Adsorption of Arsenate and Chromate from Waters on Hydrophobized Zeolitic Media

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A laboratory setup was used to examine the uptake of chromate and arsenate from aqueous solutions by octadecylammonium acetate [ODA]-modified inland clinoptilolite. In trials, a natural variety of montmorillonite was compared to organic, i.e. surfactant loaded clinoptilolite. and some inorganically substituted (Ag, Pb) monoforms. The arrangement of the surface-attached ODA chains was the important factor for differences in the adsorption states of the guest species (oxyanions). A novel nanostructure inorganic-organic composite was prepared and was characterized by SEM, thermogravimetry, HR TEM, UV-VIS diffuse reflectance and powder XRD spectral analytical methods. Finally, the adsorption isotherms of the studied system were expressed. An approach was proposed for the regeneration of exhausted surfactant-immobilized clinoptilolite with inorganic salt solutions under a dynamic regime.

Key Words: Octadecylammonium-clinoptilolite, adsorption, anion-exchange, chromate and arsenate oxyanions, montmorillonite.

Introduction

Natural zeolites are a large group of porous tectosilicates with about 50 different framework topologies that have been synthesized or found in nature. Currently, over 1000 occurrences of zeolite minerals have been reported predominantly from sedimentary rocks of volcanic origin in more than 40 countries around the world.

Due to their chemical and mineralogical variabilities, and the characteristics of local natural zeolite deposits, the properties of these minerals have not been generalized, and they have become a popular topic of research internationally[1].

Many new inclusion materials with a zeolite matrix have been prepared using various hosts of inorganic or organic molecules, and pharmaceutically or biochemically effective components have been included in the zeolitic channels and cavities. Such prepared materials often provide specific properties useful in various fields of industry, agriculture, pharmacy and environmental protection. Using the adsorption on modified natural zeolites for the removal of toxic elements and other inorganic or organic pollutants in water treatment processes appears very promising and costeffective[2].

On the basis of Slovak natural clinoptilolite (deposit Nižný Hrabovec) a row of surfactant octadecylammonium acetate (ODA)-modified clinoptilolite samples have been prepared to remove toxic inorganic

pollutants, i.e arsenate, chromate, from model aqueous solutions. Arsenic and chromium may be found in water that has flowed through metal-rich rocks. Severe health effects have been observed in populations drinking toxic metal contaminated water over long periods. The technology for arsenic and chromium removal for a piped water supply is moderately costly and requires technical expertise. Inorganic arsenic and chromium are documented human carcinogens[3,4].

A series of batch adsorption experiments as well as dynamic fixed bed runs have been performed in our laboratory to examine how the capacity data and adsorption kinetics toward the above pollutants increase in relation to raw, unmodified montmorillonite and cation exchanged Ag (Pb)-clinoptilolite.

Various simple and complex techniques including optical, scanning and transmission electron microscopic, X-ray, nuclear magnetic resonance, and UV-VIS spectroscopic analytical methods have significantly contributed to the detailed characterization of the above discussed zeolitic composites. The surface morphology and topological properties of surfactant loaded clinoptilolite rich tuff adsorbed with arsenate or chromate were simultaneously studied.

Materials and Methods

In this study, clinoptilolite tuff of Slovak origin, supplied by the Mining and Benefication Company Zeocem Bystré, was used. The industrial exploitation of zeolite in the Nižný Hrabovec opencast mine is performed by blasting a small quarry extent and transporting the disintegrated material to a hammer crushing line and thereafter to rotating drum dryer. The process of grinding the zeolite continues using a two chamber (grinding balls and bodles) mill and it falls out of the mill through the screening separator to the concrete collection bins. A small package of 6 kg, 0.3–1.0 mm grain–sized zeolite fraction, filled PE bag was supplied by the above company for laboratory experiments.

The mineral composition of the zeolite tuff was determined by a powder-XRD diffractometer (Philips APD computer controlled, equipped with APD analytical software, with set-up parameters: CuKα radiation, voltage 30 kV, intensity 15 mA, Co/Ni – filter, diaphragm 1.1.0.5, time 1 s., 0.1 step).

Freshly broken rock surfaces were scanned by electron microscope using an electron probe microanalyzer (Jeol – JXA 840A, Japan), while a high vacuum coating unit (Balzers BAE 080) was used for the production of carbon film; for fine gold coating of the well-formed single clinoptilolite crystals an ion sputtering device (JEOL JFC-1100) was used.

Thermogravimetric (TG) analysis of raw and ODA-modified clinoptilolite rich-tuff was performed using a Perkin-Elmer TGS-2 thermal analyzer at a heating rate of 10.0 °C /min and nitrogen atmosphere, between 20 and 1000 °C.

Physicochemical and mineralogical characterization of the clinoptilolite tuff under study is reported elsewhere[5]. The montmorillonite that was isolated from the bentonite by sedimentation and wet sieving was powdered below 5 μm particle-size fraction; the material originated from the Central Slovakian ore Jelšový potok [6].

UV-VIS diffuse reflectance spectra (DRS) were recorded under ambient conditions on a Cary 300 Scan (VARIAN, Australia) with a standard diffuse reflectance unit. The samples were scanned using an optical quartz cell (UV-VIS scan rate 600 nm/min, data interval 1.000 nm, beam mode double reverse, SBW 2.0 nm and average time 0.100 s).

High-resolution transmission electron microscopy (HR TEM) was carried out on a Jeol 2010. The

samples were first pretreated by ultrasonic dispersion in ethanol, while only some drops of suspension were placed on a carbon coated grid for TEM measurements. The resultant HR TEM data were compared with those of the ICDD-PDF database.

Total arsenic concentrations in water were determined using inductively coupled plasma ICP AES spectrometry (ICP 2070 Spectrometer – Baird, USA) with pneumatic nebulization and Cr concentrations were analyzed by atomic absorption spectrometry with flame atomization on a Perkin-Elmer, Model 1100 (USA).

Octadecylamine surfactant applied as modifier was of chromatography grade quality (Lachema Brno, Czech Republic). Chemicals used in the preparation of stock solutions were of analytical grade.

Laboratory trials performed with surfactant-immobilized and cation-exchanged clinoptilolites

To establish the most efficient surfactant counterion (chromate, arsenate) uptake by ODA-clinoptilolite, a batch sorption procedure using various initial ODA concentrations (all greater than the critical micelle concentration – CMC) and of the same weight/ volume ratios was set, i.e. 20 g of raw clinoptilolite rich-tuff and 100 mL of different ODA aqueous solutions (0.001, 0.01, 0.1, 0.2 M/L). These were stirred by an MLW ER 10 lab assembly for 24 h at 60 °C in a glass container. The stirring period was considered to be sufficient to achieve sorption equilibrium. The pH value of the equilibrium solutions was kept around 3.0 by the addition of 98% acetic acid. The mixture was then paper-filtered on a warmed Buchner funnel to yield a clear supernatant solution and ODA-treated clinoptilolite. Zeolite was rinsed with deionized (D.I.) water, allowed to dry in a Premed KBC–laboratory dryer at 60 °C and then ground by mortar and pestle.

The sorption of chromate and arsenate from aqueous solutions with ODA-modified clinoptilolite was measured in a laboratory setup using the above 0.2 M/L initial ODA concentration. This modification showed the most efficient counterion sorption. No significant CHN-elemental increase was recorded from ODA-clinoptilolite samples prepared with the last two, i.e. 0.1 and 0.2 M/L initial ODA concentrations. According to CHN analyses, performed on a Perkin-Elmer 2400 Elemental Analyzer (Italy), the content of ODA in all examined samples, corresponding to the used initial ODA concentrations, was 5.46, 6.70, 8.60 and 8.75% .

In our trials a natural variety of montmorillonite was compared to an organic variety, i.e. surfactant loaded clinoptilolite and some inorganically substituted (Ag, Pb) monoforms respectively, on the supposition that these will create chemically bound precipitates of silver or lead arsenates and chromates on the zeolite surface. The crushed, raw zeolite samples were loaded up with 4% silver nitrate or lead acetate aqueous solutions following a conventional ion exchange procedure analogous to that reported by many other authors[7].

A 0.5 g mass of either the organo-treated or inorganic cation exchanged zeolite and 50 mL of 10 mM/L arsenate or chromate aqueous solutions were placed into Erlenmeyer flasks and mechanically shaken in reciprocating mode to attain equilibrium. Different equilibrium periods for individual modifications and both aqueous oxyanions species were established.

The adsorption isotherm experiments were conducted using the above mass/volume ratio of samples with an initial metal concentration ranging from 0.5 to 100 mM/L at laboratory temperature. The amount of anion sorbed on the zeolite was determined from the difference between the metal concentration in solution before and after equilibrium.

Batch desorption experiments have been performed to assess the bonding strength of ODA to the zeolite and that of exchanged cation sites on the surface with the examined oxyanions in solutions of various ionic strength.

Dynamic fixed bed runs have been carried out in laboratory glass columns by changing the flow load in the range from 10 to 25 Bed Volumes per hour (BV/h). The laboratory columns were 120 mm high and had an inside diameter of 7 mm and 1 BV equaled 3.4 mL of 0.3-0.5 mm grain-sized zeolite. The initial metal concentrations in tested solutions were about 0.5 mM/L. The operation cycle until zeolite bed saturation depending on feed flow rate ranged from 6 to 15 h. To find the most effective regenerant for laboratory columns in the upflow mode, several 2% aqueous salt solutions (NaCl, NaNO$_3$, Na$_2$SO$_4$ and Na$_2$CO$_3$) were examined.

Results and Discussion

Characterization of zeolitic composites

According to mineralogical analysis, Slovak clinoptilolite-rich tuff reveals the presence of clinoptilolite (70%), volcanic glass (10%) and feldspar (10%) and minor quantities of cristobalite, quartz and plagioclase (10%). Diffractometer traces are typical of a well-crystallized clinoptilolite according to the d–spacings.

Photomicrographs of the natural (unmodified) clinoptilolite samples exhibited well-defined, tabular-shaped crystals with excellent crystal edges. As surface coverage with the polymeric compound occurred, smaller, more agglomerated crystals and poorly defined crystal edges were observed in a 1-μm scale SEM image. The apparent sharpness of the images decreased with increasing surfactant coverage (Figs. 1 and 2).


Figure 1. SEM micrograph of raw clinoptilolite-rich tuff from Nižný Hrabovec (East Slovakia); magnification x 3700.
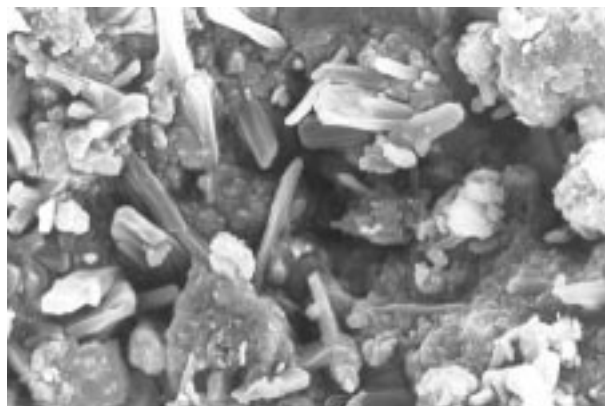

Figure 2. SEM micrograph of organomodified clinoptilolite-rich tuff from Nižný Hrabovec (East Slovakia); magnification x 3000.

Figures 3-5 show respectively the weight losses of the raw clinoptilolite, ODA and ODA–modified clinoptilolite. Almost all of the weight of ODA is lost upon heating to 230 °C, and this is seen clearly as a large, sharp peak in the derivative curve. From 30 to 400 °C a small amount of weight loss, namely 12.8%, occurs for the raw clinoptilolite due to water desorption, with characteristic endothermic peak at about 150 °C. In the weight loss curves for the ODA-modified clinoptilolite, a sequential loss of mass due to water desorption, ODA pyrolysis and desorption was observed. In the derivative curves of the modified

clinoptilolite the pronounced water-loss peak occurs at about 150 °C and the continued gradual slope of the baselines to 800 °C is due to further water loss. Weak, broad peaks at about 230 °C to 300 °C are seen in the derivative curves, corresponding probably to the pyrolysis of ODA from intermediate and higher energy bounding sites, i.e. those closely bound to the clinoptilolite surface.
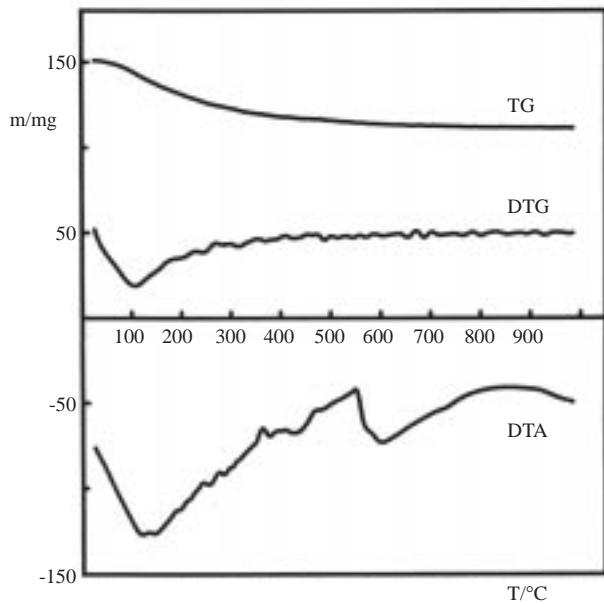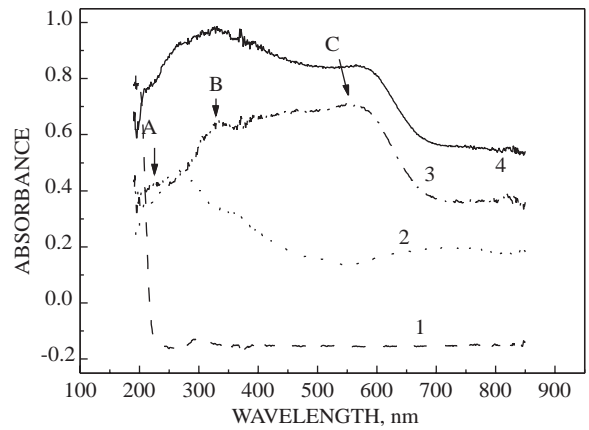

Figure 3. Derivative curves from the TGA for the raw clinoptilolite-rich tuff.
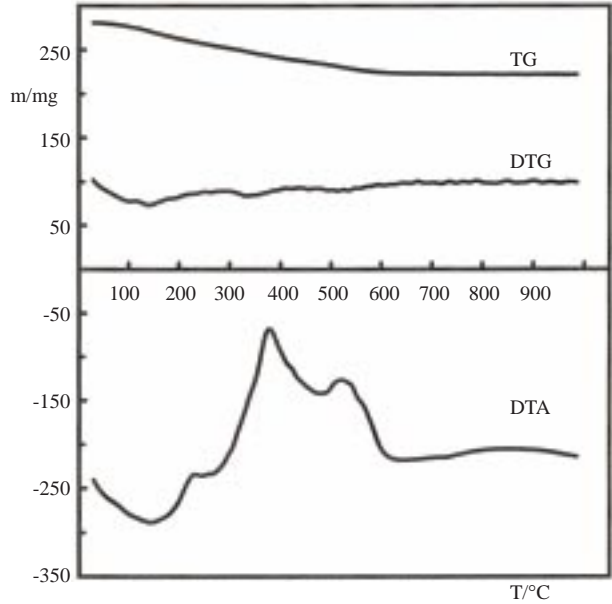
Figure 5. Derivative curves from the TGA for the ODA-modified clinoptilolite.
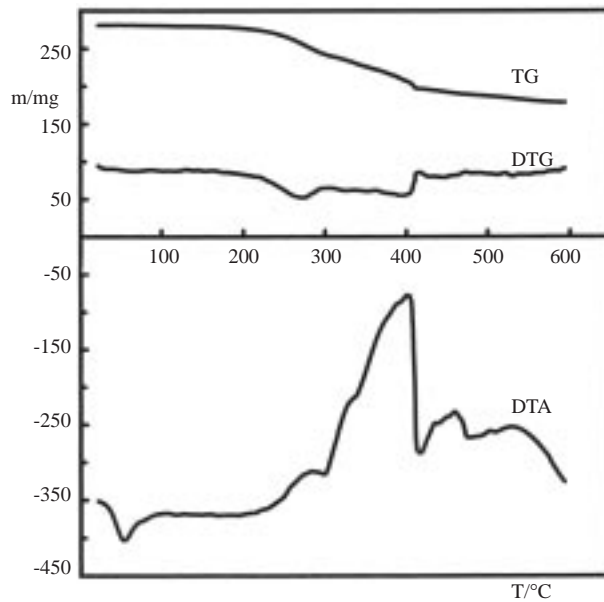
Figure 4. Derivative curves from the TGA for the ODA-modifier.

Figure 6. UV-VIS diffuse reflectance spectra for pure arsenate salt (1), raw clinoptilolite-rich tuff (2), substracted spectrum 4-2 (A-silver cations, B-silver clusters, C-silver large particles) (3), Ag-clinoptilolite – arsenate (4).

According to Figure 6 UV-VIS diffuse reflectance spectra for Ag^+ substituted clinoptilolite adsorbed with arsenate indicated clearly that silver occurs partly in Ag^+ cationic states (absorbance peak at 220 nm), in the form of small clusters (less than 10 atoms; absorbance peak at 325 nm) and in the form of large metallic particles (wide peaks at 420 and 580 nm). To summarize, the DRS results for other used modifications like ODA–clinoptilolite adsorbed either by chromate or arsenate emphasized that the samples were not homogenoeus, i.e. there were sites with or without high metal (Cr, As) content; however arsenic was present in all modifications to a significantly higher extent than chromium. Likewise, clinoptilolite and ODA probably exhibit a strong chemical interaction with adsorbed counterion that may suppress the absorbance increase typical for both chromate (at 470 nm) and arsenate species. ODA surfactant may create a dendritic, clustered sorption pattern on the clinoptilolite surface and this may lead to agglomerations of surfactant molecules.

According to HR TEM measurements the ODA-modified clinoptilolite adsorbed with arsenate also revealed the clinoptilolite's surface morphology after being affected by the attached chemicals. While the natural clinoptilolite sample was characterized mostly by a typical lattice structure enriched with numerous plates and fibers, the ODA-clinoptilolite contained small particles of high contrast and size of about 5-10 nm. The mostly changed morphology resulted from the final arsenate adsorption, i.e. the analyzed samples contained, except for the previous particles, low contrasted and flower-shaped particles and plates with some holes of about 50 nm. No such pronounced attack was observed by the adsorption of chromate on ODA-clinoptilolite (Fig. 7).

Batch equilibrium measurements

To attain equilibrium a period of about 30 h was necessary for the adsorption of oxyanions onto inorganically exchanged zeolite, whereas for organomodified zeolite and raw montmorillonite about 3 days were necessary.

Some differences in arsenate and chromate adsorption on ODA-clinoptilolite and Pb(Ag)- clinoptilolites were also recorded. ODA-clinoptilolite exhibited more efficient arsenate and chromate removal from aqueous solutions than the inorganically exchanged modifications. However, the silver-exchanged clinoptilolite revealed higher capacity values for the uptake of both oxyanions than lead-exchanged clinoptilolite. This phenomenon supports the preference silver-treated clinoptilolite utilization for specific water purification processes even on the basis of environmental acceptability. Figure 8, illustrates an extensive uptake of the studied oxyanions by montmorillonite, which is mainly based on the large interplanar dimensions of microcrystallite, while modified clinoptilolite samples gradually approached adsorption plateaus. However, it was proven that commercially cheap ODA may sufficiently enhance the capacity of inland clinoptilolite toward anionic species from aqueous solutions and the toxic oxyanions may be surface-attached by Coulombic, van der Waals and hydrocarbon chain tail-tail interactions as intercalated, respectively.

Predominantly, Freundlich adsorption isotherms fitted by simple linear regression were proposed for the mathematical desription of the studied process (Table). According to the correlation coefficients (r), only Ag-exchanged clinoptilolite in both arsenate and chromate solutions was described by Langmuir adsorption model.
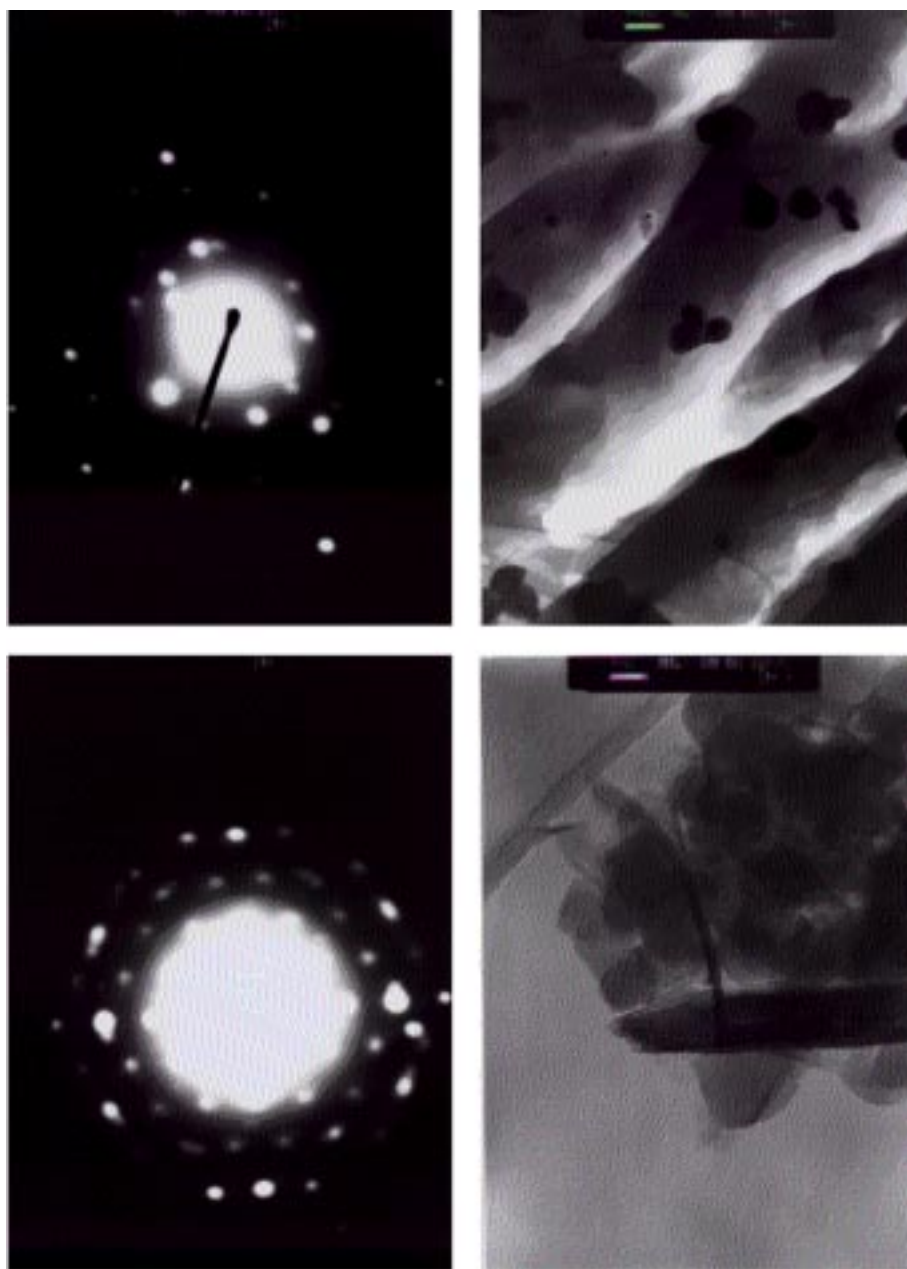
Figure 7. Electron diffraction pattern and HR TEM images of Ag-exchanged clinoptilolite-rich tuff adsorbed with arsenate (upper part) and of ODA-clinoptilolite-rich tuff adsorbed with chromate (lower part).

By batch desorption trials organo- and inorganically modified zeolite was subjected up to 24 h in distilled water, tap water and 2% NaCl aqueous solutions in a laboratory shaker to demonstrate how strongly the examined oxyanions are bound on the modified zeolite. While only a slight chromate desorption at maximum extent, i.e. about 20 mg/L, was observed, arsenate desorption approximately one order higher was found due to increased ionic strength in the water.

Nevertheless, in both cases ODA–clinoptilolite exhibited the lowest desorption characteristics. Here, the desorbed anion concentrations differed negligibly for the above proposed elution reagents.

Table. Freundlich and Langmuir adsorption constants for the studied system.

System	Freundlich model: $a = K \cdot c_{eq}^{1/n}$			Langmuir model: $1/a = 1/(a_{max} \cdot bc_{eq}) + 1/a_{max}$		
	r	K	n	r	a_{max}	b
Montmorillonite -$HAsO_4^{2-}$	0.9980	1.1501	1.9354	0.9616	140.84	0.0008
Montmorillonite - CrO_4^{2-}	0.9209	2.3757	2.5608	0.9006	142.86	0.0006
ODA-clinoptilo-lite-$HAsO_4^{2-}$	0.8648	0.8083	2.0259	0.8922	72.99	0.0014
ODA-clinoptilo-lite-CrO_4^{2-}	0.8906	0.6419	1.9512	0.8048	64.93	0.0009
Ag-clinoptilo-lite-$HAsO_4^{2-}$	0.8935	0.5310	1.9066	0.9422	39.50	0.0009
Ag-clinoptilo-lite-CrO_4^{2-}	0.8805	0.5539	1.9286	0.9920	17.66	0.0376
Pb-clinoptilo-lite-$HAsO_4^{2-}$	0.9324	0.6842	2.3742	0.7614	45.87	0.0006
Pb-clinoptilo-lite-CrO_4^{2-}	0.9394	1.3078	3.0193	0.0264	37.87	0.0009

a, b, K–constants, r–correlation coefficient
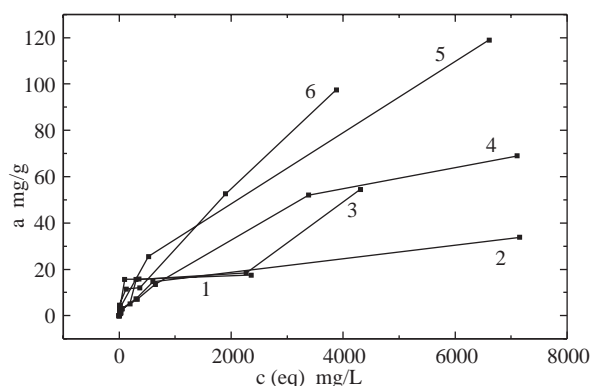
Figure 8. Arsenate and chromate uptakes vs. equilibrium metal concentrations in aqueous model solutions studied: 1 chromate vs. Ag-clinoptilolite, 2 arsenate vs. Ag-clinoptilolite, 3 chromate vs. ODA-clinoptilolite, 4 arsenate vs. ODA-clinoptilolite, 5 arsenate vs. montmorillonite, 6 chromate vs. montmorillonite.

Dynamic fixed bed experiments

The general objective of many case studies dealing with the exploitation of clinoptilolite for water treatment is mostly to define various operational parameters necessary to efficiently remove pollutants through a clinoptilolite bed, and to more accurately predict column performance and thus the costs of the process. Total exchange capacity, chemical and physical stability and major service cycle variables, i.e. hydraulic loading rate, mesh-size, bed depth, and one column vs. series column operation, are commonly verified in the laboratory before pilot-measure operation.

Furthermore, feasibility studies for mass-balance, regeneration-recycling loop by column setting were performed in the laboratory.

Figure 9 presents the partial results of dynamic regime experiments for chromate adsorption and desorption by ODA–clinoptilolite. As shown by the breakthrough curves, ODA–clinoptilolite column quantitatively removed chromate species from simulated waste water apparently more efficiently at a lower flow rate. Due to the similar configuration of chromate and sulfate anions, such a loaded column was more efficiently regenerated with Na_2SO_4 than NaCl solutions, as the elution curves in Figure 9 illustrate.

Arsenate removal by ODA-clinoptilolite proceeded almost analogously with the chromate removal. However, the front part of the breakthrough curve was fairly shallow and indicated an earlier leakage of pollutant into the adsorbate (Figure 10).
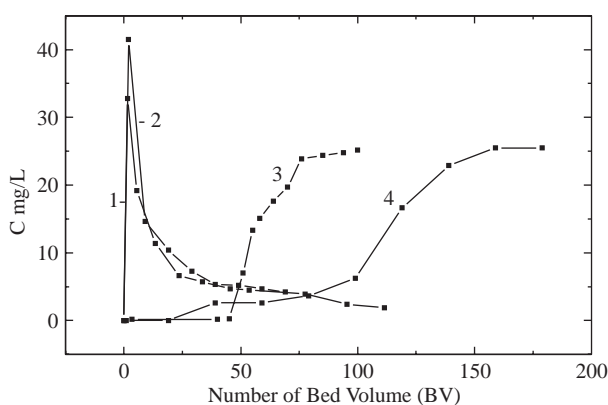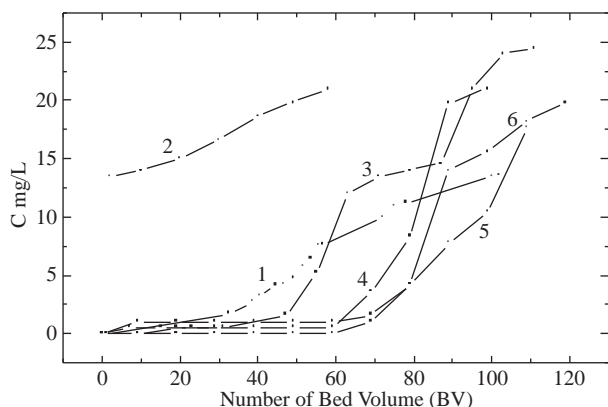

Figure 9. Regeneration of ODA-clinoptilolite columns loaded with chromate by means of 2% NaCl (1) and 2% Na_2SO_4 aqueous solutions (2) and breakthrough curves for ODA-clinoptilolite in 0.5 mM/L chromate solution by 30 BV/h (3) and 15 BV/h in downflow mode (4).
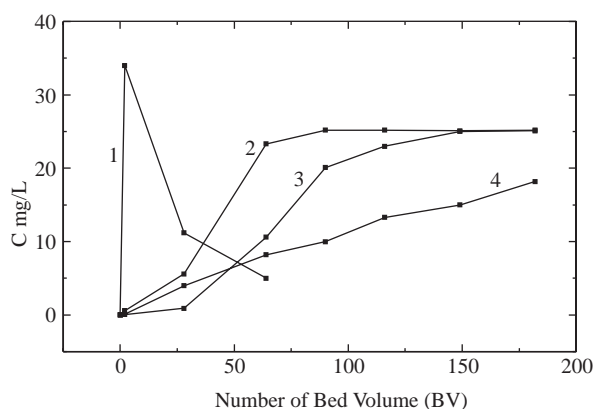
Figure 10. Regeneration of ODA-clinoptilolite column loaded with arsenate by means of 2% NaCl aqueous solution (1) and breakthrough curves for ODA-clinoptilolite for arsenate solution of $c_o = 25$ mg/L (2), repeated cycle after regeneration (3), breakthrough curve on Pb-clinoptilolite (4).

Nevertheless, the reproducible repeated breakthrough curve was recorded after exhausted column regeneration. Inorganically treated clinoptilolite, i.e. Pb-exchanged, did not prove to have such a characteristic breakthrough profile by dynamic arsenate uptake as the organoclinoptilolite had. Although ODA-clinoptilolite preferred either arsenate or chromate with respect to all other anions commonly found in water $[HAsO_4^{2-} (AsO_4^{3-}) > CrO_4^{2-} > SO_4^{2-} > Cl^- > CO_3^{2-} > NO_3^-]$, it cannot be considered absolutely selective and other anions do compete for the available adsorption sites. Figure 11 illustrates the first and second (not reproducible) breakthrough curves for chromate on Pb-clinoptilolite and competitive anions influence each 1 g/L by dynamic chromate adsorption. Figure 12 summarizes both breakthrough curves for chromate and arsenate on ODA-clinoptilolite with the reproducible second breakthrough curves recorded after column regeneration.

An approach to tailor a new natural anion exchanger from ODA–modified clinoptilolite was studied. We repeatedly verified the clinoptilolite enhanced oxyanion uptake mechanism after regeneration and have so far confirmed the feasibility at laboratory level. To set up this process for water treatment in a recycling operation, pilot-scale research is necessary.

Figure 11. Breakthrough curves for chromate on Pb-clinoptilolite: (1) first cycle, (2) second, repeated cycle after regeneration, (3) incl. competitive chloride anions, (4) incl. competitive sulfate anions, (5) incl. competitive nitrate anions, (6) incl. competive chloride, sulfate and nitrate anions.
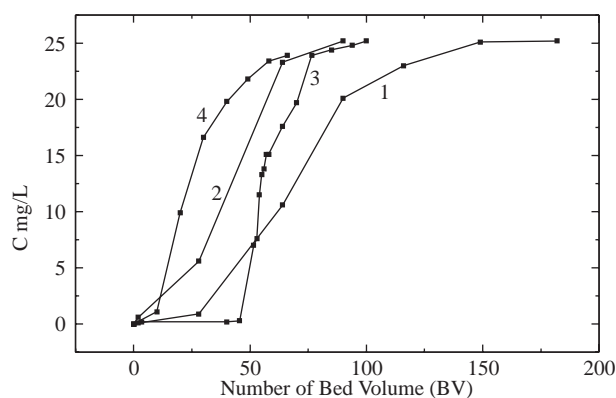
Figure 12. Breakthrough curves for arsenate (1)-first cycle, (2)-second, repeated cycle and chromate (3)-first cycle, (4)-second, repeated cycle on ODA-clinoptilolite.

Acknowledgments

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