

# CHARACTERIZATION OF DIATOMITE MODIFIED BY STRUCTURAL-CHEMICAL METHOD

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**Abstract.** A novel fluorine sorbent, modified diatomite was characterized in the study. For modification of diatomite with the goal to make it more selective towards fluoride-ions we have used structural-chemical method which consists in introduction into the diatomite matrix of elements that have a high potential for adsorption of fluorine or form with him low solubility product. Such a modifier element is aluminum. The -modified diatomite was made through surface modification treatments including NaOH treatment and aluminosilicate deposition on raw diatomite. In the NaOH treatment under heating, amorphous  $\text{SiO}_2$  of diatomite was partially dissolved in the NaOH solution. The dissolved Si contributed to form the aluminosilicate which deposited onto surface and into the macropores and mesopores of diatomite. For characterization of the original and modified diatomite chemical, thermogravimetric, X-rays, structure and adsorption (BET) and FTIR analyses were used. Blocking macropores and larger mesopores of diatomite with aluminosilicate resulted in increase of specific surface area to  $81.77 \text{ m}^2/\text{g}$  for the modified diatomite which is 2.5 times-larger than the raw diatomite ( $37.54 \text{ m}^2/\text{g}$ ). Sorbent obtained was tested to remove fluoride from model solution with initial concentration of  $\text{F}^-$   $1 \text{ mmol/l}$ . In identical conditions ( $m=0.5 \text{ g/l}$ ;  $\text{pH} = 4.9$ ;  $T=293 \text{ K}$ ; time 120min) adsorption capacity of modified diatomite was  $40 \text{ mgF/g}$  sorbent in comparison with  $4 \text{ mgF/g}$  for raw diatomite

Keywords: diatomite, modification, structural-chemical, aluminosilicate

## 1. Introduction

In recent years for natural water purification more widely used adsorption-based technologies and processes in which various natural minerals applied as a sorbent, particularly diatomaceous earth, and bentonite, which have a number of advantages over the traditional - synthetic sorbents and ion exchange resins: high stocks, availability, low price and the possibility of a single application.

Specific surface area of natural diatomite is generally low ( $15\text{-}35 \text{ m}^2/\text{g}$ ), which does not allow the diatomite to be an effective sorbent for solutes. Therefore, to increase the surface area and improve the surface characteristics substantial modification of the raw diatomite need. A high porosity (80-85% voids) makes it a suitable carrier for the materials used for inoculation.

In this work to modify the surface of diatomite and give it selectivity towards fluoride ions we have used structural-chemical method. Structural-chemical modification method (SCM) includes three consecutive stages of diatomite treatment: alkaline-based heating at constant stirring, exposure in the aluminum salt solution ( $\text{pH}$  below 3.5) and the third stage – mixing with ammonia solution in basic medium. After separation of the precipitate, it was washed, shaped and dried in open air and further at the temperature  $110\text{-}120^\circ\text{C}$ .

For characterization of the initial diatomite (D1) and the diatomite modified by structural-chemical method (DMA) X-ray, thermogravimetric, and structure of adsorption (BET), chemical and FTIR analyses were used. It was established that the initial diatomaceous earth contains  $\text{SiO}_2$  - 60%,  $\text{CaO}$  - 11.7%  $\text{Al}_2\text{O}_3$ -4.8%, and also oxides of Mg, Fe, Na, K, diatomite main phases

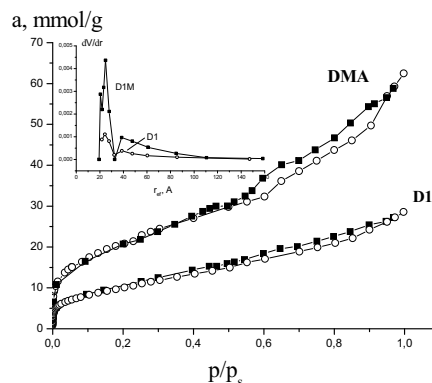
are quartz, amorphous silica, calcite, aragonite, kaolinite and montmorillonite present in small quantities.

Modification of diatomite leads to decomposition of calcite and aragonite phases and formation of a new one - aluminosilicate. During the diatomite treatment with NaOH at heating amorphous silica partially dissolved and in the second stage (interaction with a modifier) in volume and on the surface aluminosilicates formed, which probably deposited into the macropores and the larger mezopores.

## 2. Results and discussion

### 2.1. Adsorption-structural analysis (BET)

Fig. 1 shows isotherms of nitrogen adsorption-desorption by the samples D1 and DMA



**Fig. 1 Nitrogen adsorption isotherms by the natural diatomite D1 and the structural-chemical modified DMA samples**

According to Fig. 1 the initial parties of the isotherms are convex curves for both samples. The isotherms of the initial sample and the modified diatomite are both of type IV by the classification of A.V. Kiseleov, i.e. samples are mixed structure mesoporous sorbents. A special feature of the isotherms is the presence of reversible hystereses - adsorption branch coincides with the desorption one at low relative pressure  $p/p_s = 0.25$  to  $0.40$ , after the point of hysteresis beginning a larger amount of adsorbed nitrogen vapor (more than two times) is observed for the sample DMA.

This probably tells us about the formation of new active centers on the sorbent surface as a result of structural changes and the increasing of chemical interaction diatomite - nitrogen, which is characteristic for adsorption processes accompanied by capillary condensation. Both samples isotherms are satisfactorily described by the multimolecular adsorption model, specific surface values calculated following BET

equation are equal to  $37.54$  and  $81.77 \text{ m}^2/\text{g}$ , corresponding for the initial sample and modified (the area of nitrogen molecule was taken as  $16.2 \text{ \AA}$ ).

Thus specific surface of diatomite modified sample has changed 2 times higher than natural diatomite sample. According to this fact the adsorption isotherm DMA is placed above the initial sample (Fig. 1). As it seen from the curves of pore volume distribution by radii values mesoporous structure is preserved for both samples and the effective pore radius is at  $25 \text{ \AA}$ . Along with that on the pore volume distribution curves the second maximum is observed at  $r_{ef} = 39$ . The difference in pore volume distribution curves of samples studied is only the numerical values of  $dV/dr$ .

Table 1 presents the basics of the porous structure of samples D1 and DMA determined from nitrogen adsorption isotherms, and in some cases - and on the basis of benzene adsorption.

**Table 1**  
**Adsorption and structure characteristics of raw and modified diatomite**

Sample	$S_{sp}$ , BET, $\text{m}^2/\text{g}$	Mesopores		Micropores		Pore sorption volume, $V_s, \text{cm}^3/\text{g}$	Macropores		Pore total volume, $V_\Sigma, \text{cm}^3/\text{g}^*$
		$V_{me}$ , $\text{cm}^3/\text{g}$	% of $V_\Sigma$	$V_{mi}$ , $\text{cm}^3/\text{g}$	% of $V_\Sigma$		$V_{ma}$ , $\text{cm}^3/\text{g}$	% of $V_\Sigma$	
D1	37,54	0,032	6,60	0,012	2,31	0,0442	0,448	91,12	0,498
DMA	81,77	0,091	9,40	0,027	3,20	0,1058	0,739	87,5	0,845

Sorption pore volume  $V_s$  of DMA samples is  $0.105 \text{ cm}^3/\text{g}$  and total pore volume  $V_\Sigma$  -  $0.845 \text{ cm}^3/\text{g}$  (found by the method of impregnation of the samples with benzene\*). Thus the volume of macropores for the DMA is  $0.739 \text{ cm}^3/\text{g}$ . For the initial diatomite sample this value is  $0.492 \text{ cm}^3/\text{g}$ . Therefore, the initial and modified diatomite samples contain a significant amount of large pores.

Characteristics of adsorption and structure of those samples testify that the process of modification leads to increase in the sorption volume and total pore volumes of samples.

## 2.2. Physicochemical study of the raw and modified by structural-chemical method diatomite

Real density of the samples  $\gamma_r$  was determined based on impregnation with benzene\*,  $\gamma_a$  - apparent density - with the method by Herbst.  $V_\Sigma$  - total pore volume was calculated using the formula:

$$V_\Sigma = \frac{1}{\gamma_a} - \frac{1}{\gamma_r} \quad (1)$$

Simultaneously this parameter has been determined by wetting of dried at  $110^\circ\text{C}$  samples with benzene. Sorption volume was calculated from nitrogen adsorption isotherms, taking the product of maximum adsorption  $a_m$  at  $p/p_s = 1$  and molar volume of liquid adsorbate. Adsorption volumes of the samples in the base of benzene vapor saturation were also determined by the amount of vapor adsorbed by desiccator method.

The samples  $\text{pH}_{\text{PZC}}$  were found from the curves of potentiometric titration data.

Total porosity  $P$  was calculated by the formula:

$$P = \frac{\gamma_r - \gamma_a}{\gamma_a} \cdot 100\% \quad (2)$$

and technical porosity by the equation:

$$P_T = -\frac{\gamma_r - \Delta}{\gamma_r} \cdot 100\% \quad (3)$$

where  $\Delta$  - volumetric weight of the samples

Table 2 summarizes some characteristics of the samples studied. \* Determined by this method the total volume of pores  $V_\Sigma$  differs little from the data referred to the real and apparent densities (Table 2). This method should be regarded as a relative and can be used to compare the results of the same class of sorbents. Obviously, the results are reproducible after  $V_\Sigma$  values satisfactorily coincide with those obtained from density data.

The table shows that structural - chemical modification of diatomite leads to increase of real density and decrease of apparent density and volumetric weight of the samples. Diatomite modification also leads to increasing of its total and technical porosity.

It should be noted that the  $V_\Sigma$  of both initial and modified diatomite is greater than the sorption volume of their pores. It tells us about the presence in the studied samples large pore (macropores) and for modified sample this difference is more pronounced.

## 2.3. Thermogravimetric analysis

To measure the adsorption and determine physicochemical characteristics all the samples were air-dried and heated at  $110^\circ\text{C}$  to constant mass, after they

**Table 2**  
**Physicochemical characteristics of natural diatomite D1 and modified by structural-chemical method DMA**

Parameter	Sample	D1	DMA	Annotation
Humidity (hygroscopic water), %, %		7	0	Drying temperature 120 <sup>0</sup> C, 4 hours
Real density $\gamma_r$ , g/cm <sup>3</sup>		2,11	2,35	
Apparent density $\gamma_a$ , g/cm <sup>3</sup>		1,03	0,78	
Volume weight, g/cm <sup>3</sup>		0,54	0,38	
Total porosity P, %		51	67	According to the real and apparent density data
Technical porosity P <sub>T</sub> , %		74	84	
Suspension pH		8,15	7,84	
pH <sub>PZC</sub> (pH of point of zero charge)		8,8	8,5	
Total pore volume V <sub>Σ</sub> , cm <sup>3</sup> /g		0,497	0,856	After real and apparent density data

were kept in desiccator for further research. Samples drying temperature of 110<sup>0</sup>C was determined from thermogravimetric analysis data.

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**Table 3 Thermal effects on thermograms of raw D1 and modified DMA diatomite**

Sample	Type of effect	Temperature interval, <sup>0</sup> C	DTA curve peak, <sup>0</sup> C	Effect characteristic
D1	Endoeffect	40-140	90	Distinct
	Endoeffect	750-820	780	Distinct
	Endoeffect	190-330	260	Broad not deep
	Exoeffect	280-380	Widely spread	Shallow
	Endoeffect	40-190	120	Distinct, large, clear
	Endoeffect	720-950	870	Wide, shallow
DMA	Endoeffect	190-470	Small	Insignificant
	Exoeffect			
	Exoeffect	900-960	950	Visible

On the raw diatomite sample DTA curve there are two endoeffects: one in the 40-110<sup>0</sup>C with a minimum temperature at 90<sup>0</sup>C, the second - in the 750-820<sup>0</sup>C temperature range with a minimum at 780<sup>0</sup>C. First endoeffect corresponds to physically adsorbed water removal, the second - decomposition of carbon minerals present in samples of natural diatomite. The total loss of mass corresponding to these effects, determined by TG curve is 26mg, which makes up 96.2% of the total loss of mass. The part of decomposed carbonate is 6 mg. It should be marked that on the DTA curves of natural diatomite can be observed a broad endoeffect in the

temperature region 190-330<sup>0</sup>C, which is attributed probably to the structural water removal and organic impurities of samples decomposition. A shallow and wide exoeffect on the DTA curve in the temperature range 280-380<sup>0</sup>C is related to the start of combustion of organic substances. On the heating curves of the modified diatomite samples a clear and narrow endoeffect also present in the temperature range 40-190<sup>0</sup>C with a minimum at 120<sup>0</sup>C, which corresponds to physically adsorbed water elimination and an exoeffect in the temperature range 190-470<sup>0</sup>C. The nature of these peaks is similar to those for unmodified samples. These effects

correspond to the weight loss in the amount of 26mg, which makes up 89.6% of all losses of mass of the sample. After temperature 470<sup>0</sup>C on the DTA curve in

the temperature range 720-950<sup>0</sup>C a lossless mass endoeffect is observed at 870<sup>0</sup>C minimum.

This is probably due to decomposition of carbonates, remaining in the samples after diatomite modification. Most carbonates of diatomaceous earth were broken as a result of chemical treatment at the second stage with the solution of aluminum salts (aluminum salt solutions are acidic as a result of hydrolysis). But because the rest mass of carbonates is low, it corresponds to an insignificant endoeffect. Noticeable exothermic effect on the thermogram with a peak at 950<sup>0</sup>C can be attributed to the crystallization of products of acid decomposition of carbonates in the modification of diatomite (mainly calcite and aragonite). Qualitative changes in the composition of modified diatomite are confirmed by X-ray analysis and FTIR spectra: appearance of new reflexes on the diffractogram characteristic for aluminosilicates and vibration of groups Si—O—Al on the curves of infrared transmission spectra.

Sorbent obtained was tested to remove fluoride

from model solutions at the concentration of F<sup>-</sup> of 1mmol/l. Under identical conditions of adsorption (m = 0.5 g/l, pH = 4.9, T = 293 K; time 120min) adsorption capacity of modified diatomite was 40mgF/g sorbent in comparison with 4mgF / g for raw diatomaceous earth.

### 3. Conclusions

By the structural-chemical method a new selective fluoride sorbent has been synthesized. Obtained sorbent possesses both basic mineral and modifier compounds properties: it is relatively inexpensive and has high selectivity towards fluoride typical for aluminum compounds.

The structure changes in modified diatomite are accompanied by increasing of specific surface and sorption pore volume they are caused primarily by increasing of mesoporous surface area and volume of meso and micropores. The development of microporous structure of diatomite is the result of blocking macropores with aluminosilicate during structural - chemical modification.