of the ecological risk determined on the environment (covering water, air, and soil components); industrial waste management– development of advanced methodologies for identification and assessment of the environmental risks caused by waste disposal; methodologies in the fields of quality management, environmental management, and health and occupational safety management.

Keywords: *articles, conference papers, ECOLIB, patents, research results*

Introduction

Research Institutes possess high amount of valuable data that remains hidden in archives, print formats, and personal storage devices. These may be in the form of research materials, presentation, technical reports, which are nearly inaccessible to end users. Various Institutional Repositories or Digital Libraries (DL) are implemented by various institutions as an innovative way to manage institutional properties more efficiently, to disseminate the research activities and to preserve of digital assets generated by researchers (Chen & Zhang 2014).

DL refers to a collection that constitutes electronic resources, accessible on-line via internet. DL's are distributed software infrastructures that aim to collect, manage, preserve, and use digital objects (or resources) for the long term, and provide specialized services on such resources to its users. Currently, modern digital libraries include a wide range of conventional digital objects: text document, image, audio, video, software, etc.

DL have emerged since the early 1990s, distinguished by their useful content, helpful organization and a range of services that include indexing, searching, browsing. DL is associated with metadata catalogue, services, collection, digital objects (Fox 2005). The concept of DL has therefore evolved (Saracevic 2000), moving from a system for the retrieval of static information (primarily books and digitalized textual documents) to a tool useful for the collaboration and interaction between researchers and users, regarding domain-specific topics.

For implementation, a DL request a proper infrastructure and software in order to build the structure and preserve the added documents.

Open source DL software represents a system for the construction and presentation of information collections. It helps in building collections with searching and metadata-bases browsing facilities. Moreover, these software's are easily maintained and can be rebuild automatically. Commonly open source DL management software used to disseminate information to world audience are DSpace, EPrints and Greenstone. The choice of one of them usually depends on material type / format, distribution, software platform and time frame for setting up a DL (Tramboo et al. 2012). In the comparative studies are presented the performance of the software's, information on metadata format, search options, authentication, statistics, programming language (Tramboo et al 2012, Barbuti et al 2014).

DSpace was elaborated in a joint project of the Massachusetts Institute of Technology Libraries and Hewlett-Packard laboratory (Madalli 2003). It is fully customizable to meet the needs of individual institutes and archives, has been initiated and developed by academic institutions, and is nowadays the most common software used in research (DSpace 2014), with the largest community of users all over the world.

The paper present the implementation of ECOLIB Library from the starting point (building) to the indexing process using DSpace software.

Materials and Methods

Infrastructure

Server Dell, model PowerEdge T130;
CPU: Intel(R) Xeon(R) CPU E3-1230 v5 @ 3.40GHz;
Memory: 8Gb; HDD: 1x1Tb;
SO: VMware vSphare 6 Hypervisor.

Software

DSpace software was used for implementation of Institutional Repository because was compatible with various metadata standards and inter-operability protocols, uses only one programming language, complete documentation is available on-line for free and are various communities that can provide technical support (DSpace 2014).

The documents included in the repository created with DSpace software are automatically indexed in Google Scholar which represented a strong advantage.
The version of the used DSpace application is 5.5.

Structure of the Institutional Repository
The repository was structured, by the MBM Software IT specialists, in communities and collections according to the main research activities developed by the scientists from National Research and Development Institute for Industrial Ecology.
In Fig. 1 is presented the access scheme to the Institutional Repository via internet, the web address being: http://dspace.incdecoind.ro.

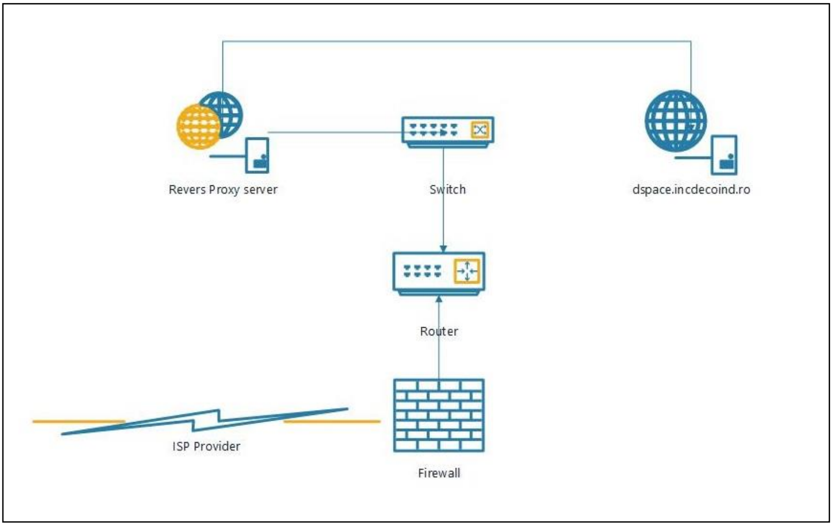

Figure 1. ECOLIB Repository access scheme

The search in the repository is performed using one of the following options: author name, publication year, title of the document, subject (keywords).
Access to the full-text of the resources is either open access or restricted in accordance with the document publication policy.
The repository has been completed in march 2017. It was launch on-line at the end of April 2017 and after that it was used for indexing within Google Scholar database.

Results and Discussion

Communities and collections
The repository is structured in six communities, four of them representing the main research areas of ECOIND. The documents included are: articles published in national and international journals, doctoral theses (abstract), conference papers, short description of the projects developed from 2006 till present, patents, presentations.
<u>Ecology and Pollution Control</u> community include research results on development / implementation of new methods, methodologies, and advanced analytical control

techniques for assessment of environmental pollution level (water, soil, sediments, air, waste products) with inorganic and organic substances and microbiological contaminants. Within this community there are also laboratory and field eco toxicological assessment studies for chemicals / polluted environmental samples regarding their biodegradability, acute and chronic toxicity on different aquatic organisms (fish, green algae, planktonic and benthic crustacean, rotifers, ciliates, plants and bacteria). 60 full-papers, 25 conference articles, 3 book chapters, 5 PhD abstracts and short description of 34 projects are included.

Environmental Assessment community contain research results related to pollution state of various environmental media with establishment of the anthropic impact and various tools and techniques for data processing and analysis, by using mathematical modelling software, in the field of environmental impact and ecological risk assessment.

This community include also research results on mobility of a wide range of hazardous substances in aquatic ecosystems, industrial waste management – development of advanced methodologies for identification and assessment of environmental risks caused by waste disposal (gases emissions, pollutants migration through soil layers and groundwater systems) and studies for the evaluation of the ecological risk upon the environment (covering water, air, and soil components). There are 40 articles, 3 book chapters, 18 conference papers, 4 PhD abstracts and summary of 35 projects.

Third community is called *Environmental Management* and cover research results regarding methodologies in the fields of quality, environmental, health and occupational safety management; food safety management and audits; research results addressed to methodologies applied to management of environmental quality costs and security. In Environmental Management are summary of 30 projects, 11 conference papers, 3 articles, one book chapter.

Environmental Technologies contains research results addressed to: substantiation of modern procedures applied for advanced removal of hazardous compounds from wastewater/water (setting up techniques, processes, mechanisms, kinetics); technologies/biotechnologies applied for wastewater/water treatment (removal of nutrients, xenobiotics / hazardous substances); solar-based environmental technologies – clean technologies with low energy inputs, and innovative biotechnologies presenting unconventional treatment processes; applied research for restructuring, revamping, and modernization of wastewater treatment plants for sustaining of legislative regulations, treatment costs reduction, and sustainable development approach. This community contain 65 articles, 35 conference papers, 56 patents, short description of 55 projects, 8 PhD abstracts and one book chapter.

Another community (*Other Topics*) belongs to Researcher's Portfolio (articles, book, conference papers and theses), results of PhD, Postdoc studies performed with other institutional affiliation than R&D Institute for Industrial Ecology and contain more than 50 documents.

The last community is assigned to the International Symposium "The Environment and the Industry", *SIMI Proceedings*, and include archives from 2011, 2013, 2015 and 2016 years, approximately 240 full-papers. This publication is edited by the National Research and Development Institute for Industrial Ecology ECOIND, has on-line ISSN (2457-8371) ISSN-L (1843-5831) and DOI for each article published in 2015 and 2016 (10.21896/simi. 2015; 10.21698/simi.2016). The papers published in the last two years are indexed in Crossref, Google Scholar, Scilit, Scipers International Databases, and can be also found on Mendeley and CiteUlike Platforms.

In the repository are included more than 800 documents, are listed 850 author names and 1750 subjects.

The metadata recorded for each document are: document title, authors, keywords, publisher, abstract, publication title, year, volume, number, other identification data for publication (e.g. ISSN, ISBN), article DOI.

These resources are available without login and access to the full-text is either open access or only abstract with the possibility to send an e-mail to administer and request an author copy.

Indexing

Starting with June 2017, ECOLIB Library is indexed in Google Scholar. Thus, the digital documents submitted in ECOLIB are indexed in Google Scholar, and as result, the citations can be counted.

In June 2017 the application for indexing in Directory of Open Access Repository (OpenDOAR), a platform containing more than 3300 repositories, it was submitted.

Until now, no answer received, the rate of acceptance is around one repository per month. In this platform are only three repository from Romania, none belongs to a research institute.

In july 2017 was applied for indexing in Registry of Open Access Repositories (ROAR), the application was admitted and so, ECOLIB is indexed in ROAR. ROAR is hosted at the University of Southampton, UK, being part of the Eprints.org network. In this platform are indexed twelve repositories from Romania belonging to some university, institutes or publications with topics in the field of administrative studies, aquaculture, business administration, economics, theology, but not regarding environmental topics.

Statistics

In Fig. 2 are presented usage statistics starting with March 2017 till July 2017.

In March and April months the repository was under construction, in the process of adding documents, so the viewers were ECOIND scientists.

Starting with end of April, ECOLIB was launched on-line. The number of visitors was low (arround 100), until July 2017 when the number increased four times, mainly do to the indexation in Google Scholar on the end of June.

The visitors come from Romania, Hungary, EU and China, the top cities are Bucharest, Cluj, Iasi, Szeged, Hangzhou, Fuzhou, Nanjing.

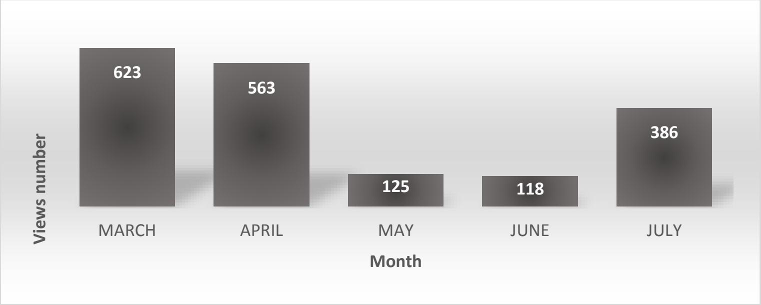

Figure 2. Resource usage statistics

Conclusions

ECOLIB represent the first Institutional Repository in the field of environmental topics from Romania and contain the research results of the scientists from National Research and Development Institute for Industrial Ecology ECOIND.

The repository contain more than 550 documents (articles, conference papers, patents, book chapters) and 240 SIMI conference papers.

ECOLIB Repository is indexed in Google Scholar and ROAR, this fact should lead to a long-term increase of the submitted documents visibility on international level.

Acknowledgements

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GLOBALIZATION AS EMPOWERMENT TOWARDS ECOLOGY

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Abstract

This paper tries to underline the need to empower ecology as part of globalization process and globalization as key ignitor of eco-economics. In these days of economic distress, we need to induce the idea of social ecological responsibility to help protect our environment and natural resources towards prolonging the life span of what we can procure from our Earth's resources and also keep something for future generations.

Keywords: *ecology, economics, globalization, natural resources*

Introduction

In the 21st century, the phenomenon of inevitable globalization is being discussed, but the opinions are also the opposite. After all, what does that mean? Is it a concept that can be adjusted or a disastrous reality? It is a phenomenon that grows as a result of the development of the new technology and its rapidity as well as the information that reaches a stunning speed from one corner to the other on Earth. It is also the consequence of cruel and careless human facts about the environment, social, economic and especially political. These are just a few of our dilemmas and we are trying to find a more plausible answer.

Starting from the premise of this quote, we realize that this process, named in the last century, "globalization" has its origins right from the beginning of civilization with the moment when the man in his desire to know more and to have as much migration to the lands Richer, in full progress.

The globalization that process level is not a new phenomenon in human experience, but the extent and the contemporary coverage of the phenomenon are unprecedented. If we look at today, the US economic crisis has left no other country unaffected because the trading systems are very dependent on each other (Bran et al. 2014).

As globalization is a complex set of processes that affect virtually every aspect of our everyday life - art, culture, economy, politics, immigration, climate, health - studies of globalization show us without a host of humanistic, social perspectives and scientific knowledge of the forms that globalization takes, the forces that shape them, their historical origins and their impact on all aspects of the lives of individuals and communities.

Without doubting this, the 18th and 19th centuries represented and now represent the most dynamic and dense periods in close connection with the unfolding of historical, social contradictory and complex facts but equally dramatic by the consequences of the processes and phenomena unfolding in the plan Spiritual, political-military, economic and social, which have led to the spread of globalization (Bran et al. 2012). We can assert that it is the "Extreme Century" in which mankind has experienced the most spectacular evolutions, from nothing to almost everything, managing both to "stop time in place" and to know the highest level of economic and cultural development of civilizations actually felt at the very high threshold today. But it is also the century in which hundreds of millions of people have been victims of wars, revolutions in different fields, and from different ideologies, whether religious, ethnic or political.

Results and Discussion

Globalization – 360

Globalization is a very common concept used to characterize the current state of the economy at a global level, but it is understood differently by every man because of the perception of the events happening in our lives. Some people perceive it as a complex and complete uniformity, others, on the contrary, that a diversification in the sense of a river of proportions, based on the observance of common principles imposed.

This is presented as a phenomenon specific to the end of the century and the millennium, globalization - or at least some of its dimensions is based on a long history. Under this latter aspect, globalization is the almost natural consequence of the increasingly accelerated course imprinted on history, the first Industrial Revolution.

What distinguishes the contemporary phenomenon of globalization from the previous integration processes since its first appearance is: - scale (formerly regional, current world); - the pace of slow but sure changes at the beginning, and now very fast for 40-50 years now, supporting more technological progress than before, with immediate and irreversible impact on the conditions of everyday life.

With the advent of the Industrial Revolution, globalization is as strong as possible with the discovery of new territories and migratory flows. But the most exciting is the synchronized development with the technological progression by which manual work has been replaced by machinery. In this mechanized process, the worker, that is, the most important actor in the globalization, has the role of supervising, regulating and feeding the machine and controlling the quality. The industrial revolution had the effect of increasing production, improving the quality of life, and making man aware that he can hold more capital, more power, which made him sacrifice himself to live a life full of reward.

It is only after the end of the Second World War that we can consider the extraordinary momentum of globalization; When the process has become a widespread phenomenon (or when the world has really become aware of it), an alarming and extremely satisfying growth in rich countries (Bran et al. 2009). From now on, we can think of globalization as a union among nations that aims to reorganize national borders and transpose them into a single one through which certain transfers can be made: a workforce called "brain theft" or intellectual theft, then leveling. Taxes unfortunately for the less developed countries that cannot keep pace with the opulent states, the establishment of standard rules that do not have a very effective impact in poor countries. Lack of capital results in environmental disintegration, falling population, increased mortality.

The chaos we face today results from the fact that, starting from the development of the most important economic and technological plans, whose origins come mainly from the United States of America, makes the potential differences of all countries to create a so-called Racing in profit and power.

The declared objectives of globalization are concretized in one: a world governance system and a world society with universal rules and thinking in unison. But there is only one question. Who is the benefit of this transformation of all national governments into a single world in fact? Rich countries that allow themselves to go through the transition or poor countries that have to go in order to go through the transitions? This paradigm of today's global society that we will discuss in the continuation of this work with solid and grounded arguments.

Globalization - a disruptive factor for the environment

Globalization is the process by which all peoples and communities "are affiliated" to experience a more and more common, yet similar, economic, social and cultural environment more or less similar. By definition, the process affects everyone in the whole world, regardless of our will or not.

Globalization, which is a word partly synonymous with the growth of trade all over the world, has favoured large-scale production, trade and consumption of unprecedented material goods unprecedented 100 years ago. This has weighed the footprint of human activities around the world, protecting her from hard work. Although it is still difficult to assess the impact of globalization on the environment, it is quite obvious to some people, but in some areas we can argue with solid and tragically real arguments that this phenomenon affects all areas by treating all such things unfortunately

Questions that have linked globalization to the environment have grown largely as a result of extraordinary economic growth in some parts of the world, and in other parts of the world it has been steadily declining, but globalization has meant a very important concept change on how we each think of the environment. Many of us today see environmental issues as being of international interest, not exclusively national interest, such as the protection of the rivers that become the tributaries of the seas and the end of the planetary ocean and, last but not least, the pollution atmosphere of each state Chosen from those with high idle share. The environment is considered to be "patrimony" and the problems connected with it are increasingly the object of international bodies' efforts due to their cross-border effects and the impossibility that only one or some of the particularly rich nations can solve these big dilemmas on their own.

Climate change is one of the main environmental problems, perhaps all the more worrying, because it is impossible to predict exactly how it will develop and what the consequences will be if it is negative. Its causes, however, are known. Climate change comes largely from the greenhouse effect - that is, the excessive retention of solar energy in the atmosphere due to the accumulation of certain gases, especially CO2. The main sources of CO2 emissions are industrial production, transport and, more indirectly, deforestation. These three human activities exist independently of globalization, but their stunning and accelerated development during the 20th century is partly related to globalization.

Globalization, the promoter of mass deforestation

Deforestation is an indirect but probably the most serious and significant cause of the greenhouse effect, landslides, and many other issues that are now threatening the

Earth. Clearing reduces the volume of CO_2 that plants convert to oxygen, this translates into an equivalent increase in the volume of CO_2 in the atmosphere and thus adds to the greenhouse effect. And the burning of the removed wood releases large amounts of CO_2.

Over the past 30 years, globalization has brought about rapid and deep changes in countries around the world, more or less. Generally, there has been a tendency to decentralize the government and reduce the role it plays in the everyday life of its citizens. In countries under development, this "change" has major implications for forests.

Whether it is driven by a market economy (consumption) or imposed by a "command" economy, forest management is usually the responsibility of forestry services in the public domain. In order to stop illicit mass deforestation, public bodies have decided to privatize these forest lands under the leadership of private firms, NGOs, etc. But this decision seems to have been and is in vain if we look around thousands of hectares of raging forests.

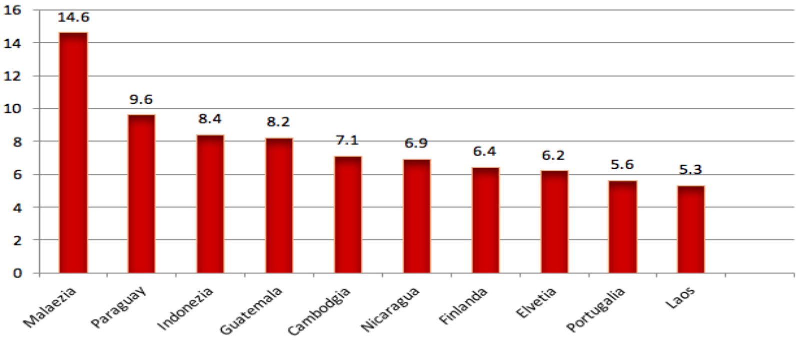

Figure 1. Top for illegal deforestation worldwide
Source: data filtered by the author using www.news.mongabay.com

On the chart we have the countries with the highest percentage of illegal deforestation in the world in descending order.

The total loss of forest in Malaysia amounted to 14.4 percent of the country's wooded cover from 2000 to 2014. The loss is 47,278 square kilometers (18,244 square miles), a larger area than Denmark.

As a critical promoter of globalization, transport systems have, along with international trade, multiplied emissions from road transport (mainly cars and trucks), which are, of course, very high, even more so within the national borders of developing countries in particular economic. As we know, the opening of regional areas (such as the total abolition of border controls between EU countries) has greatly propelled transport of goods by road. Despite recent alternatives, truck transport by train for part of the journey, trans-national road transport is an important source of CO_2 emissions.

Globalization = greenhouse effect.
The greenhouse effect increases the Earth's temperature by capturing the heat in the atmosphere. This keeps Earth's temperature higher than if the direct sunlight was the only source of light. When it reaches the surface of the Earth, part of it is absorbed, that is, that which heats the soil, then the rest riches back into space in the form of heat. The greenhouse gases that are in the atmosphere absorb and then redirect some of this heat back to Earth.

The greenhouse effect is a major factor in keeping our planet warm. In fact, without the greenhouse effect, the average global Earth's temperature would be much lower and life on Earth as we know it would not be possible.

Globalization "indirectly" promotes CO_2 emissions related to industrial activity.
While the Industrial Revolution was a vector of globalization, growth in cross-border trade and investment in its turn stimulated industrial activity. This is often a major source of GHG emissions, as in the case of electricity production, which still involves coal burning, oil and its derivatives. The intensification of globalization has then accentuated the greenhouse effect and global warming (global warming is one of the undesirable effects that would appear to be a major problem of humanity that is neglected or given to a deliberate second plan.

For decades, developed countries, pioneers of global industrialization, have been the world's largest polluters, responsible for most of GHG emissions. Today, the United States is responsible for about 20% of global emissions.

According to International Energy Agency (IEA) statements, in 2016 carbon dioxide emissions stagnated for the third consecutive year, and curiosity is that the economy globally has increased. In China and the US they have fallen, and in Europe they have stagnated.

According to the agency, the largest decrease was in the US (-3%), i.e. 160 million tons of carbon dioxide (CO_2) less than in the previous years, while the economy grew by 1.6 %.

EU carbon dioxide emissions stagnated in 2016. This happened when demand for gas increased by 8% and demand for coal fell by 10%. Renewable energy has played a significant role, but one quite small. Researchers say the decline was driven by a sharp increase in shale gas supplies and renewable energy sources that replaced coal.

In China, carbon dioxide emissions dropped by 1% in 2016. At a time when demand for coal fell, the economy grew by 6.7%. Experts say that the share of renewable energy, nuclear energy and natural gas has contributed to this (Bodislav 2012).

Globalization and behavior of multinational companies to the environment
A multinational company actually carries out an enterprise operating in several states, but it is managed from a single country. Typically, any company or group that earns a quarter of its revenue from operations outside its home country is considered a multinational corporation.

There are four categories of multinational corporations:

1. Multinational corporation, decentralized with a strong presence to the country of origin;
2. A global, centralized corporation that gains a centralized production cost advantage whenever it is cheaper;
3. International company based on R & D and its HQ's practices;

4. A transnational enterprise that combines the three previous approaches.

Industrial corporations are abundant in terms of technology innovation and investment capital in increasing their production. In the context of globalization, privatization and market liberalization, they are considered to be one of the most important factors in shaping the future of the world. However, these factors have brought not only an economic growth but also a negative effect on the environment (Bodislav 2015).

In an attempt to reduce costs, many multinational corporations have expanded their polluting export activities through subsidiaries established in less developed countries. Environment pollution does not necessarily have to cross a country's borders as a substance, it can also cross the border by a decision taken in a state that leads to environmental consequences in another. Otherwise, the environmental degradation resulting from the subsidiary's activities can often be traced back to the parent company's regulatory orders. Importantly, because multinationals are large contributors to the world economy, they enjoy significant political power on the international stage. The predominant position of these corporate giants is not equally balanced with that of victims when they seek to make multinational responsibility for environmental damage. Most often, the cost of production is required to combat by introducing non-environmentally friendly manufacturing processes and consumables used in production, which slowly, but systematically put their mark on the environment.

Ironically, all the elements of the environment still offer us the opportunity to walk clean streets and breathe fresh air, despite the fact that pollutants are rapidly multiplying every day. From multinational companies, road traffic and people who deliberately deforest and pollute, we all have our part to blame for endangering.

Conclusions

The phenomenon of globalization determines the extraordinary development of already overdeveloped economies; Developing economies are losing momentum and declining. States lose their national identity, especially the middle and small, and become parts of the regions with a strong reputation due to the regress of their national economies.

Everyday life in Europe and America, these being the continents with a predominantly high rate of development, influences the natality rate, causing the population to straighten their efforts towards economic development and career not to procreation.

The global climate will suffer very much in the next 50-100 years. The effect of the greenhouse gives rise to extremely hot summers, droughts with temperatures above 40 degrees, melting glaciers and polar fauna and mountain areas.

Measures to reduce population will have a devastating effect in developed areas, while in poor areas will have no effect and will continue the alarming rise of the population.

Deindustrialization measures will increase until most state-owned institutions that make a significant contribution to GDP will be privatized or bankrupt.

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USING TECHNOLOGY AS KEY ELEMENT IN CREATING RATIONALITY IN NATURAL RESOURCES USAGE

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Abstract

This research article starts from the premise that we need to emphasize the idea of scarcity to protect our rational way of consuming our Earth's natural resources. From Stone Age agriculture till today's Internet of Things which can used in agriculture, we came a long way. This paper presents the competitive advantage offered by technology and by human behaviour moulded by speedy communications towards creating a special path that could be seen as optimized agriculture.

Keywords: *agriculture, economics, natural resources, rationality, technology*

Introduction

Over the years, the growth was a strong force to reduce poverty, creating jobs and improving general living conditions. Before the 18th century the world economy has experienced low growth. Growth theory has its roots in the eighteenth century is developing amid the Industrial Revolution, revolution led to higher yields of production factors in a surprising manner. So, at that time, economic growth has been associated with a significant increase of production at the company level (Bodislav & Bran 2017). According to economic historian, James Bradford DeLong, global growth was 0.3% per year between 1300 and 1700, and only 0.6% per year between 1700 and 1800. But in the 19th century, growth reached 2.7% per year as a result of industrialization in UK, US, France, Germany and Japan.

Decades of research economists have emphasized the central role that innovation has in terms of generating long-term economic growth. Therefore, development of science and technological changes occurring as a result of continuing innovation is a key - the key economies today.

Innovation has played an important role in terms of employment expansion. Progress in health technology have led to a dramatic increase in life expectancy. If in the 1800s, the average life expectancy at birth was under 40 years in all developed countries by 2011, this had risen to more than 75 years, the highest average was recorded in Japan, respectively 83 years.

Currently, there are many areas of innovation to stimulate growth potential in the future, and these include: nano-biotech, intelligent robots, 3D printers, and genetics. However, in order to stimulate economic growth, it is necessary for new technologies to widely publicize the economy. It is also necessary that the current economy possess sufficient absorption capacity to hold human capital able to understand and apply new technologies, have the know-how and have the institutions to coordinate and mobilize resources to implement new technology (Bodislav & Bran 2017).

Results and Discussion

Efficiency as part of agricultural innovation

Trade between traders, agricultural producers and customers made in due time, taking into account the perishability of goods, requires a high efficiency in the distribution structure that may involve an extra cost mainly borne by the customer.

These exchanges are limited and geographical location of agricultural land use, road infrastructure and population distribution, so to have highlighted the links between traders, farmers and customers have drawn connections and competitive advantage created by technological advances (Bran & Bodislav 2012).

Technological advances created through the used transport system, the innovative agricultural systems used and the real-time distribution to the customer, to which we can add the optimal development of the farms in order not to enter into exogenous or endogenous production cycles.

The agricultural industry based on timely distribution to the trader and the customer by the farmer is based on economically efficient processes that include three evolutionary factors: creating work standards, widespread deployment and optimizing dead times. As an example, we can take the evolution of a tomato, which, although strictly natural, can be controlled and manipulated anthropically (Bodislav 2011). A tomato-based factory (tomato juice, ketchup, whole preserved tomatoes, etc.) requires an optimized technological flow to avoid creating high dead-time costs.

The working framework of the agricultural crop-process process must also be optimized through the timely distribution system. That the whole picture be complete also needs to be borne in mind that there are also the environmental and health standards of the crop (if the obtained vegetables are bio, eco or GMOs), which are now also a factor evaluated by the consumer, not only by competent agencies (Low & Vogel 2011).

If large merchants are taken as a valuation pool, with the top three at global level being in 2011: Wal-Mart, Tesco and Carrefour, they can see that they attach greater importance to offering the consumer as green as possible, through spaces addressed to the customer Depending on its preferences and area of origin.

In connection with the area of origin referring to the US market in particular (Kummer 2010) where Wal-Mart is trying to bridge the gap between the farmer and the final customer, reaching even to impose conglomerates local to introduce a policy of financial support to farmer's subcontractors (Whole Foods 2011).

These new product features result in new supply chain needs, decreasing production distance but increasing workflow. To increase the efficiency of distribution to the trader (or final customer), the work and development strategy has been attributed to the carrier as it can optimize dead times by calculating production, harvesting, processing and shipping times for the trader, and to provide it with a Life of the product so that it does not cause loss due to expiration of the shelf life.

We can introduce here the idea of a trader as a symbol of operational efficiency by the fact that the big retailers come from developed countries that have access to global distribution and development, creating a scalable model for optimum output (in terms of volume and time).

To gain access to shelf life, major retailers incorporate domestic producers, who have independence in the production decision, but not in delivery and volume. In order to lower the producer's costs, subcontracting the agricultural conglomerate and the retailer's purchase, the producer is retired on a single agricultural product or just on an agricultural class.

This chosen path has been partially imposed because studies suggest that there is a loss of quality through industrial production methods and in terms of nutritional value but also by the minimum standards reached (USDA).

Between 1950 - 2000, it had a loss of crop nutrition 6% protein and 38% riboflavin (Davis et al. 2004; Ata et al. 2012), but an increase in the level of pesticides (EWG 2011) and chemical fertilizers circuit are naturally found in ground water in the agricultural area (Berman et al. 2005).

Fresh versus rotten – the technological output for perishable natural resources

Why is there such results that affect product quality, ambient environment and consumer health? Because they have a high shelf life, productivity is above normal, and these products look very "healthy" and fresh all the time. These are the characteristics of mass production, low quality nutrition and spending a lot of time in the distribution flow. The alternative of the moment is given by the local production, which besides the indirect aid granted to the local economy and the national macroeconomic indicators also has some qualitative specific features:

1. Agricultural crops do not spend a lot of time in processing (time = money, less time spent, lower cost per piece, greater profit);
2. "Healthy" prospect (the product is freshly preserved naturally without chemical improvement);
3. The agricultural production method is environmentally friendly.

We can see such production as a component of horizontal development in the agribusiness, which is part of the vertical distribution to the final consumer that the product supports multiple payment complementary industries (Bran & Bodislav 2012). Local production is thus the first step towards agricultural health but at the expense of global production, super-industrialized or super-chemically processed.

It can be considered as one of the only viable long-term outsourcing models. In the case of a company, the outsourcing process has a long-term tendency to destroy organizational culture and block the company, creating a malicious addiction to the chances of creating a competitor in the subcontracted company.

The balance obtained through the process of outsourcing production by an agricultural conglomerate is unique because it is a long - term win - win situation. To outsource globally a global conglomerate process, it must be synchronized with the trader's distribution system by translating the distribution network's working structure, basically either by optimizing the farmer's / processor relationship with the merchant's chain of stores, or by creating continuous-flow warehouses , From which to supply the merchant's stores (there are costs of extra storage and new distribution costs on the warehouse-store relationship), and the high level of competition does not allow the use of price discrepancies. Wal-Mart has developed the Heritage Agriculture Program to highlight both distribution structures, but highlighting local character and keeping pace with competition prices.

Conclusions

In the production and development cycle of the subcontracted producer (externality) there is also the need to implement the agricultural cycle, which includes the efficiency of the crop through exogenous factors (weather and pests).

In agricultural production models, there is the Three Sisters model, which is based on alternating cultivation: corn, beans and pumpkins at the same time on the same arable land (corn provides the climbing structure for beans, the beans provide the necessary nitrogen for the corn, and the pumpkins do not allow access pests and soil covering (Fullerton 2001). This is a practical balance of the hedge agricultural base model.

For the outsourcing process, we also have major implications for the development of product and brand standards according to the conglomerate or retailer for which it is produced, here we can mainly include processed products, but in the case of unprocessed products (e.g. tomatoes delivered to traders) Have specifications according to USDA or European Commission, but not by taste or nutritional quality.

If we call into question olfactory senses, we can see major differences between the taste of a "garden" tomato and a tomato produced for the market, although both look the same. Local producers, subcontracted by agricultural conglomerates or traders, intervene here as they can bring the following features as an advantage over competition:

Natural taste;
High nutritional values;
Methods of ecological cultivation.

It should be noted that certain production processes are viable only in certain areas and therefore the implementation and feasibility process should be followed up by studying the soil, climate, anthropic environment and available infrastructure characteristics, also taking into account the relationship developed during the research: The distance between a city and city center and an agricultural producer is directly proportional to the arable land available for cultivating the necessary agricultural products. In the long term, the influence of innovation on the IT & C sector may be the one that will create a rupture in the traditional production, distribution and marketing of organic, organic, organic and natural products, which may lead to removal from the chain of retailers', but the results are to the benefit of the end user, the bio consumer. This will certainly be part of the disruption of the future when it comes to rational consumption of natural resources and maximizing their output by using the IT & C component and maybe its newest branch, the Internet of Things, this way we will reach a breakthrough like BASF did at the beginning of the 20th century when they introduced the chemical fertilizer and increasing productivity per hectare 100 times in only one year, evolution never seen since then.

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WATER RESOURCES IN THE CONTEXT OF GLOBALIZATION

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Abstract

A rational use can lead to the protection of water resources. In a community, the state of the environment is influenced by both the quality and the quantity of water resources. The state of the environment is also given by measures to protect water resources in other areas such as energy, transport, agriculture, fisheries and tourism. The supply of drinking water is influenced by water quality. A prudent and rational use of natural resources, including water resources, can help preserve, protect and improve the quality of the environment. Water management and use of water resources are very important. The importance is the multiple use of water. This may lead to deterioration in the qualitative parameters of water resources. This raises the issue of implementing rehabilitation and development measures for wastewater management systems. The application of modern and non-polluting technologies can lead to pollution prevention. In many areas, it is used in addition to surface water and groundwater. From this point of view, the article presents an analysis of the quality of surface waters and groundwater. Globalization has favoured technological transfer from developed countries to developing countries. Given the economic development of a country, globalization has made the role of human capital grow. It also had an effect on competitiveness. The article presents the evolution of the population served by the public water supply system, respectively the quantity of drinking water distributed to the consumers. In a globalized economy, increasing competitiveness is based on knowledge.

Keywords: *environment, globalization, water resources*

Introduction

Changing the physical, chemical and biological characteristics of water, in other words water pollution, has consequences for the health of the population.

Proper drinking water supply has consequences in reducing the impact on quality of life. Also, the quality of surface and underground water is influenced by the way waste is collected and stored.

In a global economy, human capital is an instrument that can lead to success. The fight against climate change and the maintenance of social cohesion can be achieved through a sustainable and highly competitive social market economy (EC 2010).

New global challenges with long-term effects are emerging globally. Due to population growth, pressure on natural resources is increasing. At European level, the aging process is proving to be an additional challenge. Increased vulnerability of crops and animals to climate change (MADR 2015). These, together with increasing urbanization, will lead to the limitation of food production. Globally, it is forecast that food demand will increase by 70% by 2050 (FAO 2011).

This trend will mostly contribute to developing countries for which demand for food will double in the coming years.

It is estimated that by 2050 the world population will grow to 9 billion and 95% of this growth will be in the least developed countries (in 50 of the least developed countries around the world, where the population will double) (EC 2008). Also, by 2050, 70% of the world's population will live in urban areas (FAO 2009).

EU water policies have contributed to the protection of water resources. However, fresh water accounts for only about 2% of the total amount of water in the planet (McKinsey 2009). Thus, the estimated supply of water supply worldwide is approximately 40% (EEA 2012).

Surface water

Food security is affected by climate change. Through impacts on water resources, local effects can be generated for different areas around the globe. Thus, some areas may benefit from productivity gains in the vegetable sector, as well as from crop and farmland expansion. For other areas, global warming and water scarcity can affect productivity and production in the vegetable sector, thus affecting food security. In order to prevent such situations, both low-water irrigation systems and renewable energy systems can be developed. There is also the possibility of creating water reserves as well as afforestation. Climate change and extreme weather phenomena generate negative effects. For example, in the agricultural sector, they influence the resistance and adaptability of some plants. Under these circumstances, measures to support water supply, as well as increasing the efficiency of its use, are necessary and welcome. In this case, it is important both effective access to water resources and access to drought resistant varieties (MADR 2015).

Climate change can help reduce water and food resources. This could contribute to triggering regional conflicts, hunger and refugee flows (EC 2014).

Thus, at the level of local communities, measures supporting water management activities are also important.

Afforestation activities are designed to protect water resources. In water resource management, consideration should also be given to the non-use of all water in the production processes. Thus, by not using all the water, part of the water returns to the water source. In this way, the qualitative parameters of this source deteriorate. The importance of this observation is necessary because, later, this water source can be a water resource for other communities.

Worldwide, people are in increasing interdependence. The manifestation of the globalization process has allowed markets to expand globally, as well as the opening of new markets. However, negative effects, which are more and more dangerous than positive effects, must be considered (Zaman & Gherasim 2007). Thus, positive effects can be cancelled by the duration and amplitude of seizures. In crisis situations, even if wealth is produced, there are still prerequisites for more poverty. Some social categories may be affected more than ever by such problems.

Effective water resource management enables local and regional communities to better prepare for extreme weather events. Due to climate change, these extreme weather phenomena are becoming more common and cause serious damage.

At the EU level, the water resources sector comprises 9,000 active SMEs and offers almost 500,000 full-time equivalent jobs (EC 2015).

In order to support a sustainable economic recovery and adaptation to climate change, the European Commission launched in 2012 the European Water Innovation Partnership.

At European Union level, the Europe's Water Rescue Plan was developed. It aims at removing obstacles to Europe's water resources and is based on an extensive assessment of existing policy. Europe's water security plan provides some key themes. These include topics addressing better land use, water pollution, increasing water use efficiency, and resilience of water resources (EC 2012).

Depending on the level of development, for 2015, Table 1 contains data on water resources. It is noticed that, among the surface waters, Jiu hydrographic basin has the highest flow of 2,109 million m^3 / year.

Table 1. Water resources depending on the degree of amenity

Water sources/ Hydrographic basin	million m^3 / year
Total	38346
Surface waters	33679
Inland rivers	13679
Tisa	256
Someş	715
Crişuri	395
Mureş	1,044
Banat Space	608
Jiu	2,109
Olt	1,682
Vedea	40
Argeş	1,672
Ialomiţa	430
Siret	1,956
Prut	726
Other basins	2,046
The Danube	20000
Underground waters	4667

Source: Authors' elaboration based on National Institute of Statistics (NSI) 2017 data

Certain activities may contribute to adverse effects on water status. Climate change and land use have such negative effects. Negative influences on water status also arise through energy production, industry, agriculture and tourism.

However, water, through natural retention measures, contributes to limiting the negative effects of drought and floods. Water transfers or desalination have a high impact on the environment. Thus, measures for treating wastewater or industrial wastewater make reuse of water applicable to both irrigation and industrial purposes.

The assessment of surface water quality involves monitoring the hydro morphological, physicochemical biological parameters of the priority pollutants as well as other pollutants discharged in significant quantities. According to the regulations, the 5 quality classes are the following: I (very good condition), II (good condition), III (moderate), IV (weak) and V (poor).

The following table presents the comparative situation (1995-2015) of the length (km) of the main river basins.

Table 2. Comparative situation of the main river basins

River basins	1995	2015
Tisa	467	1294
Somes	1602	3169
Crisuri	1093	1926
Mures	2402	5124
Banat Space	1241	2815
Jiu	944	2141
Olt	1567	3539
Vedea	875	1101
Arges	2221	2257
Ialomita	1193	1371
Siret	4135	5439
Prut	1655	3492
Dunărea	1903	2491
Litoral	69	349
Total	21367	37111

Source: Authors' elaboration based on NSI 2017 data

It is noted that in 1995, the Siret Basin had 4135 km, and the Mures Basin had 2402 km. Compared to 1995, the situation remains in 2015. However, in 2015 there are also increases for other basins (Litoral, Jiu, Banat Area).

From the point of view of surface water quality, the following table presents the comparative situation (1995-2015) for hydrographic basins with the highest lengths in 2015, as well as correspondence with the respective quality classes.

Table 3. Comparative situation for hydrographic basins with the largest lengths

	Siret		**Mureș**		**Olt**		**Prut**	
	1995	**2015**	**1995**	**2015**	**1995**	**2015**	**1995**	**2015**
Total lengths	4135	5439	2402	5124	1567	3539	1655	3492
Category I	2464	-	1073	-	543	-	584	-
Category II	776	3801	713	3457	582	2072	425	1322
Category III	235	1638	163	1659	264	1287	335	2062
Category IV	-	-	-	-	-	161	-	108
Category V	-	-	-	8	-	19	-	-
Above 3rd category limits	660	-	453	-	178	-	311	-

Source: Authors' elaboration based on NSI 2017 data

It is noticed that, compared to 1995, in 2015 we no longer find the classification in the first grade (very good condition). For the first three hydrographic basins, it is found that the majority is the classification in the quality class II (good condition). For the Prut River Basin, the majority is the grade III (moderate) class.

Distribution of drinking water

For areas related to water quality and nature protection, European Union legislation includes provisions requiring high levels of protection (EC 2016b).

At the same time, the EU's environmental policy also covers the protection of water resources, aquatic ecosystems and the water we drink, as well as bathing water. This approach is foreseen in the Seventh Environment Action Program (the framework agreed for EU environmental policy by 2020) (EC 2016a).

In the field of water, the European Union's environmental policies aim to achieve a good environmental status for inland surface waters, transitional waters, coastal waters and groundwater. The regulations on drinking water, bathing water and urban wastewater monitor the pollution caused by nitrates, industrial emissions, pesticides and persistent organic pollutants. The importance of sustainable water management is also addressed in the EU Strategy on Adaptation to Climate Change. Thus, in order to achieve sustainable water management, account must be taken of the impact of climate change. Increasing the efficiency of water resources, by improving the conditions for its reuse, can be achieved by moving to the circular economy.

Inadequate water supply, sanitation and hygiene are the causes of various diseases that affect the health of members of any community. Food security is affected both by the lack of water resources and the poor quality of water. They exert a negative influence on how people choose their livelihoods, but also on educational opportunities (EC 2014).

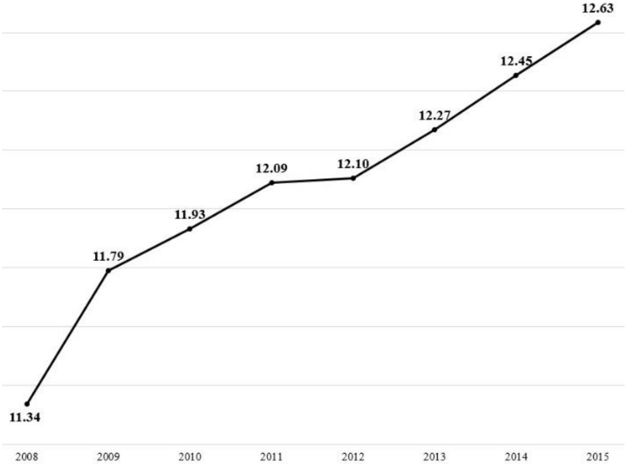

Figure 1. Evolution of the population served by the public water supply system
Source: Authors' elaboration based on NSI 2017 data

Water supply is considered to be a service of general interest. Thus, water resources must be protected and defended. They cannot be classified as commercial goods.

The provisions of the Directive establishing a Community Water Policy Framework can only be successful through cooperative and coherent community action (EP 2000).

Supplying the population with drinking water is guaranteed by the good quality of water resources. Thus, the protection of water resources promotes the sustainable use of water.

Worldwide, it is noted that mankind faces the danger of lack of water resources, but also the degradation of the quality of these water resources.

The Fig. 1 shows the evolution of the population served by the public water supply system, for the period 2008-2015 (million people).

There is a continuous increase in the number of people who have access to the public water supply system.

According to the data presented on the NIS website, the highest increases are registered in the following counties: Ilfov (+ 43.30%), Damboviţa (+60.22%), Iaşi (+51.22%), Gorj (+50.01%), Salaj (+31.63%). Even if the national increase was 11.45%, there are counties where the number of people served by the public water supply system has decreased. These counties are the following: Braila (-8.62%), Dolj (-7.44%), Botosani (-1.94%), Vaslui (-1.80%).

The following figure (Fig. 2) shows the evolution of the amount of drinking water distributed to consumers in 2000-2015 (thousands of cubic meters).

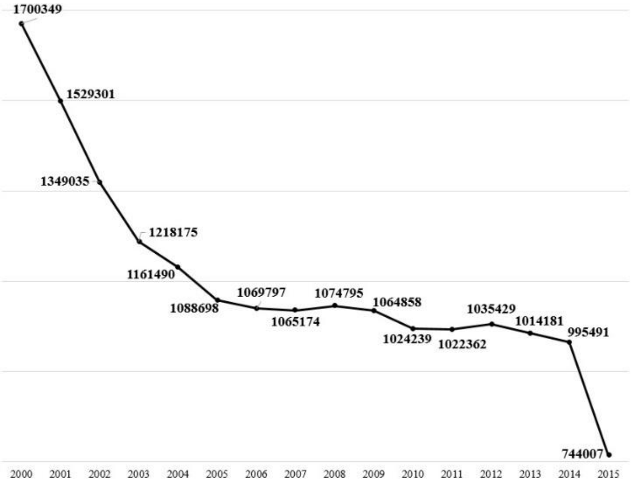

Figure 2. Evolution of the amount of drinking water distributed to consumers
Source: Authors' elaboration based on NSI 2017 data

There is a steady decrease in the amount of drinking water distributed. Thus, as compared to 2000, a quantity of 56.24% was distributed in 2015.

Although this decrease is observed, as compared to 2000, in 2015 the quantity of drinking water distributed for household use in the total quantity distributed increased as shown in the following figure (%) (Fig. 3).

According to the data published on the NIS site, at county level, the counties where the share of household drinking water has increased is: Alba (+39.48%), Botosani (+36.37%), Giurgiu (+29.54%), Bistrita- Nasaud (+25.73%), Suceava (+25.51%). Also, the counties where the share of domestic drinking water dropped were: Valcea (-12.05%), Damboviţa (-10.60%), Sălaj (-9.53%), Covasna (-9.39%), Argeş (-8.84%).

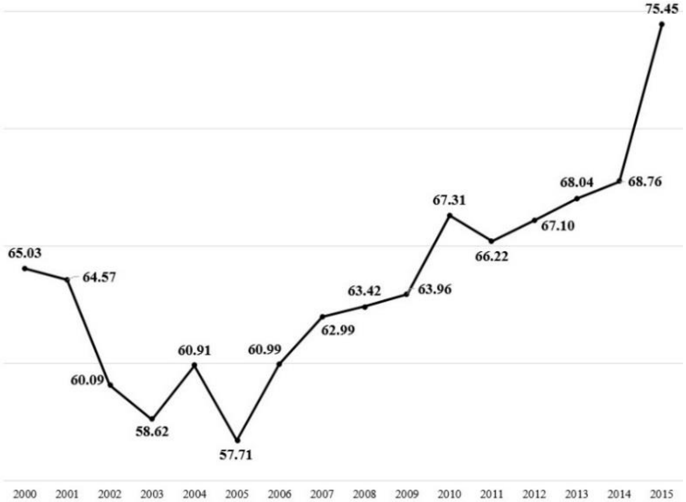

Figure 3. Evolution of the amount of drinking water distributed for household use out of the total quantity distributed
Source: Authors' elaboration based on NSI 2017 data

Conclusions

Climate change can help reduce water and food resources. This could contribute to triggering regional conflicts, hunger and refugee flows (EC 2014). Due to population growth in the coming years, global demand for water will increase. The manifestation of this pressure can be amplified by climate change (EC 2017a).

At national level, as compared to 1995, in 2015, the waters of the main four hydrographic basins (Siret, Mureş, Olt and Prut) are no longer in Class I (very good condition), but in Class II (good condition), respectively in the quality class III (moderate state).

In recent years, there has been a steady increase in the number of people who have access to the public water supply system. However, the amount of drinking water distributed decreases.

Access to clean water, clean cooking, education and healthcare, job creation and support for local businesses are activities that need energy. Climate change disproportionately affects the poor (EC 2017b). Thus, inclusive growth and, at the same time, limiting climate change can be achieved by investing in sustainable energy. In this way, affordable, modern, reliable and sustainable energy services can be based on renewable energy.

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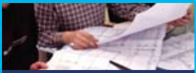
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- *•1998 - Redox opened the first warehouse*
- *•2000 - Signed exclusive distributor agreement with Sigma-Aldrich*
- *•2003 - Signed exclusive distributor agreement with DAKO*
- *•2003 - Expand the sales force , warehouse and all the other departments*
- *•2005 - Obtain ISO 9001:2000 certification*
- *•2008 - Implement the ERP system in all operations*
- *•2009 - Finished the new offices and warehouse building*
- *•2011 - Signed distributor agreement with Eppendorf*
- *•2013 - Signed exclusive distributor agreement with ArcDIA*
- *•2015 - Merck Completes Sigma-Aldrich Acquisition*
- *•2017 - Start distribution of Merck Millipore products*

Products

- *·Life Science Products*
- *·Analytical Reagents and Supplies*
- *·Essential Reagents (Commodities) and Consumables*
- *·Materials Science Fine Chemicals*
- *·Diagnostics*
- *·General Laboratory Instruments*

Services

- *•Laboratory Consultancy Services*
- *•Instruments installations and staff training*
- *•Stock products accordingly with agreed yearly planners*

Watchword

WE HAVE THE KNOWLEDGE, ENERGY AND WILL !

25 ANI DE PERFORMANTA
25 years
RONEXPRIM
WE DELIVER PERFORMANCE

Ronexprim has over 25 years of uninterrupted activity on the Romanian laboratory equipment market for materials science, life science, research, environment, industry, and others areas of activity.

The company was founded in 1991 as the Agency and Service for Philips Industrial Departments in Romania and now represents most of the market – leading international manufacturers, including Thermo Fischer Scientific, FEI (part of Thermo Fischer Scientific), Malvern Instruments, Edinburgh Instruments, SpectroScientific, Nanonics, Milestone, Stanhope Seta, Trace Elemental Instruments, etc.

Ronexprim is specialized on consultancy and technical assistance for equipment, configuration, integration and installation, covering warranty and post-warranty maintenance and customer employee's professional trainings.

The company is offering an extensive portfolio of products which are integrating the world's latest technologies**:** electronic microscopes, spectrometers, laboratory and process equipment for physio-chemical analysis and also sample preparation systems, consumable and certified reference materials.

Producers: cutting-edge technology and devices

FEI part of Thermo Fisher Scientific
EDAX Smart Insight AMETEK MATERIALS ANALYSIS DIVISION
Xenemetrix The Power to Change Energy into Information
Trace Elemental Instruments
ThermoFisher SCIENTIFIC
EDINBURGH INSTRUMENTS
LANCER GETINGE GROUP
Malvern
Spectro Scientific Confidence in knowing
MILESTONE HELPING CHEMISTS
LGC Standards Excellence through measurement
SPEX SamplePrep Laboratory Equipment for Sample Preparation & Handling
LAARMANN Innovators in Solids
NANONICS IMAGING Ltd.
SETA STANHOPE-SETA
PSL
Sonel
Thermoteknix Systems Ltd
BEHA AMPROBE
KEYSIGHT TECHNOLOGIES
FLUKE
FLUKE Biomedical
FLUKE Calibration
Raytek Fluke Process Instruments
ELSPEC When Power Meets Quality

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