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STUDY OF SOME INORGANIC OXYANION-LOADED ODA- AND Ag-CLINOPTILOLITE-RICH TUFF BY HR TEM, SEM AND XRD SPECTRAL ANALYTICAL TECHNIQUES

A novel nanostructure organic-inorganic composite material on the base of clinoptilolite-rich tuff of Slovakian origin has been investigated using SEM, HR TEM and XRD spectral analytical techniques.

As organic guest species cationic surfactant, i.e. octadecylammonium, on clinoptilolite matrix was used. As inorganic guest silver arsenate or chromate was attached to the surface of clinoptilolite-rich tuff. Both ODA and Ag-substituted clinoptilolite modifications exhibited high adsorption capacities for the inorganic oxyanions examined.

1. INTRODUCTION

Zeolites are microporous, high-internal-surface-area crystalline, hydrated aluminosilicates of alkali and alkaline earth cations having an infinite, open, rigid and three-dimensional structure as well. Their three-dimensional framework consists of tetrahedral AlO_4^{5-} and SiO_4^{4-} units linked through shared oxygens. The clinoptilolite topology consists of crosslinked sheets of complex tetrahedral units containing 4- and 5-member ring and 8- and 10-member ring pores. The diameters of the windows or pores leading the voids range only from 2.6 to 7.6 Å [1].

Zeolite tuffs in huge deposits are widely distributed all over the world. A few small regions of them are known in Slovakia. So far the clinoptilolite tuff is the most abundant and represents only one industrial opencast mine in Eastern Slovakia, i.e., in the locality of Nižný Hrabovec, currently possessed by Zeocem Ltd. Bystré. The annual production reaches up to 200 000 tonnes of powder-ground and 20 000 tonnes of the grain-sized-ground clinoptilolites [2].

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Because of its high cation-exchange capacity and selectivity for ammonium and some metals, clinoptilolite, a naturally occurring zeolite, has often been used as an inexpensive cation exchanger for controlling a release of NH_4^+ or some other cations like Pb^{2+} , Ag^+ , Cs^+ , Sr^{2+} in waters [3]. It has been found recently that surfactant-modified zeolite, a type of inexpensive organo-zeolite composite, can fulfill the requirements for adsorption of organic and inorganic pollutants contaminating waters [4].

On the basis of Slovakian natural clinoptilolite a series of surfactant (octadecylammonium (ODA))-modified clinoptilolite samples has been prepared in order to remove toxic organic compounds such as PCE, DCE, TCE, phenol and inorganic compounds, e.g. arsenate, chromate pollutants, from model aqueous solutions.

A series of batch adsorption experiments as well as dynamic fixed bed runs have been performed at laboratory to examine how the capacity data and adsorption kinetics of the above pollutants increase compared to the raw, unmodified clinoptilolite samples [5]. Various simple and complex techniques from optical, scanning and transmission electron microscopic methods to X-ray, nuclear magnetic resonance, UV-IR spectroscopic analytical methods significantly contribute to the detailed characterization of the above zeolitic composites, enriched with the hydrophobic long hydrocarbon chains attached to the zeolite surface [6], [7].

The surface morphology and topological properties of surfactant-loaded clinoptilolite-rich tuff after adsorption of arsenate or chromate have been studied and presented in this paper.

2. EXPERIMENTAL

The zeolitic tuff used in this study was native clinoptilolite (Slovakian quarry Nižný Hrabovec) supplied by the Zeocem Bystré company in grain-sized fraction ranging from 0.3 to 1.0 mm.

Mineral composition of zeolitic rock and powder diffractograms were attained with a Philips PW1710 diffractometer coupled to a copper anode X-ray tube. The $\text{CuK}\alpha$ -radiation was selected with a diffracted beam monochromator. Mineral components were identified by comparison with JC PDF cards in a conventional way. Mineralogical analysis has revealed that the tuff contains about 70% of clinoptilolite and minor quantities of volcanic glass, feldspar, cristobalite and quartz.

Chemical composition of clinoptilolite-rich tuff used in the experiments and determined by X-ray fluorescence analysis (Fluorescence Spectrophotometer Hitachi F-2000) is presented in the table.

The high-resolution transmission electron microscope (HR TEM), Jeol 2010 instrument, was used for sample investigation. The samples were first pretreated by ultrasonic dispersion in ethanol, and then only some drops of suspension were placed on a carbon-coated grid for TEM measurements. The HR TEM data obtained were compared with that of ICDD-PDF database.

Table
Chemical composition of clinoptilolite-rich tuff

Component	% w/w
SiO ₂	67.16
Al ₂ O ₃	12.30
Fe ₂ O ₃	2.30
Na ₂ O	0.66
CaO	2.91
MgO	1.10
K ₂ O	2.28
P ₂ O ₅	0.11
MnO	0.14
TiO ₂	0.17
Sr, Ba, Pb, Zn	less than 0.01
H ₂ O	10.9

Scanning electron microscope (SEM) equipped with Electron Probe Microanalyser JEOL – JXA 840A (Japan) was applied, while a high-vacuum coating unit Balzers BAE 080 was used for production of a carbon film, and an ion sputtering device JEOL JFC-1100 – for fine gold coating of the well-formed single clinoptilolite crystals.

3. RESULTS AND DISCUSSION

A wide scientific research on hydrophobization of natural clinoptilolite-dominated zeolites has been accelerated recently, and many organic bases like hexadecyltrimethylammonium (HDTMA), hexadecylpyridinium (HDPY), benzothonium (BE), polyhexamethylguanidinium (PHMG) and the others have been employed to promote the uptake capacity of natural zeolite for multivalent heavy metal anions.

A 0.5 g mass of either the organo-treated or inorganic cation exchanged zeolite-clinoptilolite and 50 cm³ of 10 mmol/dm³ arsenate or chromate aqueous solutions were placed into Erlenmeyer flasks and mechanically shaken to reach equilibrium. The adsorption isotherm experiments were carried out analogously using the initial metal concentrations ranging from 0.5 to 100 mmol/dm³, measured at ambient temperature. The quantity of metal adsorbed on clinoptilolite was determined from the difference between the initial and equilibrium concentrations in solutions, using the atomic absorption spectrometry method (AAS).

Using the samples of clinoptilolite enriched with octadecylammonium and Ag-modified clinoptilolite-rich tuff of Slovakian origin in order to investigate the removal of arsenate and chromate from aqueous solutions, we also undertook their complementary analytical screening by XRD, SEM and HR TEM which allows us to characterize the new-tailored nanostructure organic-inorganic composites with clinoptilolite matrix.

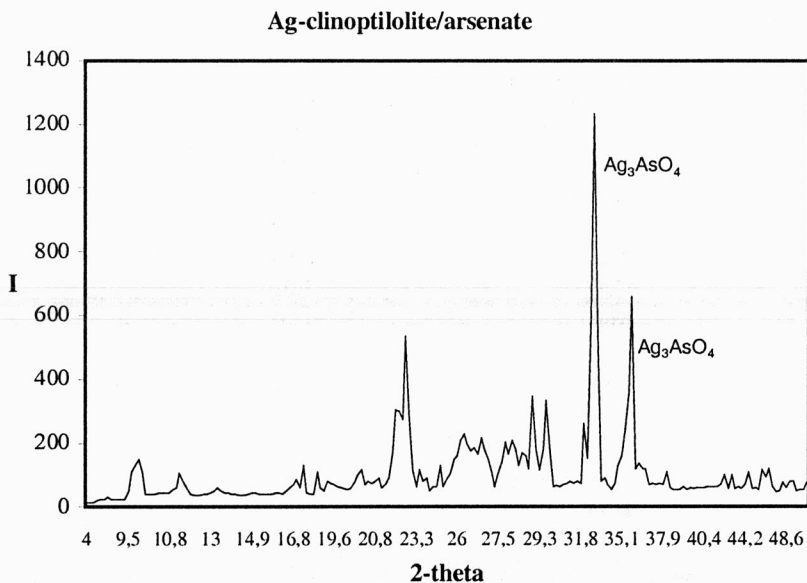


Fig. 1. XRD pattern of Ag-exchanged clinoptilolite-rich tuff after arsenate adsorption

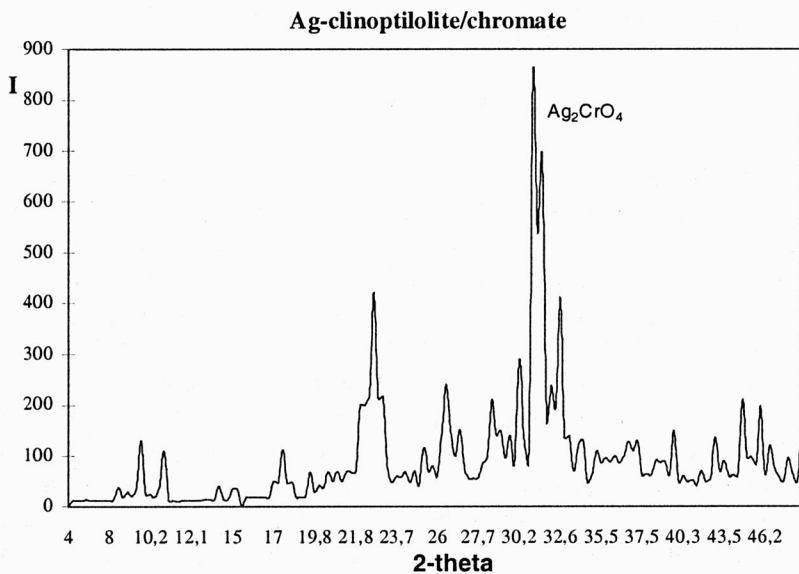


Fig. 2. XRD pattern of Ag-exchanged clinoptilolite-rich tuff after chromate adsorption

As previously stated, the batch and column experiments demonstrated considerably higher adsorption capacities of ODA-clinoptilolite for the above oxyanions compared to the Ag-substituted cation or natural (untreated) clinoptilolite varieties [5].

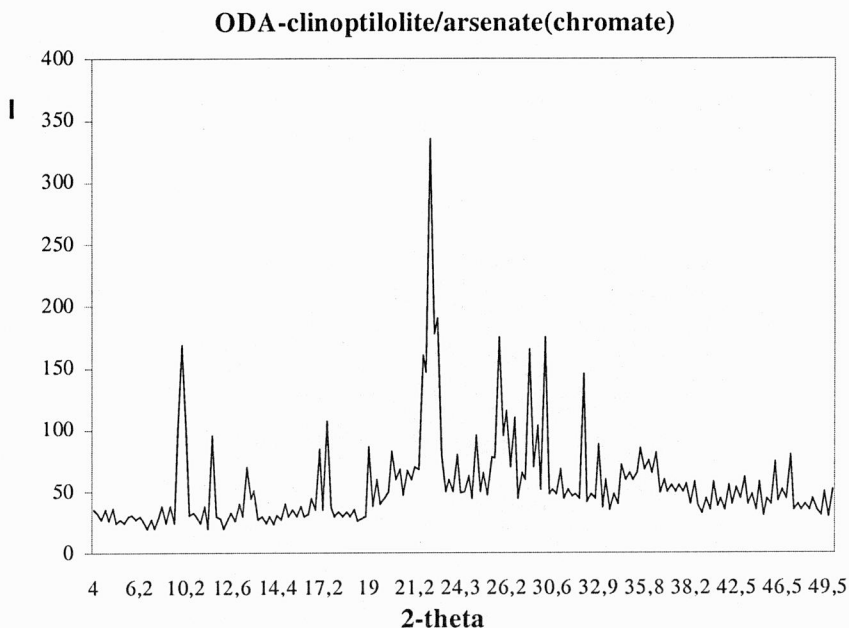


Fig. 3. XRD pattern of ODA-clinoptilolite-rich tuff after arsenate (chromate) adsorption

The arrangements of the surface-attached ODA-chains were an important factor influencing the adsorption states of guest species, i.e. inorganic oxyanions. The 18-carbon ODA chains with ammonium head groups predictably intercalated into each other on the clinoptilolite surface, while the down- and upwarded positive charged ammonium head groups interacted with the negative oxyanions and the negative SiO_4^{4-} (AlO_4^{5-}) clinoptilolite skeleton by electrostatic Coulomb forces.

In order to determine the most efficient surfactant counterion (chromate, arsenate) uptake by ODA-clinoptilolite, we established a batch sorption procedure using various initial concentrations of ODA whose weight/volume ratios were the same, i.e. 20 g of raw clinoptilolite-rich tuff and 100 cm³ of different ODA aqueous solutions (0.001; 0.01; 0.1; 0.2 mol/dm³). These mixtures were stirred by an MLW ER10 lab assembly for 24 hr at 60 °C, considering this time period to be sufficient for equilibrium attainment. The pH of solutions was kept ca. 3.0 by addition of 98% acetic acid. The mixture was then paper-filtered through a warmed Büchner funnel to yield a clear supernatant and ODA-treated clinoptilolite, afterwards rinsed sufficiently with distilled water, dried and ground with a pestle.

The data being published formerly confirmed the highest counterion uptake with that ODA-surfactant-loaded clinoptilolite which was prepared from the initial octadecylammonium acetate solution of 0.2 mol/dm³ (greater than critical micelle concentration (CMC)). According to CHN analyses carried out using Perkin-Elmer 2400 Elemental Analyser, the ODA content in that sample reached 8.75%.

The XRD results checked the presence of large crystals of Ag_3AsO_4 according to JC PDF 6-493 (figure 1) and chromate (tarapacaite*) according to JC PDF 15-365 with Ag-substituted clinoptilolite (figure 2); however, the polymerous ODA-surfactant attached to the clinoptilolite surface makes the appearance of the characteristic arsenate or chromate peaks at the X-ray diffractogram impossible except the typical clinoptilolite ones (JC PDF 25-1349) (figure 3).

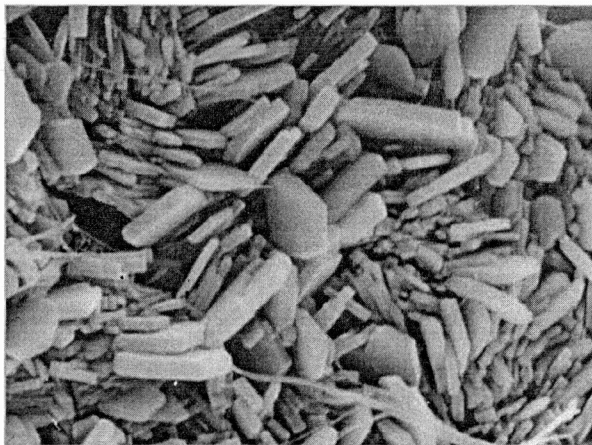


Fig. 4. SEM image of clinoptilolite-rich tuff of Slovakian origin (untreated); magnification 3700 \times



Fig. 5. SEM image of ODA-modified clinoptilolite-rich tuff; magnification 3000 \times

* A mineral consisting of a native potassium chromate and occurring in Chilean nitrate deposits (Editor's footnote).

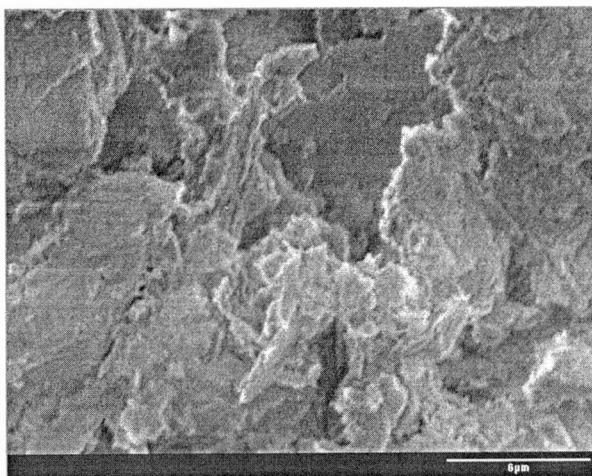


Fig. 6. SEM image of ODA-modified clinoptilolite-rich tuff after chromate adsorption

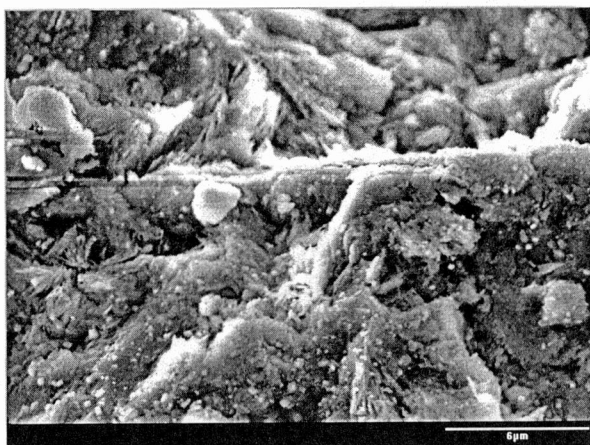


Fig. 7. SEM image of Ag-exchanged clinoptilolite-rich tuff after arsenate adsorption

In other words, the XRD pattern shown in figure 3 is identical with that representing an unmodified, natural clinoptilolite. A similar case concerns an inorganically modified Ag-clinoptilolite; however, on the basis of crystalline nature, i.e. large crystals of silver arsenate and silver chromate adsorbed on clinoptilolite matrix, only the XRD spectra presented in figures 1 and 2 are enriched with the above new host species. No silver-exchanged cations were found in clinoptilolite microstructure using this method.

The morphology and structure of the natural, Ag-exchanged and ODA-modified clinoptilolites with adsorbed arsenate and chromate were investigated making use of electron microscope. SEM images of untreated clinoptilolite-rich tuff (figure 4)

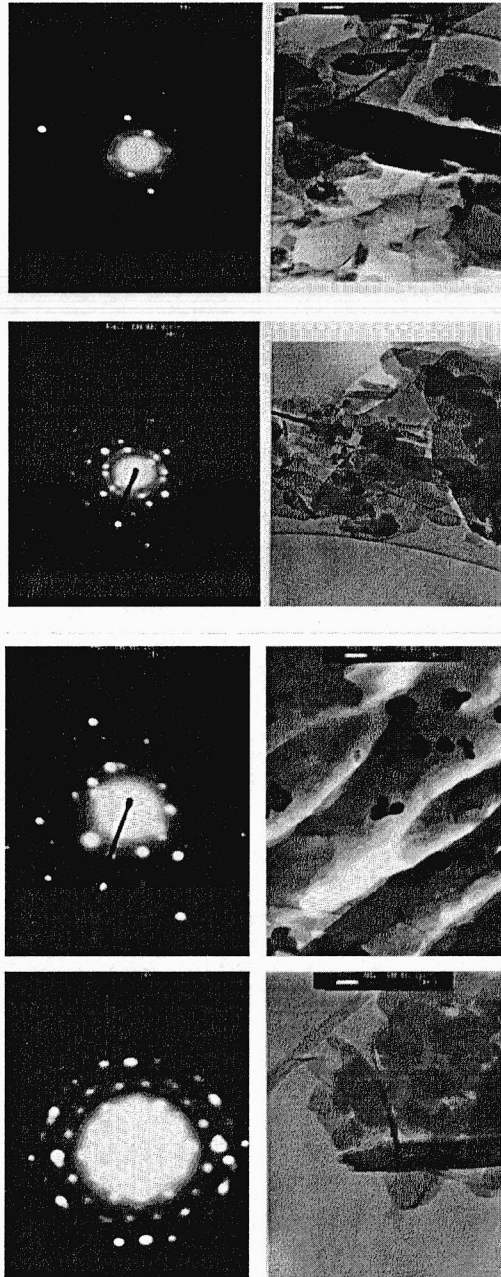


Fig. 8. ED pattern and HR TEM micrograph of an ODA-modified clinoptilolite-rich tuff, untreated clinoptilolite-rich tuff, Ag-exchanged clinoptilolite-rich tuff after arsenate adsorption, ODA-modified clinoptilolite-rich tuff after chromate adsorption (downwards)

exhibited well-defined tabular-shaped crystals with distinct crystal edges, whereas more agglomerated, poorly defined crystal edges appeared after the surface covering with organic surfactant (figure 5). The slightly undulated surface may be indicative of the surfactant presence. Such a surfactant formed a dendritic, clustered sorption pattern and thus agglomerations of surfactant molecules on the clinoptilolite surface. The quite smooth leaflets or tablets disappeared and some quasi-little pits appeared or some impregnation was found on the surface after adsorption of chromate onto ODA-clinoptilolite (figure 6) or arsenate onto Ag-clinoptilolite (figure 7). Scanning electron micrograph (figure 7) resembles some kind of foaming structure.

According to the HR TEM measurements the modified forms of clinoptilolite after arsenate adsorption were also more influenced, i.e. by attached chemicals that changed clinoptilolite surface morphology (figure 8). At the same time the natural clinoptilolite sample was characterized mostly by a typical lattice structure enriched with numerous plates and fibres visible in bright and dark field images, the ODA-clinoptilolite contained additionally small particles of high contrast and size of about 5–10 nm.

The mostly changed morphology resulted in the final arsenate adsorption onto Ag-substituted clinoptilolite, i.e. the analysed samples except the previous particles contained low contrasted and flower-shaped aggregates (subcolloidal and colloidal Ag-particles) and plates with some holes of about 50 nm size. Such a pronounced effect of the adsorption of chromate on ODA-clinoptilolite was not observed. From an electron diffraction (ED) pattern the presence of periodically ordered structure in all more or less analysed samples was detected.

4. CONCLUSIONS

This work is a part of the study dealing with new nanostructure organic–inorganic composites prepared on the basis of clinoptilolite-rich tuff of Slovakian origin. Novel composite material tailored for inorganic oxyanion removal from water, enriched with adsorbates (arsenate or chromate), was analysed by SEM, HR TEM and XRD experimental techniques. All spectral analytical methods used confirmed the presence of the above guest species in the clinoptilolite-rich tuff matrix and contributed to a better understanding of ongoing surface phenomena.

All the experimental results lead to the following conclusions:

- ODA-clinoptilolite exhibited more efficient uptake of arsenate and chromate from model solutions than inorganically exchanged Ag-forms (up to 50–70% higher capacity).
- Adsorption of the above inorganic species on clinoptilolite was reversible and batch desorption trials in the media of various ionic strength testified to the highest bonding ability of ODA-clinoptilolite for arsenate and chromate.

- Likewise, clinoptilolite and ODA exhibit a strong chemical interaction with adsorbed counterion that suppressed the characteristic reflections in some other spectral analyses (e.g. XRD).

- Electron micrographs revealed a dendritic, clustered sorption pattern on the clinoptilolite surface and some agglomerations of surfactant molecules.

- The conventional laboratory column experiments demonstrated a quantitative removal of arsenate and chromate from model solutions by a hydrophobic (ODA)-grain-size zeolitic adsorbent. Ag-pretreated clinoptilolite did not prove to have a typical breakthrough profile caused by dynamic species uptake such as that of the ODA-clinoptilolite.

- In the case of a simple linear regression, the Freundlich adsorption isotherm is appropriate for description of counterion adsorption on ODA-clinoptilolite; however, the Langmuir model was used for Ag-clinoptilolite.

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BADANIE TUFÓW BOGATYCH W KLILOPTILOLITY, KTÓRE OBCIĄŻONO NIEORGANICZNYMI UTLENIONYMI ANIONAMI, ZA POMOCĄ ELEKTRONOWEJ MIKROSKOPII TRANSMISYJNEJ I SKANINGOWEJ ORAZ TECHNIK ANALIZY WIDMOWEJ

Nowoczesny organiczno-nieorganiczny kompozyt nanostrukturalny, którego zasadniczym składnikiem jest słowacki tuf wulkaniczny bogaty w klinoptilolit, badano, korzystając z elektronowej mikroskopii transmisyjnej i skaningowej oraz technik analizy widmowej. Jako dodatku organicznego na podłożu klinoptilolitu użyto kationowego środka powierzchniowo czynnego, którym był ODA. Dodatkiem nieorganicznym natomiast był arsenian srebra lub chromu przyłączony do tufu bogatego w klinoptilolit. Oba dodatki wykazały dużą zdolność adsorpcji utlenionych nieorganicznych anionów.