

Surface charging or templating by carbonaceous substances to broaden the adsorption performance of clinoptilolite-rich tuff

E. Chmielewska, L. Sabová, A. Wu*, M. Aranyosiová** and D. Velič**

*Faculty of Natural Sciences, Comenius University,
Mlynská dolina, 842 15 Bratislava, Slovakia*

**Department of Ceramics and Glass Engineering,
University of Aveiro, 3810-193 Aveiro, Portugal*

***International Laser Centre, Ilkovičova 3, 812 19 Bratislava, Slovakia*

In order to develop novel adsorption materials, economically feasible, with the sufficiently high adsorption performance, a series of experiments has been performed to verify the function of the native zeolite combined adsorbents. A report on the detailed structural investigation using XRD, SEM, SIMS and FT IR analyses has been provided in order to get a better insight understanding of the examined pollutants uptake mechanisms by the prepared hybrid adsorption materials.

1. INTRODUCTION

Surface and interface structure incl. compositions are the primary factors controlling chemical, electronic or mechanical properties of materials in many technologically important applications. The study of biomineralization offers valuable insights into the scope and nature of material chemistry at the inorgano-organic interfaces. Potential applications of new, recently fabricated materials with specific surface deposition in nanoelectronics and nanoinformatics for ultrahigh density of magnetic recording or in biological sensor production are another important field of interest nowadays [1,2,3].

The objective of our study was to characterize the interfacial phenomena and the surface architecture of new organo-inorganic clinoptilolite-rich tuff based adsorbents prepared by means of hydrophobization, carbonization and alginate-biopolymer coating onto the external zeolite surface, using the complementary SEM, XRD, SIMS, and FTIR spectral analytical techniques. Above surface

modified polyoxide based adsorbents were used for removal of nitrate, phosphate, chloride, sulfate, chromate and arsenate from aqueous model solutions [4,5].

A native zeolite of clinoptilolite type has been chosen as the support (matrix) for the above combined adsorbents fabrication on the base of its solid skeleton composed of Al and Si polyoxides, sufficiently large hydrophilic, polar, microporous, temperature and radiation resistant surface, economical feasibility, easier accessibility on the domestic market, a low mechanical attrition and appropriate hydraulic properties.

The adsorption isotherms of the systems: nitrate, phosphate, sulfate, chloride, chromate and arsenate on the hydrophobized, carbonized and alginate zeolites were drawn to confirm and quantify the adsorption functionalities of the examined zeolite samples.

2. EXPERIMENTAL

2.1. Materials. The natural clinoptilolite-rich tuff, crushed and ground into the fraction of 0.4–1 mm (35–16 mesh) has been supplied for laboratory experiments by Zeocem, Share Holding Company, mining at the East-Slovakian sedimentary, commercialized rock quarries (Nižný Hrabovec). The mineralogical and chemical compositions of the raw zeolite was published elsewhere [5].

2.2. Methods. Carbonization was accomplished with the waste, mostly vegetable substratum, inside a middle range temperature pyrolytic combustion chamber, which used direct heating by exhaust gas flow in an oxygen free atmosphere. The process had a lot of similarities with biomass pyrolysis [4].

Hydrophobization of clinoptilolite with ODA-surfactant to enable anions removal from water was thoroughly described in paper [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 examined nutrients removal [4,5]. Zeolite was beneficiated with ODA-surfactant and biopolymeric alginate using the sol-gel method.

Equilibrium adsorption and isotherm measurements in the laboratory were done with aqueous model solutions of sulfate, nitrate, phosphate, chloride, arsenate and chromate salts on the surface of modified clinoptilolite-rich tuff (hydrophobized, carbonized and alginate covered one) with the solid-to-liquid ratio 1g/100 ml, at $T = 23 \pm 0.1^\circ\text{C}$. All experiments were run in triplicate, keeping the suspensions equilibrated up to 7 hrs.

2.3. Surface area measurements. External surface area and porosity of zeolite samples were determined at liquid nitrogen temperature (76 K) using Micromeritics ASAP 2400 Apparatus with enhanced gas analysis manifold, a lower pressure transducer, by applying static volumetric technique and t-plot methods incl. BHJ pore diameter computation.

Prior to the measurements the samples were vacuum degassed at 2 Pa overnight and by $T = 623.15$ K. Some S_{BET} values of relevant composite samples were compared to the surface area values verified by different methods, i.e. porosimetry method (Porosimeter P 2000, Carlo Erba, Italy) and surface area determination according to Blaine [6].

2.4. Analytical procedure. Chromate and arsenate concentrations in aqueous solutions were analysed by atomic absorption spectrometry (AAS) with flame atomization on a Perkin-Elmer apparatus, model 1100. Phosphate, sulfate, chloride and nitrate concentrations were analysed on Isotachophoresis ZKI 02 (Villa Labeco). The other pollutants like Acid Red (AR) pigment and phenol have been determined using the Diode Array HP Spectrometer 8452A. Infra red spectra of the samples were made on FT IR system and Perkin-Elmer Spectrometer 781 using the KBr disc technique.

Time-of-Flight Mass Spectrometry (TOF MS) was based on the simple fact that ions with the same energy but different masses travel with different velocities. In its simplest set-up, ions formed by a short ionisation event were accelerated by an electrostatic field to a common energy and travel over a certain drift path to the detector. Measuring the flight time for each ion allowed the determination of its mass.

The actual TOF-SIMS instrument (TOF-SIMS IV), installed at the International Laser Centre (ILC) in Bratislava has been manufactured by IONTOF, Germany. It was equipped with ion guns for analytical and sputtering purposes and a reflectron type TOF analyser. The main analytical gun was gold liquid metal ion one. The oxygen sputter gun was used for depth profiling in positive polarity. All SIMS analyses have been carried out under ultra high vacuum of 10^{-9} mbar.

The X-ray powder diffraction (XRPD) patterns were accomplished at room temperature on a Phillips 1830 diffractometer using CuK_α radiation only for carbonized clinoptilolite-rich tuff in order to promote the identity as well as any change of XRD spectra regarding the original clinoptilolite-rich tuff. The resulted patterns were compared with the JCPDS Catalogue (Joint Committee on Powder Diffraction Standards).

Surface morphology and topography were visualized by scanning electron microscopy (SEM) on JEOL-JXA 840A integrated with the energy dispersive multichannel X-ray (EDX) microanalyser KEVEX equipped with the Si(Li)

detector. The polished crystallite samples were pretreated by ultrasonic dispersion in ethanol and then only some drops of suspension were placed on a carbon coated grid for the SEM measurements.

3. RESULTS AND DISCUSSION

In the recent years attention has been focused on the design, synthesis and fabrication of combined organo-inorganic adsorbents, mostly on the natural basis. Taking into account the fact that Slovakia has extraordinarily high clinoptilolite-rich tuff deposit, which is practically low-cost aluminosilicate, a suitable and potential supporter (matrix) for grafting or embedding of a broad spectrum of functional groups, due to a sufficiently large surface area, some experimental results concerning aqueous pollutant removal by this zeolite based adsorbent are reported.

Many up-to-date technologies appeared in literature for preparation of such adsorbents, nevertheless most often cited one was the sol-gel method, which was used for synthesis of ODA and alginate clinoptilolite-rich tuff also in our study.

Clinoptilolite (HEU topology) is one of the most abundant natural zeolite species, mainly occurring in sedimentary rock deposits, associated with clays or similar (alumino)silicates phases. The crystals accommodate two different systems of micropores interconnected within the lattice and capable of hosting extra-framework, i.e. exchangeable cations like Na, Ca, Mg and K in association with mobile water molecules. In our case, those cations were supposed to act as the reaction centres for grafting of long chain ODA cation and alginate biomolecules, respectively. A totally different procedure was used for carbon immobilization onto clinoptilolite-rich tuff.

A lot of laboratory bench-scale trials designed for adsorption-desorption characterization testified a higher efficiency of inorganic oxyanions removal from aqueous solutions by ODA hydrophobized zeolite, where the anionic species remained adsorbed irreversibly, regarding the carbonized zeolite (Figures 1, 2, 3, 4, 5).

Nevertheless, a satisfying abatement of phenol and AR pigment by means of the carbonized clinoptilolite-rich tuff in respect to the active charcoal (Slovak industrial product trademark HYS-N) has been achieved on the laboratory scale, testing numerous aqueous model solutions in static and dynamic arrangements (Figure 5). Obviously, no adsorption of examined anions except phosphate was observed by means of untreated clinoptilolite-rich tuff.

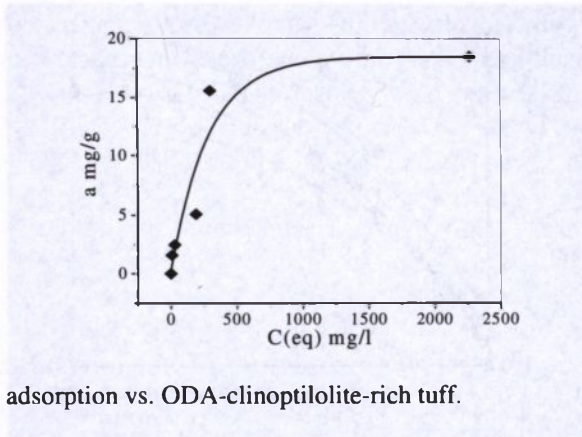


Fig. 1. Chromate adsorption vs. ODA-clinoptilolite-rich tuff.

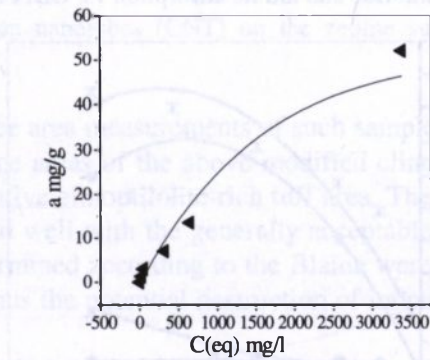


Fig. 2. Arsenate adsorption vs. ODA-clinoptilolite-rich tuff.

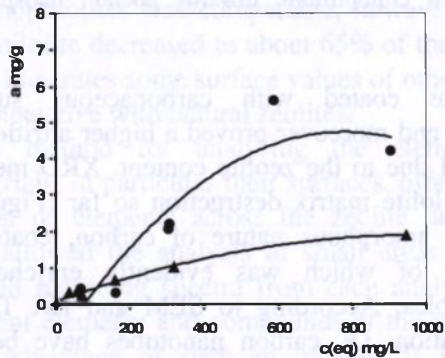


Fig. 3. Nitrate adsorption vs. ODA-zeolite and alginate coated zeolite (downwards).

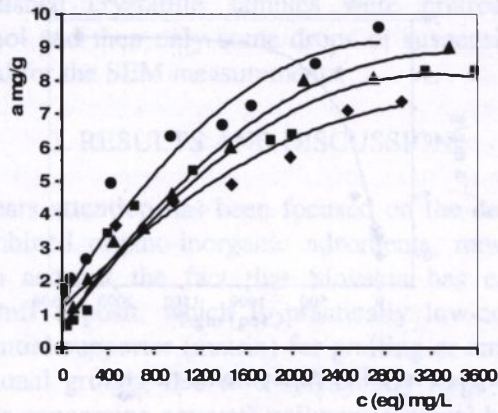


Fig. 4. Phosphate, sulfate, chloride and nitrate adsorption vs. ODA-zeolite (downwards).

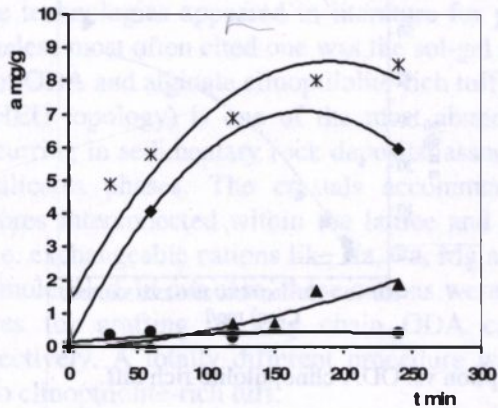


Fig. 5. Adsorption capacity vs. time dependence of activated charcoal towards AR pigment and carbonized clinoptilolite towards phenol, phosphate and AR pigment (downwards).

Raw clinoptilolite coated with carbonaceous substances resembled an activated charcoal and moreover proved a higher attrition resistance than the conventional charcoal due to the zeolite content. XRD measurements have not recorded any clinoptilolite matrix destruction so far (Figure 6). SEM analysis supported mostly an amorphous nature of carbon, coated on the adsorbent surface, morphology of which was evidently enriched with meso- and macroporous-sized holes. According to SEM and HR TEM analyses a new allotropic C-modification, i.e. carbon nanotubes have been explored on the external zeolite surface after the above described carbonization process (Figure 7).

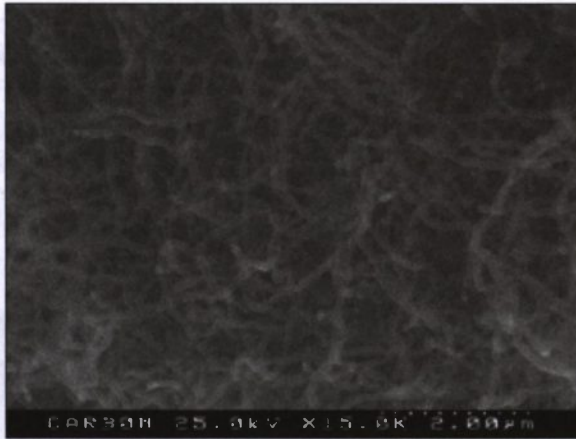


Fig. 7. SEM of carbon nanotubes (CNT) on the zeolite surface of Nižný Hrabovec quarries.

The active surface area measurements of such samples were accomplished to find out if the surface areas of the above modified clinoptilolites were changed with regard to the native clinoptilolite-rich tuff area. The mentioned porosimetry method corresponded well with the generally acceptable BET isotherm method, only the values determined according to the Blaine were different, probably due to pulverizing and thus the potential destruction of immobilized carbon enriched substances [6].

Nevertheless, while a tendency of the surface areas lowering into $2/3$ and $1/3$ of the natural clinoptilolite area by the carbonized and hydrophobized clinoptilolites as well was observed (Table 1), the Blaine method did not prove such significant surface area decrease. By this method the surface area of the natural and ODA-clinoptilolites was comparable, however, the surface area of the carbonized clinoptilolite decreased to about 65% of the natural clinoptilolite surface area. Table 1 illustrates some surface values of other comparable, mostly natural materials, competitive with natural zeolites.

The used SIMS method for analysing the elemental and chemical compositions of materials, in particular their surfaces, offered some information about the distribution of elements across the zeolite depth. Applications of focused beams also allowed the analysis of small areas and by rastering the primary ion beam and recording spectra from each analysis point, the lateral distribution of different elements and compounds at the surface was visualized (ion imaging). The advantage of such an imaging is to display with light coloured spots the homogeneous distribution of elements on the surface and with dark coloured spots the poor covering of detected constituents [10].

Tab. 1. Specific surface areas and porosity values of some materials studied.

Sample	S_{BET} (m^2/g)	S_t (m^2/g)	V_{micro} (cm^3/g)	d_{BJH} (\AA)
Slovakian clinoptilolite-rich tuff (Nižný Hrabovec)	31.7	21.4	0.0045	145
US Death-Valley clinoptilolite-rich tuff	14.3	14.5	0	92
Synthetic clinoptilolite (University of Wolverhampton, GB)	99.7	65.5	0.015	140
Carbonized Slovakian clinoptilolite-rich tuff	23.7	17.6	0.0026	83.9
ODA-hydrophobized Slovakian clinoptilolite-rich tuff	10.8	-	-	-
Alginite (Pinciná, Slovakia)	27	27	0	111
Shungite rock silicate (St. Peterburg, Russia)	18.3	17.8	<0.001	75
Mordenite (Blue Pacific Minerals, New Zealand)	125	34.3	0.042	200-900
Perlite (Eastern Slovakia)	1.24	-	-	-
Expanded perlite (Vapex, KERKO Košice)	2.11	-	-	700-1000

$S(\text{BET})$ – active surface area determined by the nitrogen adsorption and the BET isotherm

$S(t)$ – surface area of mesopores plus external surface area determined by the t-plot method

$V(\text{micro})$ – volume of micropores determined by the t-plot method

d_{BJH} – average pores diameter

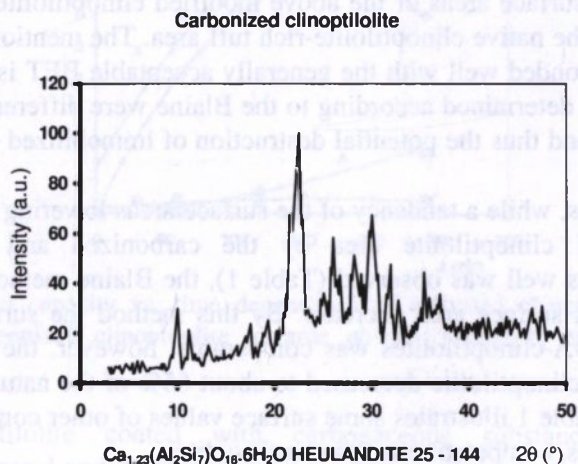


Fig. 6. XRD of carbonized clinoptilolite-rich tuff.

SIMS and Fourier Transform IR analyses of the studied zeolite combined adsorbents helped to define the new engineered surfaces of the materials as follows: The external surface of zeolite was homogeneously covered with the primary building elements, such as Al, Si and K, however, the distribution of surface Na, Ca, Mg cations as well as Li and Cs was inhomogeneous. By ODA-hydrophobized zeolite the SIMS method indicated the characteristic

peaks of $C_{18} H_{40} N^+$ i.e. amine, even some lower fragments and dimers of relatively high intensities originating from the above organic amine breakdown were recorded. The inhomogeneous dispersion of ODA compound on the surface may consequently copy the inhomogeneity of zeolite surface. The carbonized zeolite exhibited mostly peaks of low organic fragments, Ca and its compounds remaining from pyrolysis substratum according to the SIMS analysis. Some significant peaks of P-compounds were identified, too (Figure 8).

Field of view: 121.0 x 121.0 μm^2

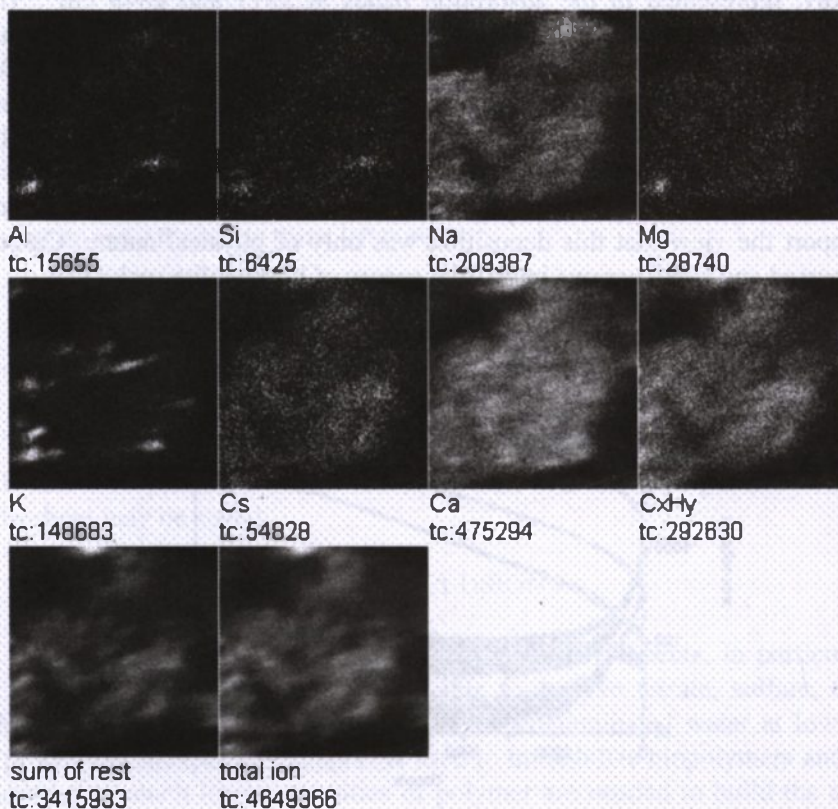


Fig. 8. Lateral surface imaging of the components present in carbonized clinoptilolite-rich tuff.

According to the depth profile measurements, surface carbonization was neither by chemical composition, nor by thickness of the carbon deposited layers in such an extent homogeneous as the ODA-surface. Disordered carbon deposition on the zeolite surface reached up to 5 μm thickness, which is about one order of

magnitude higher than in the case of ODA-surface covering. By depth profiling (Figure 9) of the carbonized clinoptilolite, using the oxygen sputter gun, two different forms of surface composed layers have been observed, in which the intensity of the basic Si, Al and K elements and organic fragments with the depth proportionally increased and the inhomogeneous one, were opposite, the intensity of organic fragments with the depth decreased.

The FT IR spectra of alginate coated clinoptilolite-rich tuff confirmed the covalent bonds between the polymers and the Ca cations of zeolite very profoundly, represented in the adsorption bands at 2917 and 2848 cm^{-1} . The ODA-clinoptilolite presented the adsorption bands at $2917\text{--}2921$ and 2848 cm^{-1} , corresponding to the assigned intense vibrations of the surface attached ODA groups, respectively. It was assumed that octadecylammonium chains were bounded onto zeolite $(\text{SiO}_4)^{4-} - (\text{AlO}_4)^{5-}$ skeleton electrostatically and alginate by means of surface accessible Ca^{2+} ions covalently. Carbon deposition from biomass pyrolysis did not prove almost any IR signals with zeolite matrix, which may support the view that this deposition was only of physical nature. Carbon was dispersed and filled various interstitial spaces of host zeolite rock [11].

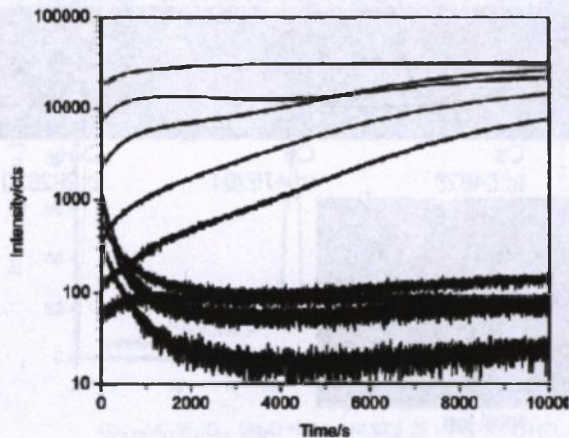


Fig. 9. SIMS depth profile of the carbonized clinoptilolite using Au (downwards Ca, Na, K, Al, Si, CH_3 , C_3H_5 , C_4H_5 curves).

Finally, the reaction order of adsorption process of ODA-clinoptilolite-rich tuff vs. phosphate as well as AR pigment was estimated by graphical presentation of the following relations:

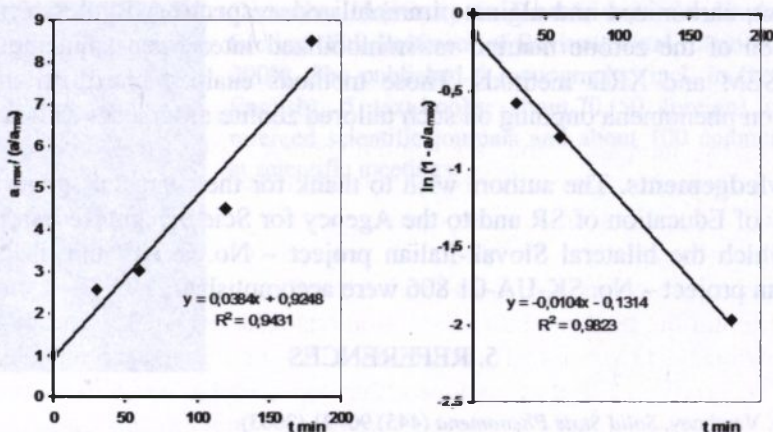


Fig. 10. Graphical determination of the reaction order of ODA-clinoptilolite-rich tuff vs. phosphate and AR pigment (from left to right).

$$\ln [1 - a/a_{\max}] = f(t)$$

$$a_{\max}/a_{\max} - a = f(t)$$

According to the computed correlation coefficient, the first order reaction for AR onto clinoptilolite-rich tuff and the second order for phosphate onto the same adsorbent may be stated.

4. CONCLUSIONS

Attention was focused on various combined adsorbents, in particular with a natural solid support, which were able to remove nitrate, sulfate, chloride, phosphate, chromate and arsenate from the contaminated water at low cost. If a proper and inexpensive support is used to immobilize biopolymers and similar substances, much lower quantities of polymer are needed to build the adsorbed material. Thus, such hybrid materials containing carbonaceous substances display much better adsorption capacity than any of its components used alone.

Based upon these results it was concluded that the best properties and the highest functionality towards aqueous solutions of phosphate, nitrate, chloride, sulfate, chromate and arsenate are exhibited by ODA-hydrophobized zeolite of clinoptilolite type, whereas the lowest one regarding the carbon-rich substratum, the coke similar carbonized zeolite.

Moreover, the scope of the present study was to characterize the novel clinoptilolite based adsorbents, surface hydrophobized with octadecylammonium

surfactant, carbonized and alginate immobilized, respectively and to define the interaction of the zeolite matrix vs. immobilized interfaces, using the FT IR, SIMS, SEM and XRD methods. Those methods enabled clarification of the interaction phenomena ongoing on such tailored zeolite adsorbents satisfactorily.

Acknowledgements. The authors wish to thank for the financial support to the Ministry of Education of SR and to the Agency for Science and Research of SR under which the bilateral Slovak-Italian project – No. 09105 and the Slovak-Ukrainian project – No. SK-UA-01 806 were accomplished.

5. REFERENCES

- [1] K. G. Varshney, *Solid State Phenomena* (445) 90–91 (2003).
- [2] S. E. Manahan, *Environmental Chem.*; 6th Ed. Lewis Publishers Boca Raton 1994.
- [3] E. Chmielewská, K. Jesenák, K. Gáplovská, *Collection of Czechoslovak Chemical Communications* 68 (4), 823 (2003).
- [4] E. Chmielewská, W. Tylus, M. Morvová, Supplementary Research of Clinoptilolite-rich Tuff Composites after adsorption trials using the XPS technique, *Central European J. of Chemistry* 4 (1)1 2006.
- [5] M. Reháková, S. Čuvanová, M. Dživák, J. Rimár, Z. Gavaľová, *Current Opinion in Solid State and Materials Science* 8, 397 (2004).
- [6] Slovak Technical Norm STN 72, 2114: Surface determination of some building materials (Permeability Method).
- [7] M. Stöcker, *Microporous Materials* (6) 235 (1996).
- [8] Š. C. Stefanovič, N. Z. Logar, K. Margeta, N. N. Tušar, I. Arčon, K. Maver et al., Structural investigation of Zn sorption on clinoptilolite tuff from the Vranjska Banja deposit in Serbia, *Microporous and Mesoporous Materials* 105, 251 (2007).
- [9] A. Godelitsas, T. Armbruster, HEU-type zeolites modified by transition elements and lead, *Microporous and Mesoporous Materials* 61, 3 (2007).
- [10] D. Velič, M. Aranyosiová, *Research Report of SIMS*, International Laser Center in Bratislava (Slovakia) 2005.
- [11] E. Chmielewská, D. Velič, M. Aranyosiová.: FT IR and SIMS Studies for active Surface induced Mechanism of Pollutants Abatement on the native Clinoptilolite based Composites, *10th Ukrainian-Polish Symposium: Theoretical and Experimental Studies of Interfacial Phenomena and their Technological Applications*, September 26–30, Proceedings, pp. 50–53, 2006.

CURRICULA VITAE

Prof. Eva Chmielewská, Ph.D. obtained M.Sc. Diploma in Technical Chemistry in 1977 at Martin Luther University (THC Merseburg) Germany; Ph.D. Degree of Inorganic Technology at Faculty of Chemical and Food Technology in Bratislava & Water Research Institute (Bratislava) in 1985, where she was employed for over 10 years; in 1992–1994 worked as the Regional Director of US–Swiss Company Comco Martech, which provided remediation and environmental protection activities for the Central Europe Region; since 1994 she has been working in the Faculty of Natural Sciences of



Comenius University in Bratislava in the Environmental Section (Full Professor of Environmental Engineering since 2005). She published 6 monographs (incl. in German and English), 5 text-books; about 70 (50 foreign) papers in refereed scientific journals and about 100 communications at scientific meetings.



Dr. Lenka Sabová graduated from Comenius University Bratislava, Slovakia, Faculty of Natural Sciences, Department of Environmental Chemistry in 2005. She is currently Ph.D. Student at Faculty of Natural Sciences, Department of Inorganic Chemistry.



Dr. Aiyong Wu joined the Centre for Research in Ceramics and Composite Materials – CICECO, University of Aveiro (UA) in 2002. She got her Ph.D. degree from UA in Jan. 2000. She is currently involved in various R&D activities being responsible and collaborating in several scientific projects. Her current scientific interests are mainly focused on the study of wet chemical reactions and material synthesis, nano-powder, thin and thick film technologies, dielectric and ferroelectric materials, microstructural (AFM, TEM & SEM) characterizations, electric properties from macroscopic and microscopic (nano-scale). Besides two patents and a book chapter, she has published over 40 SCI cited scientific papers in this field.



Dr. Monika Aranyosiova graduated from Comenius University in Bratislava, Slovakia, Faculty of Natural Sciences, Department of Physical and Theoretical Chemistry in 2004. She is currently a junior scientist at International Laser Center, Bratislava responsible for the SIMS-Lab operation.



Assoc. Prof. Dusan Velic graduated from Wayne State University in Detroit, USA in 1996 and after a postdoc stay at Fritz Haber Institute in Berlin, Germany, he joined Comenius University in Bratislava, Slovakia, Faculty of Natural Sciences, Department of Physical and Theoretical Chemistry. He is currently teaching at Comenius University along with a senior scientist position at the International Laser Center in Bratislava.