# HYBRID STRUCTURES BASED ON MONODIMENSIONAL OXIDE NANOSTRUCTURES AND EXTREMOZYMES WITH APPLICATIONS IN AGRICULTURE

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## Introduction

Soil is an important part of a terrestrial ecosystem and provides the fundamental support for all forms of terrestrial life. In this way, adequate soil protection programs are very necessary to avoid erosion, infertility, contamination of subterranean waters and, last but not least, loss of biodiversity. Soil quality is correlated with its biological properties that are affected by any changes in the environment. Also, soil microbiology is sensitive and changes rapidly in response to any changes in the environment. Soil microbiota profiles and enzymatic systems are closely correlated and represent an important indicator of soil health and quality (Pajares et al., 2011; Joshi et al., 2018). Soil enzymes, which are mainly synthesized by soil microorganisms, play a crucial role in the nutrient circuit and reflect microbiological soil activity and fertility (Bentez et al., 2000). Soil microorganisms mediate biochemical processes together with plants (their roots) and animals present in the soil. Biochemical processes are catalyzed by a series of enzymes found in the soil, including: glucosidases, xylozidases, amylase, dehydrogenase, chitinase, urease, proteases, phenol oxidases, aminopeptidases, phosphatases.

There it is of high scientific and economical interest to modulate and bring together one of the most efficient and fragile natural mechanism (the enzymatic one) with a synthetic well defined and very promising oxidic (tubular/1D) nanostructure. Many attempts are done in order to immobilize and encapsulate biological active species, especially enzymes, in appropriate inorganic matrices, usually mesoporous silica with pore diameters covering a range of 15-300 Å, this range being compatible with molecular diameters of enzymes (Takahashi et al., 2000). We have obtained highly reproducible $SiO_2$ nanotubes by sol gel method using the tartaric acid as organic template in the reaction mixture, in mild conditions. The hollow tubes have an external diameter of about 350 nm, an internal one of about 200 nm, open ends, a high surface area ($300m^2/g$) and lenghts around micrometers (Anastasescu et al., 2010). The tubular $SiO_2$ matrix is appropriate for doping and catalytic reactions (Anastasescu et al., 2012), has an intrinsic chemical reactivity (because of its large band gap, up to now was considered just a good support material) and is also a light sensitive material, a slight photocatalytic activity being registered even for pure silica (Anastasescu et al., 2009). The obtained TiNTs nanotubes had also reproducible tubular morphology but much smaller diameters, and a high surface area (Preda et al., 2013). We considered the morphological characteristics of $SiO_2$ and TiNTs appropriate for bioremediation processes conducted in the presence of halotolerant bacteria (Merciu et al., 2009). Based on these results, we managed to go further looking for a protease imobilization on $SiO_2$ and $TiO_2$ nanotubes (Merciu et al., 2014).

**Results**

The obtained results demonstrate a more pronounced alkaline phosphatase activity in the soil samples coupled to the hybrid system formed on the basis of the immobilization of the proteases on the inorganic support, compared to the soil samples coupled to the immobilized amylases and lipases on the oxide substrate. The same manifestation of the activity of alkaline phosphatase was also observed with respect to the anthropic soil sample, but also to the soil treated with the inorganic structure materials. The results were comparable for both inorganic matrices tested, the highest value being obtained for variant which has titanium dioxide as an inorganic substrate. The urease activity of the hybrid system based on the immobilization of the enzymes of interest on the inorganic support (silica) was noted by values superior to the anthropogenic soil sample. Dehydrogenase recorded activity in all tested variants. Compared to the activity value in the anthropogenic soil sample, a significant increase in activity values in soil treated only with nanomaterials variants was observed.

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