

# BATCH-WISE ADSORPTION, SAXS AND MICROSCOPIC STUDIES OF ZEOLITE PELLETIZED WITH BIOPOLYMERIC ALGINATE

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**Abstract** - Removal of nitrates, sulfate and Zn(II) ions from aqueous solutions through adsorption onto biopolymeric alginate/clinoptilolite-rich tuff pellets was studied by using an equilibrium batch technique. The idea of this approach of biosorbent fabrication is to promote the native zeolite adsorption performance and thus to prepare more efficient amphoteric tailor-made products for specific environmental targets. A flexible component, i.e., alginate biopolymer, and a rigid component (pulverized) zeolite were crosslinked using Fe(III) and Ca(II) chlorides, additively. The extent of adsorption was found to be considerably higher than with the other mostly natural adsorbents examined towards similar pollutants. The equilibrium adsorption data for the above pollutants were satisfactorily fitted to Freundlich and Langmuir isotherms, respectively. According to the linscale SAXS pattern, there was a strong background visible, which may indicate the presence of a considerable amount of biopolymeric phase in the composite samples analysed. Scanning Tunneling, Electron and Atomic Force Microscopies helped visualize their surface texture and morphology.

**Keywords:** Zeolite; Removal of nitrates; Sulfate and Zn(II) ions; Biopolymeric alginate/ clinoptilolite-rich tuff pellets; Freundlich and Langmuir isotherms; SAXS, SEM, STM, AFM.

## INTRODUCTION

Zeolites are highly porous, hydrated aluminosilicates with a rigid crystalline structure and a network of interconnected tunnels and cages. Their structures consist of a three-dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations that are exchangeable with certain cations of the surrounding solutions. Based upon these facts and according to some new definitions, zeolites are also clathrates or inclusion compounds, able to host various guest substances in their versatile structure (Ambruster, 2001, Roskill, 2010, Baerlocher et al., 2007).

The characteristics and applications of natural zeolites have been reviewed by many authors. High ion-exchange capacity, relatively high specific surface areas and, more importantly, their relatively low prices, make natural zeolites attractive adsorbents. Zeolite's unique market position has progressed mostly by continued development of their ion exchange and adsorption properties and especially through their surface treatment. Indeed, even opportunities for hybrid organic-inorganic materials and multifunctional designs are now emerging in the literature. Many of these strategies are evident in biological materials and are inspiring exciting new directions in materials design and

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synthesis of soft and biomimetic materials, starting from the molecular level [4-8]. To achieve a high application potential for the alginate gel adsorbent, activated carbon-containing alginate bead adsorbent was developed by Park et al. (2007). Those authors tried to remove a broad range of heavy metal cations from model solutions. Removal of Ni(II) cations from aqueous solutions through adsorption onto biopolymeric adsorbents, such as calcium alginate, chitosan-coated calcium alginate and chitosan-coated silica was studied by Vijaya et al. (2008). Nevertheless, Min and Hering (1988) examined the fundamental aspects of a possible remediation strategy and removal of anionic metal species (arsenate) employing the biopolymer alginic acid pretreated with Ca(II) and Fe(III) cations, respectively.

From the treatment methods considered, it is apparent that there is usually no single available solution for the efficient removal of a broad variety of pollutants that is both economically and technologically feasible. To overcome these drawbacks, we tried to combine several conventional and environmentally sound substances with the natural zeolite of the clinoptilolite type to develop an advanced and effective biosorbent that was efficient for removal of both cationic and anionic aqueous pollutants, respectively (Vijaya et al., 2008; Crini, 2005; Park et al., 2007).

Zeolitic aluminosilicates, composed of negatively charged sheets of  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  tetrahedra and balanced by some mobile hydrated cations, are able, on the basis of electrostatic, van der Waals, hydrogen bonding, dipole-dipole and neighboring surface  $\text{SiO}^-$  or  $\text{SiOH}$  group interactions, to host various biopolymeric exterior surface templates (Min and Hering, 1998; Huddleston et al., 1998; Saleem et al., 2005; Wu and Tseng, 2006; Derylo-Marczewska et al., 2005; Shawabkeh, 2004). Based upon the above broad variety of interactions and good mechanical strength and rigidity, we used natural zeolite for a design and synthesis of a new zeocomposed biosorbent, the performance of which towards various environmental pollutants is discussed here. Some useful analytical methods, preferentially SAXS, SEM, STM and AFM, were chosen for detailed characterization of the biosorbent and visualization of its surface texture.

## EXPERIMENTAL

### Materials

Clinoptilolite-rich tuff occurs in an Eastern Slovakian commercial deposit, nearby Nižný Hrabovec municipality, as the most abundant natural

zeolite. The details of the mineralogical and chemical compositions of the examined zeolitic mineral are published elsewhere (Chmielewska et al., 2003). Prior to use, the zeolite as received was pretreated according to the specific procedure described below.

Ultrapure sodium alginate polymer was purchased as *Protanal XLRB* from NovaMatrix/FMC BioPolymer (Belgium). Other chemicals necessary for the stock solution preparation were purchased mostly from Lachema Brno (made in the Czech Republic) with analytical grade quality.

### Analytical Equipment

The size and the morphology of the crystals in the studied samples were analyzed with a Jeol-JXA 840A Scanning Electron Microscope (SEM) integrated with a Kevex energy dispersive multichannel X-ray (EDX) microanalyser equipped with the Si(Li) detector. The polished crystallites were pretreated in epoxy film, cut with a fine grid diamond and coated with a carbon.

The surface texture of the biosorbent was visualized by means of Atomic Force Microscopy, using the AFM tapping mode with a supersharp silicon tip of 2 nm radius. Scanning Tunneling Microscopy was provided by the company Biont on NT-MDT equipment (Solver P47 with a head 50 x 50 x 3  $\mu\text{m}$ ) using the non-contact mode.

Characterization of the new prepared adsorbents, including the natural grained and powdered zeolite samples, was performed by small-angle X-ray scattering (SAXS) using a rotating anode generator equipped with a pinhole camera and  $\text{CuK}\alpha$  radiation collimated and monochromatized from crossed Göbel mirrors (Nanostar from Bruker AXS, Karlsruhe). All SAXS patterns were recorded with a two-dimensional position sensitive detector, radially averaged and corrected for background scattering to obtain the scattering intensity dependence on the scattering vector  $q$ , where  $q = 4\pi \sin\theta / \lambda$ , with  $2\theta$  being the scattering angle and  $\lambda = 0.1542$  nm the X-ray wavelength. The measurements were performed at two different sample-to-detector distances of 1.07 m and 0.11 m to cover a wide range of the scattering vector.

Aqueous model solutions of the chosen pollutants examined in the adsorption experiments were determined by means of isotachopheresis on a ZKI 02 Analyser (Villa Labeco). The measured data were processed by ITP PRO 32 program (Kas Comp, Ltd. Bratislava). The dyes Acid Red 1 (AR) and Acid Blue

74 (AB) were analysed spectrometrically by means of a Hewlett Packard 8452A Diode Array Spectrometer.

### Procedure for Batch-Wise Adsorption Experiments

Batch adsorption experiments were carried out as follows: Usually a 50 mL aliquot of model solution with variable pollutant concentration and 0.5 g of biosorbent (weight with analytical precision) were equilibrated for the designated time interval in 125 mL glass stoppered bottles, after which the supernatant solutions were separated by centrifugation and the residual pollutants analyzed by means of isotachopheresis. The aliquot suspensions were agitated in a horizontal Elpan Water Bath Shaker, type 357, equipped with variable speed, at 190 rpm for 240 minutes at room temperature and the pH value of distilled water. All solutions were prepared with distilled water of pH  $\sim$  6.7, measured on Präcitronic model MV 870 digital pH meter. All experiments were run in duplicate.

The equilibrium uptake capacity  $a$  (in mg/g) for each sample was calculated according to the following mass balance equation:

$$a(\text{eq}) = [ \{c(i) - c(\text{eq})\} / m ] \cdot V \quad (1)$$

where  $c(i)$  and  $c(\text{eq})$  were the initial and equilibrium concentrations of the studied pollutant (in mg/L),  $m$  was the mass of biosorbent (in g) and  $V$  was the volume of the solution in liters (L).

### Gel Bead Synthesis

The 1% sodium alginate solution was prepared by dissolving and gentle warming of 1 g of solid alginate salt in 100 mL of distilled water. This was mixed with 2 g of natural zeolite powder of the clinoptilolite type (0.01 – 0.2 mm) for a time interval of 1 hour. The resultant liquid suspension was then dropped through the tip of a 1 mL pipette into 500 mL of 0.1 M  $\text{CaCl}_2$  solution, which caused the immediate formation of insoluble gel beads about 3 mm in diameter. The beads were allowed to cure in mother solution overnight, then washed thoroughly with distilled water (about 3 hrs) to remove the excess of chlorides. The beads were left in the laboratory to dry on filter paper to soak up the external water content or were dried for 2 hours in a drying oven at 60°C. However, the weights between the slow and fast oven-drying procedures differed by approximately 20-fold, due to water content differences. It must be pointed out that, in all measurements, the weight of the prepared biosorbent

was calculated on the basis of the oven-dried mass (external water minimized while simultaneously maintaining the original structure). Ca alginate gel-clinoptilolite biosorbent was designed for enhanced metal cation ( $\text{Zn}^{2+}$ ) removal (its performance was significantly improved compared to the native or homoionic exchanged clinoptilolites) and Fe (III) alginate gel-clinoptilolite was tailor-made for aqueous oxyanions (nitrate and sulfate) removal, thus adjusting simultaneously an amphoteric biosorbent synthesis. The latter synthesis differed with the previous one only in curing of the freshly prepared (30 min) beads overnight in 500 mL of 0.1 M  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  solution instead of  $\text{CaCl}_2$  solution. Although several alginate to zeolite weights ratios were examined, the best adsorption performance towards the examined pollutants proved to be the biosorbent consisting of an alginate to zeolite weight ratio of 1:2. Based upon these results, all the subsequent experiments were done using the 1:2 ratio of alginate to zeolite in the bead synthesis.

## RESULTS AND DISCUSSION

### SEM, STM and AFM Studies

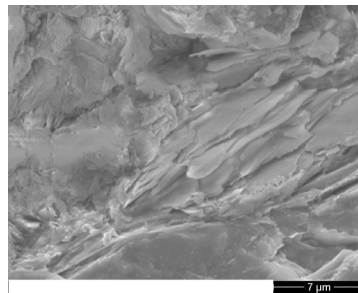
The SEM image of the synthesized alginate zeolitic bead in Fig. 1 (d) displays a rough, nearly rope-like surface morphology and thus a profound change of the original tablet-like zeolite morphology (Fig. 1 (a)). Examination of the SEM micrographs indicates the presence of many pores, cracks and oval shaped objects on the surface. Fig. 1 (b) displays, for comparison, the pure alginate biopolymer with a characteristic layer morphology. The more swollen alginate coated zeolitic beads were observed after curing the beads in calcium or iron solutions overnight (Fig. 1 (c) versus Fig. 1(d)).

Regarding the two natural zeolite micrographs in Fig. 1 (a) (SEM) and Fig. 1 (e) (STM), considerable morphology differences could be seen. Scanning Tunneling Microscopy displays the zeolite surface with not so sharp-edged crystals as Scanning Electron Microscopy, but rather with rounded edges; however, the typical layered texture of the pure alginate remains in the STM micrograph of the alginate zeolitic bead in Fig. 1 (f).

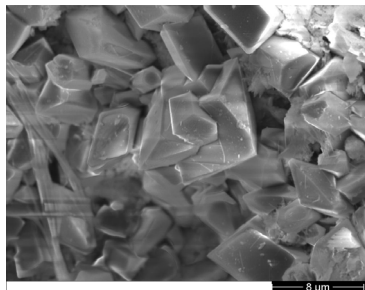
The surface texture of the Fe-alginate zeolitic bead studied presents, according to the AFM image and 2D topography, sharp-edged parallel rods growing from inside the bead to the outside surface, which are observed also in the 3D topography and the phase images (Fig. 1(g)).



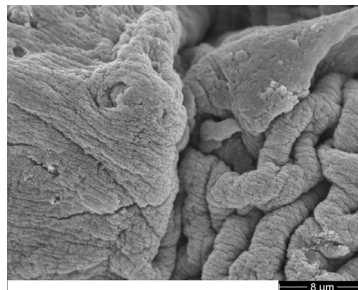
**Figure 1 (a):** SEM image of natural zeolite of the clinoptilolite type (magnification 3700x)



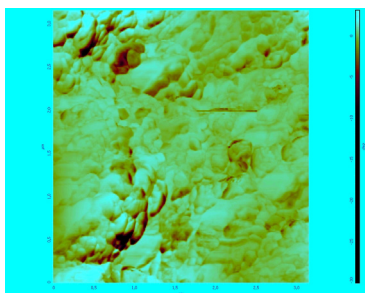
**Figure 1 (b):** SEM image of the alginate biopolymer used.



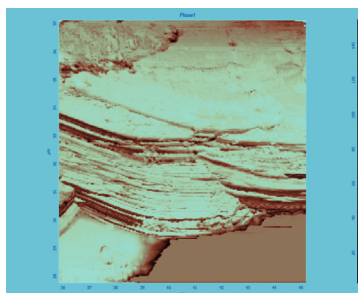
**Figure 1 (c):** SEM image of natural zeolite coated with the alginate biopolymer.



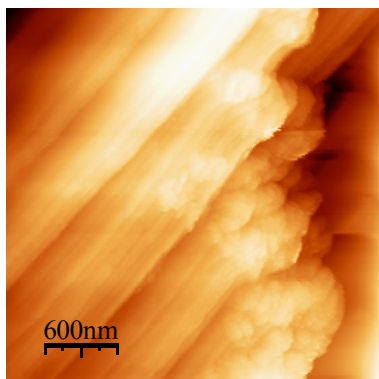
**Figure 1 (d):** SEM image of the Fe-alginate zeolitic pellet



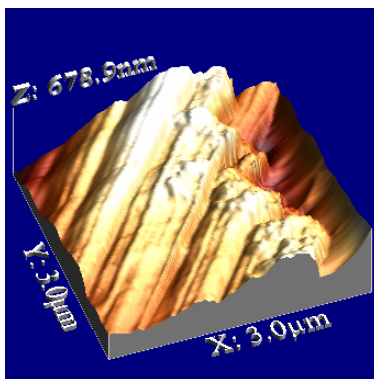
**Figure 1 (e):** STM image of natural zeolite



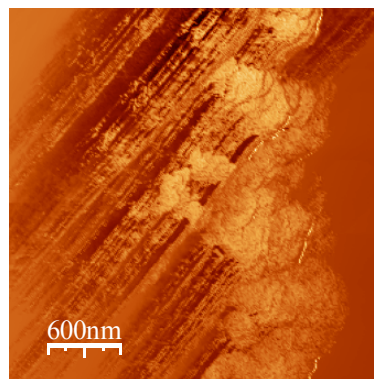
**Figure 1 (f):** STM image of the Fe-alginate zeolitic pellet



(i) 2D topography



(ii) 3D topography

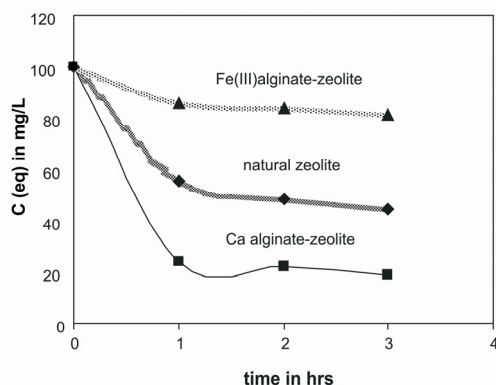


(iii) phase image

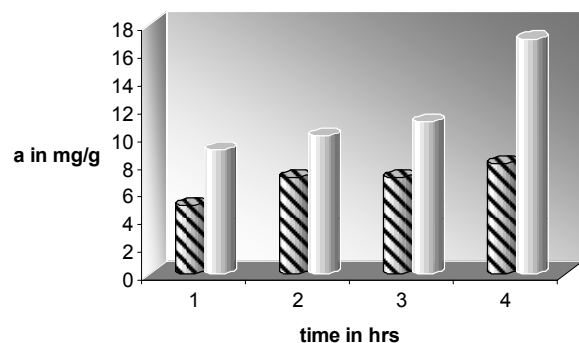
**Figure 1 (g):** AFM image (i)2D topography, (ii) 3D topography, (iii) phase image of Fe-alginate zeolitic pellet.

## Kinetic Studies

To understand the effect of time on the extent of adsorption and to obtain supporting equilibrium data for isotherm construction, the equilibrium concentrations of Zn(II), sulfate and nitrate ions were determined at different time intervals with initial concentrations of 100 mg/L and 400 mg/L. The results are graphically presented in Figs. 2 and 3 for Zn(II) and oxyanions uptakes. The data in all cases show that the adsorption efficiency increases with time, attaining the equilibrium within 4 hours. The data were used for the subsequent isotherm measurements, respectively.



**Figure 2:** Kinetic plots of Zn ion uptake by natural zeolite, Ca-alginate and Fe-alginate zeolitic pellets



**Figure 3:** Capacity vs. time dependance for uptake of sulfate (higher column) and nitrate (lower column) onto Fe-alginate zeolitic pellets

To compare all kinetic measurements, it can be stated that the highest capacity is provided by the Ca alginate gel – zeolitic adsorbent towards Zn(II) ion (Fig. 2). Neither natural zeolite nor Fe(III) alginate gel – zeolite adsorbents became saturated with Zn(II) ions to such an extent as the Ca alginate gel zeolite adsorbent did, probably due to a faster exchange between Ca(II) and Zn(II) ions in comparison to Fe(III) and Zn(II). With regard to the time vs. capacity

dependence in Fig. 3, the equilibrium capacity values for sulfate are higher than for nitrate. The major reason why the oxyanionic nitrate and sulfate adsorption onto Fe(III) alginate-zeolite proceeds most successfully is the presence of Fe(III) cationic sites, responsible for electrostatic forces between adsorbate and adsorbent in the process studied.

## Adsorption Isotherms

Conventional Freundlich and Langmuir isotherms were used to fit the experimental data. The variation of the extent of adsorption with concentration of solutes in Figs. 4 to 6 illustrates the fact that the biosorbents provide high solute uptake capacity at higher initial concentration. The Langmuir isotherm assumes a surface with homogenous binding sites, equivalent sorption energies and no interaction between adsorbed entities. In mathematical terms, it may be written as:

$$\frac{1}{a} = \left( \frac{1}{a(\max) \cdot b \cdot c(\text{eq})} \right) + \left( \frac{1}{a(\max)} \right) \quad (2)$$

where

- $a$  is the specific solute uptake capacity;
- $a(\max)$  the maximum adsorption capacity in mg/g;
- $c(\text{eq})$  the equilibrium concentration in the solution in mg/L and;
- $b$  relates to the affinity of the solute for the binding sites, expressed in L/mg.

The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies and its form is represented as:

$$a = K \cdot c(\text{eq})^{1/n} \quad (3)$$

$$\log a = \log K + \frac{1}{n} \log c(\text{eq}) \quad (4)$$

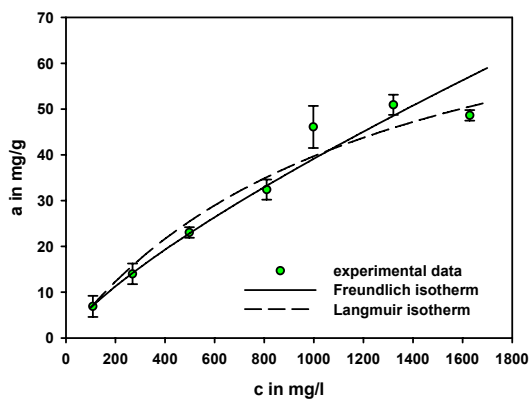
where  $K$  and  $1/n$  are terms related to the adsorbent capacity and adsorption intensity, respectively. Nevertheless, both the Langmuir and Freundlich isotherms represent the data satisfactorily, although the Langmuir model seems to fit better. The computed values of the Langmuir and Freundlich constants using the statistical least square method (*MW XP, Microsoft Office Excel 2003, Regression Analysis*) are presented in Table 1. The Langmuir parameter  $b$  predicts the affinity of adsorbate vs. adsorbent as the dimensionless separation factor  $f(s)$ :

$$f(s) = \frac{1}{(1 + b \cdot c_0)} \quad (5)$$

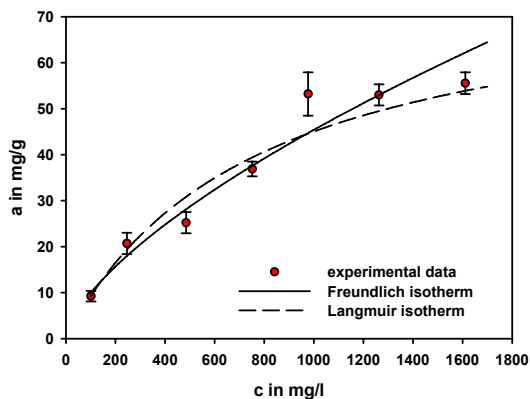
where

- $c_0$  is the initial solute concentration in mg/L and
- $b$  is the Langmuir adsorption equilibrium constant in L/mg.

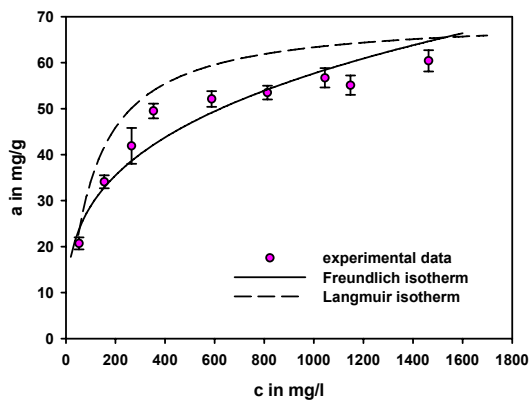
If the  $f(s)$  values are equal to zero or one, the adsorption is either linear or irreversible and, if the values are in between zero and one, adsorption is favourable to chemisorption. Our values are situated between 0 and 1, which means that the process was always favourable. All adsorption isotherms were determined at the laboratory temperature of  $23 \pm 0,2^\circ\text{C}$ .



**Figure 4:** Adsorption isotherms for nitrate and Fe-alginate zeolitic pellets.



**Figure 5:** Adsorption isotherms for sulfate and Fe-alginate zeolitic pellets.



**Figure 6:** Adsorption isotherms for Zn cations and Ca-alginate zeolitic pellets.

**Table 1: Freundlich and Langmuir isotherm data of the systems studied**

Adsorbent	pollutant	Freundlich isotherm				Langmuir isotherm		
		K L/mg	n	R <sup>2</sup>	f(s)	a <sub>max</sub> mg/g	b L/mg	R <sup>2</sup>
Fe-alg-zeo (1:2)	NO <sub>3</sub> <sup>-</sup>	0.188	1.294	0.9832	0.42	89.3	0.0008	0.9947
Fe-alg-zeo (1:2)	SO <sub>4</sub> <sup>2-</sup>	0.474	1.514	0.9687	0.32	79.4	0.0013	0.9868
Ca-alg-zeo (1:1)	Zn <sup>2+</sup>	7.201	3.321	0.9913	0.05	70	0.0095	0.9245

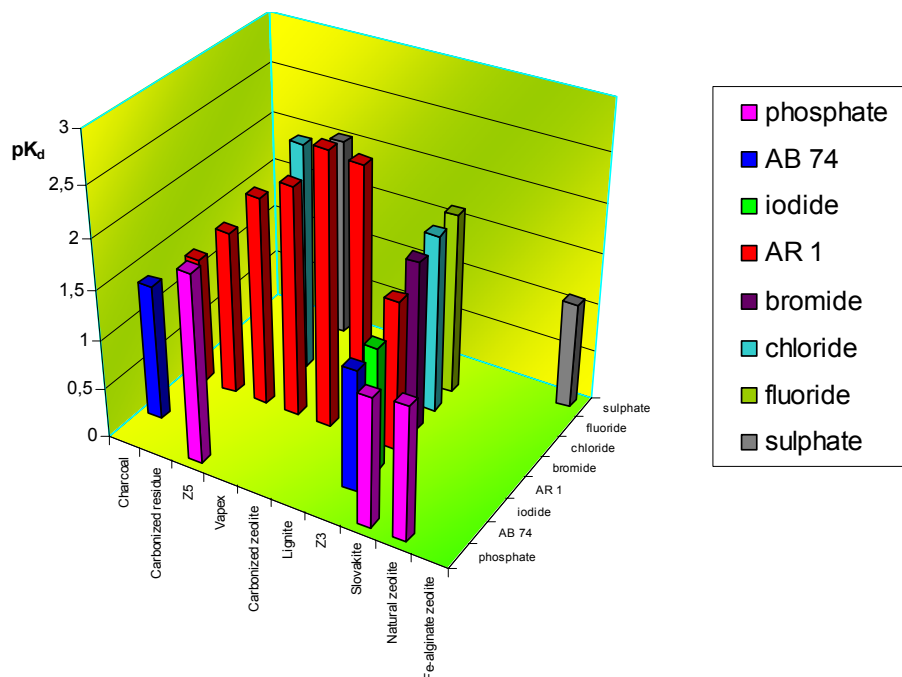
**Figure 7: pK<sub>D</sub> for various adsorbents and environmental pollutants**

Fig. 7 summarizes the adsorption performance of several competitive adsorbents towards Acid Red AR, Acid Blue AB, halogenides, sulfate and phosphate. The distribution coefficient  $K_D$  (hereafter expressed as the negative logarithm of  $K_D = pK_D$ ) in Fig. 7 was computed using the relation:

$$K_D = (C_0 - C) / C \cdot V / M \quad (6)$$

As show in Fig. 7, the alginate zeolitic beads exhibited the best performance among the mostly natural adsorption materials examined, according to following sequence:

Fe alginate/zeolite (sulfate) > ODA-zeolite (Acid Blue 74, iodide) > active charcoal (Acid Red 1) > geocomposed slovakite, natural zeolite (phosphate).

Commercial adsorbent, purchased under the trademark Vapex, was expanded and hydrophobized volcanic perlite from Eastern Slovakian quarries. Granular activated charcoal trademarked HYS-N

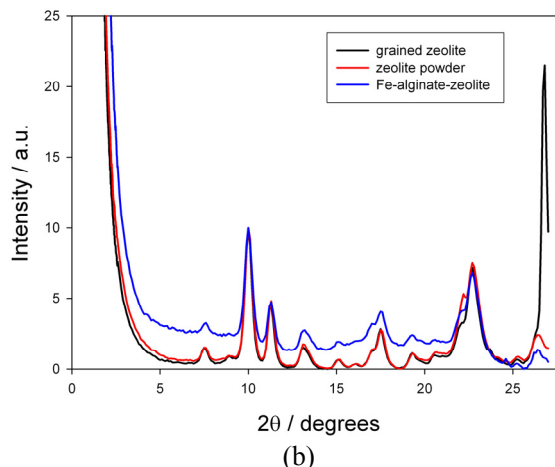
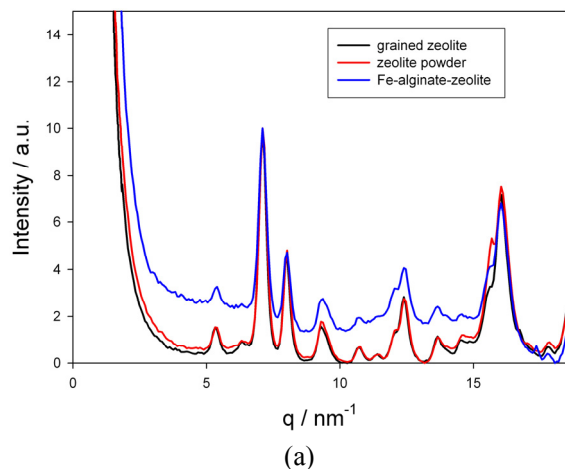
was produced at an inland chemical factory in size-granulation of 0.3 – 1.5 mm and with a S(BET) surface area of 850 m<sup>2</sup>/g. It was manufactured from black coal as the main component and some lignocellulose substrates, using activation with water steam. Carbonized char originated from the same pyrolysis matter as the carbonized zeolite enriched surface, however without any addition of zeolite as support. ODA- hydrophobized zeolite, denoted as Z3 and Z5 in Fig. 7, was coated with a mono- or bilayer of octadecylammonium (ODA) surfactant on the zeolite surface using the common sol-gel technique (Chmielewska et al., 2003). The commercial product Slovakite refers to an adsorbent manufactured from domestic dolomite, bentonite, diatomaceous clays, alginite and zeolite, with clinker and final pressurizing. Carbonaceous fossil-like lignite was of domestic origin and in general possesses some specific properties due to rich humic components, low toxic metal content, suitable physical structure, sorption properties and sensorial features, which support its usage as a fertiliser, soil conditioner, bio-

and humidity regulator and other agrochemical agents. This fossil material was considered to be the first product of the coalification processes on the globe and a potential intermediate between peat and bituminous coal. The product contains about 60 – 80% organic carbon.

### SAXS Measurements

X-ray scattering techniques are a family of non-destructive analytical techniques that reveal information about the crystallographic structure, chemical composition and physical properties of materials and thin films. These analyses are based on observing the scattered intensity of an X-ray beam hitting the sample as a function of incident and scattered angle, polarization, wavelength or energy. Small angle X-ray scattering (SAXS) usually probes structure in the nanometer to micrometer range by measuring scattering intensity at scattering angles  $2\theta$  close to  $0^\circ$ .

According to the linscale SAXS pattern in the Fig. 8 (a), (b), the grained and powdered zeolites give nearly similar results. For the alginate Fe(III)-zeolitic pellets, there is a strong background visible, which may signify the presence of a considerable amount of alginate biopolymer in the composite samples analysed. Such information supports the synthesis composition of the alginate pelletized zeolite, where the zeolite matrix content and alginate biopolymer in the final adsorbent product were in the weight ratio of 2 : 1. While the measured porosity of powdered natural zeolite is reported to be around 28%, according to the SAXS porosity calculations, the alginate pelletization increased the total composite adsorbent porosity to 37%. It is presumed that this increase was due to new mesopores.



**Figure 8:** SAXS pattern of zeolitic biosorbent: (a) intensity versus scattering vector  $q$  in  $\text{nm}^{-1}$ ; (b) intensity versus scattering angles  $2\theta$

### CONCLUSIONS

An advance in the development of new zeobiopolymeric pellets for water purification has been reported. The highest capacity was provided by the Fe alginate gel – zeolitic adsorbent towards nitrate ion, with a maximum capacity of 89.3 mg/g, then towards sulfate ion with a maximum capacity of 79.4 mg/g. Fe(III) cationic sites were responsible for electrostatic forces between oxyanions and pelletized biosorbent in the process studied, while Ca ions were responsible for Zn cation exchange in the Ca – alginate zeolitic pellets.

The best adsorption performance towards the oxyanionic pollutants and adequate rigidity of the adsorbent was obtained for an alginate to zeolite weight ratio of 1 : 2.

Summing up, among the mostly natural adsorption materials or other surface modified zeolites examined, the alginate zeolitic beads exhibited the best performance in the following sequence:

Fe alginate/zeolite (sulfate) > ODA-zeolite (Acid Blue 74, iodide) > active charcoal (Acid Red 1) > geocomposed slovakite, natural zeolite (phosphate).

Complementary analytical methods, i.e., SAXS, SEM, STM and AFM, helped to clarify and visualize several important features of new biosorbent. Both AFM and STM confirmed the typical layer structure of alginic biopolymers. According to SAXS porosity calculations, the alginate pelletization increased the total composite adsorbent porosity to 37%.



## ACKNOWLEDGMENT

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