

CONTEMPORARY AND PROSPECTS FOR NEW GENERATION OF ENVIRONMENTAL NANOCOMPOSED ZEOADSORBENTS

E. Chmielewská, L. Sabová

*Comenius University, Faculty of Natural Sciences, Mlynská dolina,
842 15 Bratislava, Slovakia, Eva Chmielewska
[eva.chmielewska@fns.uniba.sk]*

Received December 27, 2005; received in revised form January 23, 2006; accepted January 27, 2006

Abstract

Over the last few years, there has been a significant development in interest for P and N recycling, particularly within the water industry concerning sewage, but also agricultural and industrial wastes. Where nutrients cannot be recycled by agricultural spreading of biosolids, a number of pathways and innovative technologies have been developed and are accessible on the market or at the design level, world-wide currently. The paper deals with some alternative adsorption process for nutrients removal examined at the laboratory level, whereas the novel zeolite based adsorbent was characterized by AFM and SEM techniques. The paper tries to outline simultaneously the tremendous potential of the zeolitic material modifications, which due to their cost effectiveness, may push them as newly developed sustainable systems, to the forefront of state of the art technologies.

Key words: clinoptilolite, biomineralisation, nutrients removal, biomimetics, nanomaterials, adsorption

Introduction

The Water Framework Directive (2000/60/EC) adopted by the European Union in 2000 requires member states to take a river basin approach to qualitative and quantitative aspects of water management. An increasing demand for sustainable resources and more stringent nutrients discharge limits into surface water bodies have prompted the waste water technology industry to explore alternatives to conventional nutrient removal technologies.

Consequently, a number of scenario evaluations for nutrients recovery from waste waters (calcium phosphate and struvite precipitations, REM-NUT process for P-recovery, ion exchange, coagulation, sludge incineration ashes, biologically-driven phosphate and nitrate removal etc.) have been proposed and examined in last 2 - 3 decades^[1].

Current state of the art technology in water treatment sector which is or will be more or less implemented almost at all conventional waste water treatment facilities is considered primarily biological nitrification - denitrification (N-D) with luxury uptake (LU) nutrients removal systems^[2].

The study of biomineralization offers valuable insights into the scope and nature of materials chemistry at the inorganic-organic interface. Here, the interest is in how these organic architectures like e.g. collagen in bone can be associated (grafted) with inorganic solids to produce an unique biominerals.

The objective of our study was to characterize the interfacial phenomena and the surface architecture of novel biomineral zeolitic products synthesized by hydrophobization, carbonization or biopolymer coating, using AFM and spectral SEM techniques incl. targeted inorganic nutrients adsorption examinations.

Exemplified human body biomimetics for adsorption material tectonics

Generally, nanoscale biomineralization involves the molecular construction of discrete self-assembled organic supramolecular systems (e.g. ferritin) that are used as pre-organized environments for controlling the formation of finally divided inorganic materials, 1-100 nm in size.

As example, the iron-storage protein ferritin consists of an 8 nm diameter spherical cage formed by the self-assembly of 24-polypeptide subunits. In the native protein, the cavity is filled with an iron oxide core consisting of no more than 4500 iron atoms.

In enclosed systems such as ferritin, the level of molecular recognition (templating) is relatively imprecise. Redox-active metal-binding sites (ferroxidase) and negatively charged patches of glutamate are involved in generating and stabilizing mineral clusters specifically within the protein cavity. The assembly of mineral nuclei is generally governed by electrostatic, structural and stereochemical complementarity at the inorganic-organic interface^[3].

The hierarchical structure of bone is also well documented. The primary unit is based on the nucleation of calcium phosphate in nanoscale spaces organized within the supramolecular assembly of collagen fibrils. The precise hole arrangement is governed by the strong covalent crosslinks that exist between the triplehelical molecules when they are staggered by 68 nm along their long axis. The fabrication of consolidated biominerals, such as bone, also involves the construction of pre-organized organic frameworks, but the length scale is in micrometers and the matrix is polymeric such as collagen^[4].

The three constructional processes of biomineralization - supramolecular pre-organization, interfacial molecular recognition (templating) and cellular processing - represent a sequence of increasing tectonic complexity. However, the level of organizational complexity for biocompatible materials preparation can be enormous.

Obstacles and beneficial aspects of some abio-technological P-recovery processes

Precipitation of phosphates as calcium phosphates or as struvites (magnesium ammonium phosphates) currently appears as the most likely route to both achieving effective precipitation in accessible operating conditions in waste water treatment.

Calcium phosphate is essentially the same material as the mined phosphate rock used as feedstock in fertiliser industry (it has high P-content, limited levels of heavy metals, low water and organics content, physical and handling properties). Struvite, on the other hand cannot be accepted by either existing or realistically modified phosphate industry processes, but is claimed by many authors to be a marketable fertiliser^[1,2].

Precipitation can take place in several different ways: spontaneous growth of individual crystallites in solution (homogeneous nucleation process) or aggregation of crystallites on existing surfaces (e.g. seed crystals, heterogeneous process which is less energetically demanding, using a multitude of surfaces - Crystalactor technology with fluidised bed principles).

Many municipal sewage treatment plants use iron salts for phosphorus removal. Sometimes it is the only phosphate removal process, in other cases iron salts are added in addition to biological processes. Most of the phosphorous precipitated as iron salts are not available for plants and therefore such sewage sludge has a very limited use as a natural fertiliser. Also, iron content is an obstacle to industrial reuse.

An approach to constrain organic carbon rich substratum onto clinoptilolite surface

Adsorption is one of the technologies which is potentially attractive not only from the technical but also from economical point of view for inorganic nutrients removal from waters. The main benefits are that no additional sludge is produced, reagents are not needed and waste water pH is unaffected.

Arnot^[5] found that fly ash is a good conditioner for sewage sludge as well as for heavy metal removal from waste waters, so that it can be land filled or land applied.

Sengupta^[6] used a polymeric ligand exchanger (selective anion exchanger) at Pennsylvania sewage works which limitations were that sulphate anions always present in waste waters in much higher concentrations than phosphate, were preferred by the anion exchange resin over the phosphate.

REM NUT process^[7] was based on the use of ammonium selective natural zeolite and phosphate selective commercial anion exchanger, able to remove nutrient ions from sewage down to the discharge limits. Both ion exchangers were regenerated by closed-loop recirculation of neutral 0,6 M salt (NaCl) from which, after stoichiometric addition of magnesium and phosphate ions to give Mg : NH₄ : PO₄ ratio of 1 : 1 : 1 molar ratio, struvite was precipitated. The process did not reach full scale application yet due to unbalanced N : P ratio in most sewages, requiring expensive addition of P and Mg to achieve stoichiometry for the precipitation and poor attitude of water industry toward technological innovations.

The goal of our study was stressed to the examination of three types of surface engineered clinoptilolite-rich tufts, i.e. the hydrophobized, carbonized and biomolecularly immobilized ones for the phosphate and nitrate removal from the model aqueous solutions.

Clinoptilolite dominated zeolite is in Slovakia naturally abundant mineral species which found a broad industrial application especially in agriculture and animal feeding as ingredient and multifunctional feed additive for detoxication of organism, climate improvement of the stables, animal protector against mycotoxins, multicomponent mineral fertilizer and the others^[8].

Hydrophobization of the clinoptilolite external surface was done with primary octadecylamine. The scanning electron micrograph (SEM) of such as modified surface presents the Fig. 1. Carbonization was accomplished with the waste vegetable substratum inside a high temperature pyrolytic combustion chamber installed at the laboratory, which used direct heating by exhaust gas flow in an oxygen free atmosphere^[9]. Atomic force microscope (AFM) and SEM of this surface modification show the Figs. 2 and 3. A simple biopolymeric alginate coating of the zeolite external surface by sufficient contacting of both liquid and solid phases resulted in cross-linked interpenetrated structured polysaccharide based zeolite composite, that was active for above nutrients removal (Fig. 4).

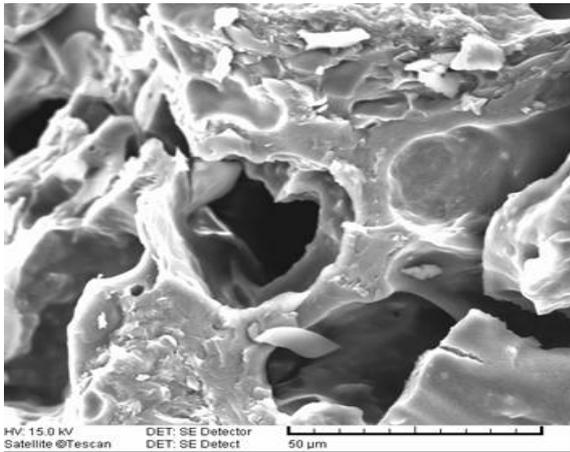


Fig. 1 Scanning Electron Micrograph of hydrophobized zeolite-clinoptilolite type

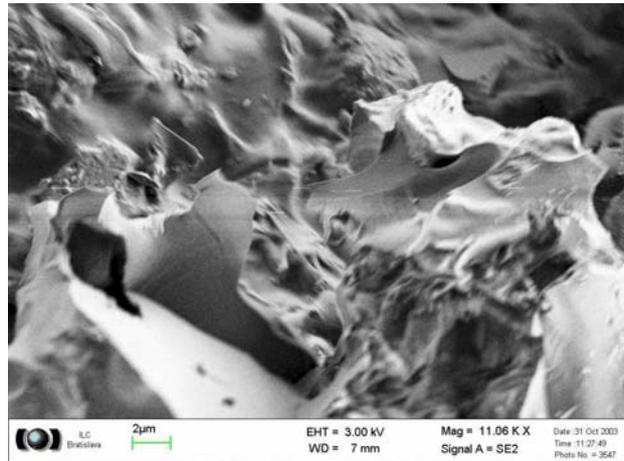


Fig. 2 AFM image of carbonized zeolite

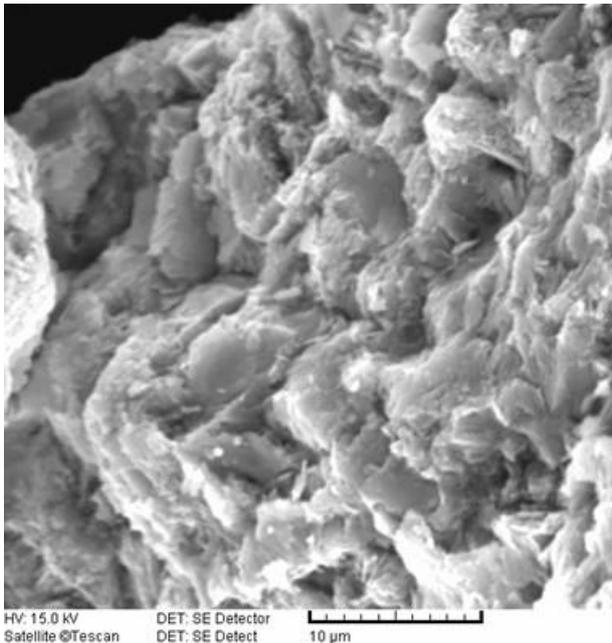


Fig 3 Scanning Electron Micrograph of carbonized zeolite-clinoptilolite type

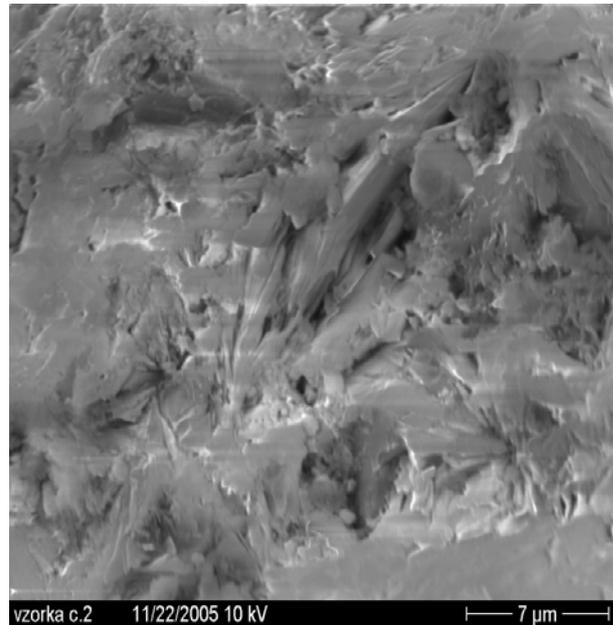
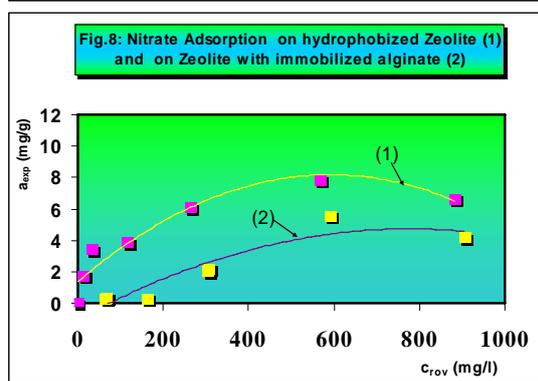
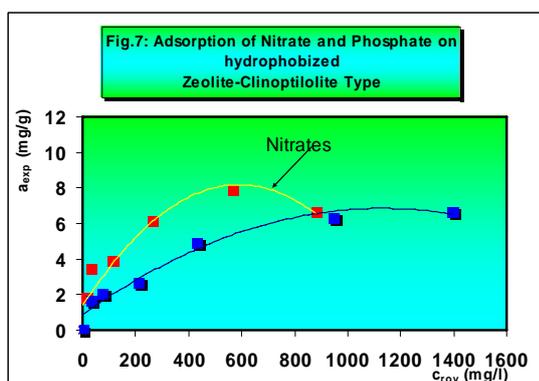
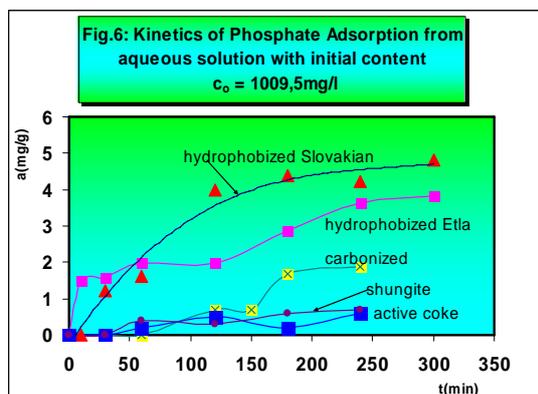
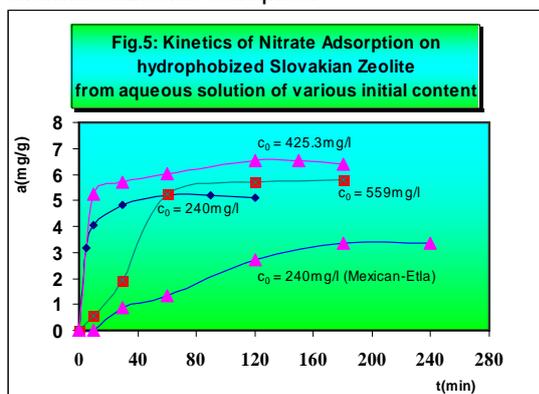


Fig. 4 Scanning Electron Micrograph of alginate coated clinoptilolite

The laboratory adsorption trials according to the Fig. 5,6 testify a better kinetics of Slovakian than Mexican (Etla) hydrophobized zeolite towards nitrate, using the three different initial concentrations. Kinetics of phosphate adsorption onto various, however compatible carbon-rich adsorbents, demonstrate the highest efficiency of the P-species removal in the following sequence:

Hydrophobized Slovakian zeolite > Mexican hydrophobized zeolite > carbonized Slovakian zeolite > shungite > active coke, what may support the statement that the last two nature of materials are more appropriate for organic pollutants removal from waters. Finally, the adsorption isotherms of the systems nitrate, phosphate vs. hydrophobized clinoptilolite (Fig. 7) and nitrate vs. hydrophobized and alginate coated zeolites (Fig. 8) were drawn to confirm and quantify the adsorption abilities of the examined zeolite samples.



Based upon these results It may be concluded that the best properties and the highest functionality towards aqueous nutrients phosphate and nitrate exhibits ODA-hydrophobized zeolite of clinoptilolite type, whereas the lowest one in coincidence to the carbon-rich substrate nature immobilized onto the carrier surface, the coke similar carbonized zeolite.

Acknowledgements

The work is supported by the Slovak Grant Agency VEGA under the projects Nos. 1/1373/04 and 1/1385/04 as well as by the bilateral Slovak-Italian project No.09 105.

References

- [1] <http://www.nhm.ac.uk./mineralogy/phos/index.htm>
- [2] Manahan, S.E.: Environmental Chemistry, Lewis Publ. Boca Raton . Ann Arbor, London, Tokyo 1994.
- [3] Mann, S.: Molecular tectonics in biomineral. and biomimetic materials chemistry, Nature 365, 7, pp. 499-505, 1993.
- [4] Wegner, G.: Functional Polymers, Acta mater. 48, pp. 253-62, 2000.
- [5] Arnot, T.: An integrated Biological/Adsorption Process for Phosphorus Recovery, Scope Newsletter 41/2001, Special Edition CEEP Bruxelles.
- [6] Sengupta, A.: Conference Summery, 2. Intern. Conf. on the Recovery of Phosphorus from Sewage and Animal Wastes, Noordwijkerhout 12-13.3.2001, Netherlands.
- [7] Liberti, L.: Ion Exchange followed by struvite precipitation, Adapting the REM-NUT process for P-recovery, Scope New letter in Europe 41, March 2001.
- [8] <http://www.zeocem.sk>
- [9] Morvová, M.; Morva, I.; Janda, M.; Hanic, F.; Lukáč, P.: Combustion and carbonization exhaust utilization in electric discharge and its relation to prebiotic chemistry, Intern. Journal of Mass Spectrometry 223-4, pp. 613-25, 2003.