ARSENATE AND CHROMATE REMOVAL WITH CATIONIC SURFACTANT-LOADED AND CATION-EXCHANGED CLINOPTILOLITE-RICH TUFF *vs* MONTMORILLONITE

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Using a laboratory set-up, sorption of chromate and arsenate from aqueous solutions with the octadecylammonium acetate (ODA)-modified clinoptilolite was examined. In the experiments, a natural montmorillonite was compared with organically, *i.e.* surfactant-loaded clinoptilolite and with some inorganically substituted (Ag, Pb)-monoforms. The arrangements of the surface-attached ODA chains have been an important factor for the difference in the adsorption states of the guest species (oxyanions). A novel nanostructure inorganic-organic composite prepared has been investigated using SEM, thermogravimetry, UV-VIS diffuse reflectance and powder XRD spectral analytical methods. Finally, adsorption isotherms for the system studied have been measured. An approach for regeneration of exhausted surfactant-immobilized clinoptilolite with inorganic salt solutions under dynamic regime has been proposed.

Keywords: Octadecylammonium clinoptilolite; Adsorption; Anion-exchange; Chromate and arsenate oxyanions; Montmorillonite; Zeolites; Ion exchangers.

Long-chain quaternary ammonium salts on clay minerals have been applied to remove petrochemical spills and to protect ground-water contaminant migration by construction of subsurface impermeable barriers since several decades. In contrast to clays the surface of which has been so far altered by surfactant modifiers, natural zeolitic minerals modified with hydrophobic long-chain amines possess a fairly large potential in future environment protection, especially due to their superior hydraulic characteristics. Organo-modified natural zeolites as new organic-inorganic composites are expected to be used for sorption of anions and organic pollutants from various industrial wastes[1].

Although the process of ion exchange was discovered around the year 1850, it was not applied as an industrial separation process until 1905, when the German scientist R. Gans demonstrated its usefulness for water

softening and removal of iron as well as manganese. Extensive development of new organic ion exchangers predominantly after Second World War enabled a rapid expansion of industrial applications of the ion-exchange processes. However, the greater stability of some natural zeolites in comparison with organic ion exchangers under certain conditions and their high selectivity to particular ions have combined to allow the development of new environmental applications of natural zeolites. Although, as noted above, natural zeolites possess attractive ion-exchange properties, they have not found significant use as ion exchangers until the early 1960's when the pioneering work of U.S. scientists L. L. Ames and B. W. Mercer was done[2]. Those scientists who verified ion exchange and selectivity properties of clinoptilolite in ^{137}Cs and ^{90}Sr radioisotopes recovery and ammonium salts removal from municipal waste waters.

Arsenic and chromium may be found in water which flowed through metal-rich rocks. Serious health effects have been observed in populations drinking toxic metal-contaminated water over long periods in countries worldwide. The technology of arsenic and chromium removal for water supply is moderately costly and requires technical expertise. Inorganic arsenic and chromium are documented human carcinogens[3,4].

Chromate sorption with cationic surfactant-loaded clinoptilolite from New Mexico (U.S.A.) was studied by Li and Bowman[5], chromate, selenate and sulfate removal from aqueous model solutions by Haggerty and Bowman[1], however, using the different hexadecyltrimethylammonium (HDTMA)-modified clinoptilolite. Arsenate sorption with HDTA-modified clinoptilolite of Greek origin was investigated by Misaelides *et al.*[6] Industrial water treatment processes for the above pollutants removal are so far the enhanced coagulation and precipitation, ion exchange, adsorption on iron oxide-coated sand or costly membrane technologies[7].

The objective of our study was to examine the arsenate and chromate removal with cationic surfactant-loaded and cation-exchanged clinoptilolite-rich tuff of Slovak origin compared with domestic montmorillonite. A primary ammonium instead of quaternary ammonium salt was selected due to a long-term tradition of ODA-bentonite production in the Kremnica plant in Slovakia. Thus in analogy, a small costs of future industrial zeolite hydrophobization may be expected.

EXPERIMENTAL

In this study, clinoptilolite tuff of domestic origin, supplied by the Company Zeocem Bystré, was used. Industrial exploitation of zeolite in the Nižný Hrabovec quarry is performed by

transporting the disintegrated material to a hammer crushing line and thereafter to a rotating drum drier. The process continues by grinding zeolite in a two-chamber mill (grinding balls) and screening. A grain-sized zeolite fraction (0.3–1.0 mm) was obtained for laboratory experiments.

Mineral composition of zeolite tuff was determined using a computer controlled (Philips) diffractometer, equipped with APD analytical software, with the parameters: CuKα radiation, voltage 30 kV, intensity 15 mA, Co/Ni filter, time 1 s, 0.1-s step.

Freshly broken rock surfaces were scanned with an electron microscope Electron Probe Microanalyser JEOL JXA 840A (Japan), 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.

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

Physico-chemical and mineralogical characterization of the clinoptilolite tuff studied is reported elsewhere[8]. Montmorillonite isolated from bentonite by sedimentation, wet sieved and powdered, (<5 μm particle size) originated from the Central Slovakian deposit Jelšový potok[9]. Montmorillonite content in the bentonite ore ranges from 40 to 80%.

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, at UV-VIS scan rate 600 nm/min, data interval 1000 nm, beam mode double reverse, SBW 2.0 nm and average time 0.100 s.

All water analyses were performed in accordance with the procedure described in standard methods for examination of water and wastewater[10]. Total arsenic concentrations were determined using inductively coupled plasma ICP AES spectrometry (ICP 2070 Spectrometer – Baird, U.S.A.) with pneumatic nebulisation. Cr concentrations were analysed by atomic absorption spectrometry with flame atomization on a Perkin–Elmer apparatus, model 1100 (U.S.A.).

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

Apparent Equilibrium and Feasibility Studies

To establish the most efficient surfactant counterion (chromate, arsenate) in sorption with ODA clinoptilolite, a batch sorption procedure was performed using various initial ODA concentrations (all greater than the critical micelle concentration (CMC)) and the same weight/volume ratios. A mixture of 20 g of raw clinoptilolite-rich tuff and 100 ml of an aqueous ODA solution (0.001, 0.01, 0.1, 0.2 mol/l) was stirred in a glass vessel at 60 °C for 24 h using an MLW ER 10 lab assembly.

This time was considered sufficient to achieve sorption equilibrium. pH of the equilibrium solutions was kept at 3.0 on average by addition of 98% acetic acid. The mixture was then paper-filtered using a heated Buchner funnel to yield a clear supernatant solution and ODA-treated clinoptilolite. The zeolite was washed with distilled water, dried in a Premed KBC laboratory drier at 60 °C and ground in a mortar.

The sorption of chromate and arsenate from aqueous solutions with ODA-modified clinoptilolite was measured in a laboratory set-up using the above 0.2 mol/l initial ODA

concentration. This modification showed the most efficient counterion sorption. No significant CHN-elemental increase by that ODA-clinoptilolite samples was recorded, which were prepared with the last two, *i.e.* 0.1 and 0.2 mol/l initial ODA concentrations. According to the CHN analyses, performed on a Perkin–Elmer 2400 Elemental Analyser (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 the experiments, a natural variety of montmorillonite was compared with surfactant-loaded clinoptilolite and with some inorganically substituted (Ag, Pb)-monoforms, assumming they form on the zeolite surface chemically bound precipitates of silver or lead arsenates and chromates[11]. The crushed, raw zeolite samples were loaded with 4% silver nitrate or lead acetate aqueous solutions following conventional ion exchange procedures, reported by many other authors[12]. This chemical treatment ensured the maximum saturation of natural clinoptilolite with silver cations (86 mg/g) and lead cations (64 mg/g) according to our previous study[13].

A mixture of 0.5 g of either the organo-treated or cation-exchanged zeolite and 50 ml of 10 mmol/l arsenate or chromate aqueous solutions in an Erlenmeyer flask was mechanically shaken to attain equilibrium. Different equilibrium periods for individual modifications and both aqueous oxyanion species have been established.

Adsorption isotherm experiments were conducted using above mass/volume ratio of samples with initial metal concentrations ranging from 0.5 to 100 mmol/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 the equilibrium.

Batch desorption experiments have been performed to assess the bounding 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 initial metal concentrations in tested solutions were about 0.5 mmol/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_2SO_4, Na_2CO_3) were examined.

RESULTS AND DISCUSSION

Zeolite Characterization

Mineralogical analysis of the Slovak clinoptilolite-rich tuff reveals the presence of clinoptilolite (60%), volcanic glass (10%), feldspar (10%) and minor quantities of cristobalite, quartz and plagioclase (20%). Diffractometer traces are typical of well-crystallized clinoptilolite corresponding with d-spacings (Fig. 1).

Physico-chemical properties of the used montmorillonite are published in ref.[14] On the basis of crystallochemical analyses following formula of the montmorillonite was drawn:

$$(Si_{7.98}Al_{0.02})(Al_{3.01}Fe_{0.23}Mg_{0.76})(Ca_{0.37}Mg_{0.01}Na_{0.02}K_{0.01})O_{20}(OH)_4.$$

Photomicrographs of the natural (unmodified) clinoptilolite samples exhibited well-defined tabular-shaped crystals with excellent crystal edges. On surface covering with a polymerous, smaller, more agglomerated crystals and more poorly defined crystal edges were observed in *ca* 1-μm scale SEM image. The apparent sharpness of the images decreased with increasing surfactant coverage (Figs 2, 3).

Figures 4, 5 and 6 show weight losses for raw clinoptilolite, ODA and ODA-modified clinoptilolite. Almost all the ODA is lost upon heating to

2 theta
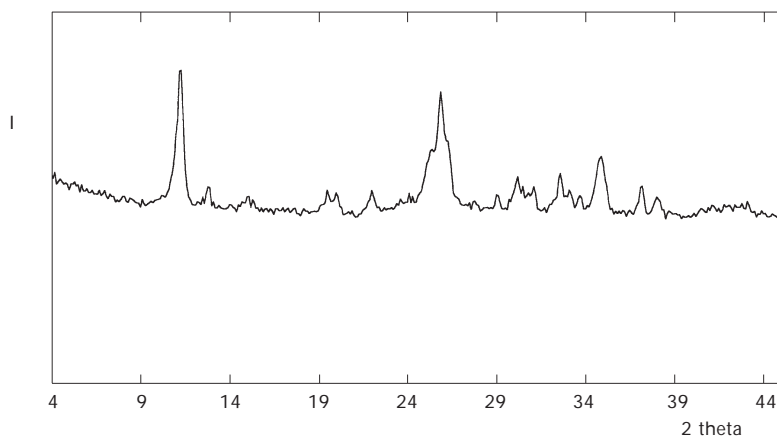
FIG. 1
XRD pattern of clinoptilolite-rich tuff from the deposit Nižný Hrabovec

FIG. 2
SEM micrograph of raw clinoptilolite-rich tuff from Nižný Hrabovec (East Slovakia); magnification 3700 X

230 °C as can be observed in the derivative curve. A part of the weight loss, 12.8%, occurs for the raw clinoptilolite from 30 to 400 °C due to water desorption, with a characteristic endothermic peak at about 150 °C. In the weight loss curves for the ODA-modified clinoptilolite, a gradual loss due to both water desorption, ODA pyrolysis and desorption was observed. In the derivative curves of the modified clinoptilolite, pronounced water-loss peak occurs at about 150 °C; further water loss is the cause of the continuous gradual slope rise of the baselines up to 800 °C. Weak, broad peaks at about 230–300 °C are seen on the derivative curves, corresponding probably to pyrolysis of ODA from intermediate and higher-energy bonding sites, *i.e.* those closely bound to the clinoptilolite surface.
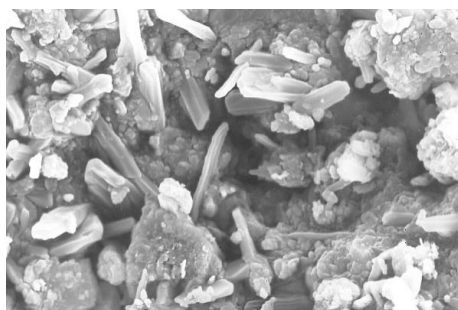

Fig. 3
SEM micrograph of organo-modified clinoptilolite-rich tuff from Nižný Hrabovec (East Slovakia); magnification 3000 X
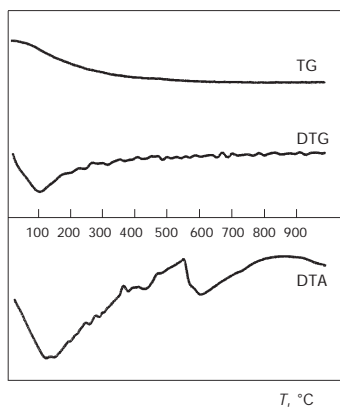

Fig. 4
TGA derivative curves of raw clinoptilolite-rich tuff

According to Fig. 7, UV-VIS diffuse reflectance spectra for Ag^+-substituted clinoptilolite with adsorbed arsenate clearly indicated that silver occurs partly in the Ag^+ states (absorbance peak at 220 nm), in the form of small clusters (less than 10 atoms; the absorbance peak at 325 nm) and in the form of large metallic particles (broad peaks at 420 and 580 nm). Summarizing, DRS results for other used modifications such as ODA clinoptilolite with adsorbed chromate or arsenate showed that the samples were not homogenous, *i.e.* there were sites without or sites with high metal (Cr, As) contents; however, arsenic was present in all modifications to a signifi-
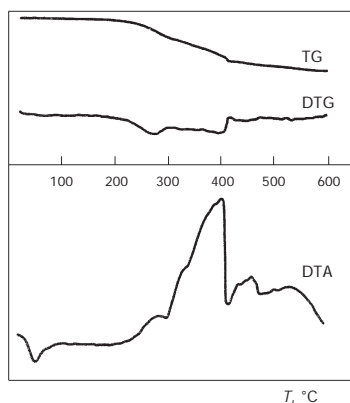

FIG. 5
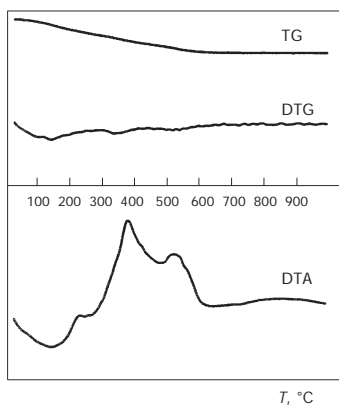TGA derivative curves of ODA modifier

FIG. 6
TGA derivative curves of ODA-modified clinoptilolite

cantly higher extent than chromium. Likewise, clinoptilolite and ODA exhibit probably a strong chemical interaction with the adsorbed counterion, which may suppress an absorbance increase typical of both chromate (at 470 nm) and arsenate species. The ODA surfactant may form on the clinoptilolite surface dendritic, clustered sorption pattern and thus agglomerations of surfactant molecules.

Batch Adsorption and Desorption Experiments

To attain equilibrium, *ca* 30-h period was necessary for oxyanion adsorption on inorganically exchanged zeolite, whereas about 3 days for the organo-modified zeolite and raw montmorillonite.

Some differences in arsenate and chromate adsorption with ODA clinoptilolite and Pb(Ag)-clinoptilolites as well were 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 sorption of both oxyanions uptake than the lead-exchanged clinoptilolite did. This phenomenon supports the preferable use of silver-treated clinoptilolite for specific water purification processes, also on the basis of environmental acceptability[15]. As the Fig. 8 illustrates, based chiefly on the interplanar dimensions of large microcrystallites, an extensive sorption of
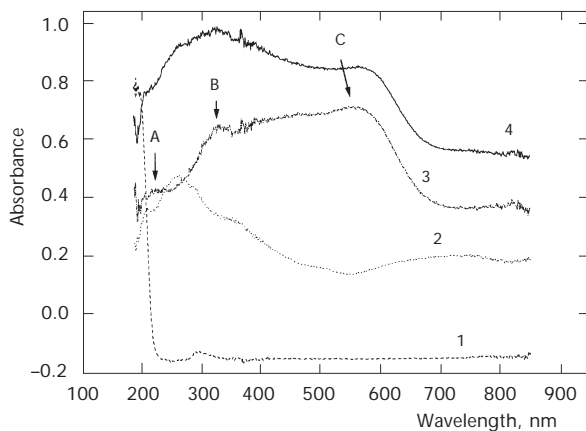

FIG. 7
UV-VIS diffuse reflectance spectra of pure arsenate salt (1), raw clinoptilolite-rich tuff (2), subtracted spectrum 4-2 (A, silver cations; B, silver clusters; C, silver large particles) (3), Ag-clinoptilolite–arsenate (4)

oxyanions with montmorillonite was observed, while modified clinoptilolite samples gradually approached adsorption plateaus. However, it was proved that cheap ODA may sufficiently enhance the capacity of domestic clinoptilolite for anionic species from aqueous solutions. The toxic oxyanions may be surface-attached by Coulombic, van der Waals and hydrocarbon chain interactions.

Predominantly, Freundlich adsorption isotherms fitted by simple linear regression were proposed for the description of the process studied (Table I). The constants of adsorption isotherms were calculated from the mean values of parallel measurements for each curve.

In batch desorption experiments, organo-modified and inorganically modified zeolites with adsorbed oxyanions were treated for 24 h with distilled water, tap water or 2% NaCl aqueous solution on a laboratory agitator to demonstrate how strongly the examined oxyanions are bound on the modified zeolite. While only slight chromate desorption was observed (max. 20 mg/l), one order higher arsenate desorption was found, proportionally to increasing ionic strength of the media.

Nevertheless, in both cases ODA clinoptilolite exhibited the lowest desorption characteristics. The desorbed anion concentrations negligibly differed for the above media.
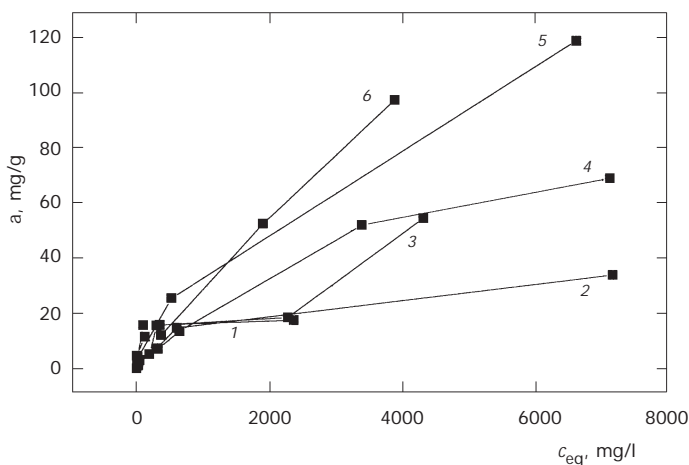

FIG. 8
Arsenate and chromate adsorption *vs* equilibrium metal concentrations in aqueous model solutions studied: *1* chromate *vs* Ag-clinoptilolite, *2* arsenate *vs* Ag-clinoptilolite, *3* chromate *vs* ODA clinoptilolite, *4* arsenate *vs* ODA clinoptilolite, *5* arsenate *vs* montmorillonite, *6* chromate *vs* montmorillonite

TABLE I
Freundlich and Langmuir adsorption constants computed for the system studied

System studied	Freundlich model: $a = K c_{eq}^{1/n}$					Langmuir model: $1/a = 1/(a_{max} b c_{eq}) + 1/a_{max}$				
	A	B	r	K	n	A	B	r	a_{max}	b
montmorillonite–$HAsO_4^{2-}$	0.0607	0.5167	0.9980	1.1501	1.9354	9.1378	0.0071	0.9616	140.84	0.0008
montmorillonite–CrO_4^{2-}	0.3758	0.3905	0.9209	2.3757	2.5608	11.8358	0.0070	0.9006	142.86	0.0006
ODA–clinoptilolite–$HAsO_4^{2-}$	−0.0924	0.4936	0.8648	0.8083	2.0259	12.0265	0.0137	0.8922	72.99	0.0014
ODA–clinoptilolite–CrO_4^{2-}	−0.1925	0.5125	0.8906	0.6419	1.9512	16.2135	0.0154	0.8048	64.93	0.0009
Ag–clinoptilolite–$HAsO_4^{2-}$	−0.2749	0.5245	0.8935	0.5310	1.9066	27.88	0.0253	0.9422	39.50	0.0009
Ag–clinoptilolite–CrO_4^{2-}	−0.2565	0.5158	0.8805	0.5539	1.9286	1.5063	0.0566	0.9920	17.66	0.0376
Pb–clinoptilolite–$HAsO_4^{2-}$	−0.1648	0.4212	0.9324	0.6842	2.3742	34.0961	0.0218	0.7614	45.87	0.0006
Pb–clinoptilolite–CrO_4^{2-}	0.1165	0.3312	0.9394	1.3078	3.0193	29.8988	0.0264	0.0264	37.87	0.0009

Laboratory Column Runs

The general objective of many studies dealing with exploitation of clinoptilolite for water treatment is mostly to define various operational parameters to efficiently remove the pollutant and to predict more accurately the column performance and thus the process costs. Total exchange capacity, chemical and physical stability and major service cycle variables, such as hydraulic loading rate, mesh-size, bed depth, single-column *vs* column-series operation, are commonly verified in laboratory and pilot-plant operation.

Mass-balance and regeneration-recycling cycles were investigated by column in laboratory. Figure 9 presents partial results of dynamic experiments for chromate adsorption and desorption with ODA clinoptilolite. As shown by breakthrough curves, the ODA-clinoptilolite column quantitatively removed chromate species from simulated waste water, apparently more efficiently at lower flow rates. Due to similar configuration of chromate and sulfate anions, such a loaded column was more efficiently regenerated with Na_2SO_4 than NaCl solutions, as elution curves in Fig. 9 illustrate. Arsenate removal with ODA clinoptilolite proceeded almost analogously to chromate removal; however, the front part of the breakthrough curve was fairly shallow and indicated earlier leakage of pollutant into adsorbate
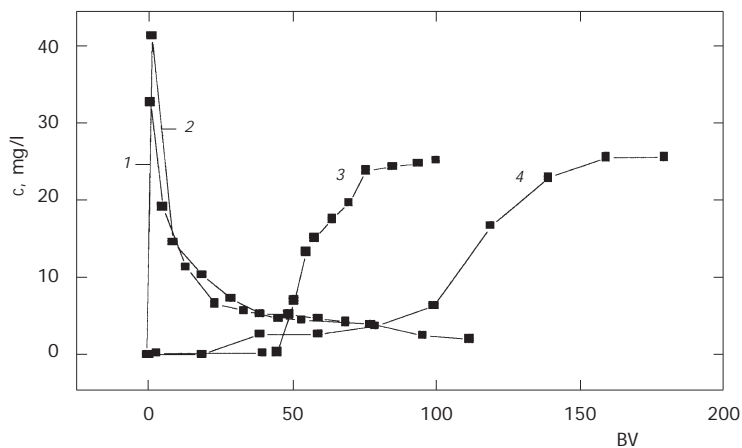
F<small>IG</small>. 9
Regeneration of chromate-loaded ODA-clinoptilolite columns with 2% NaCl (*1*) and 2% Na_2SO_4 aqueous solutions (*2*) and breakthrough curves for ODA clinoptilolite with 0.5 mmol/l chromate solution at 30 BV/h (*3*) and 15 BV/h in the downflow mode (*4*)

(Fig. 10). Nevertheless, reproducible repeated breakthrough curve was recorded after regeneration of the exhausted column. Inorganically treated clinoptilolite, namely the Pb-exchanged did not show such a characteristic breakthrough profile in the dynamic arsenate sorption as the organo-clinoptilolite did. Although ODA clinoptilolite preferred arsenate or chromate to all other anions commonly found in waters the order was [$HAsO_4^{2-}$ (AsO_4^{3-}) > CrO_4^{2-} > SO_4^{2-} > Cl^- > CO_3^{2-} > NO_3^-], it cannot be considered as absolutely selective and other anions do compete for available adsorption sites. As the last two plots show, an enhanced oxyanion sorption mechanism of ODA clinoptilolite was repeatedly verified after regeneration and thus confirmed the feasibility of the column operation on laboratory level. However, to design this process for water treatment in recycling operation, a pilot-plant research is necessary.

CONCLUSIONS

On the basis of realized experimental work and the analyses performed, following conclusions can be made.

An approach to tailor a new natural anion exchanger from ODA-modified clinoptilolite was studied. ODA opposite to long-chain quaternary ammonium salts is cheap and commercially available.
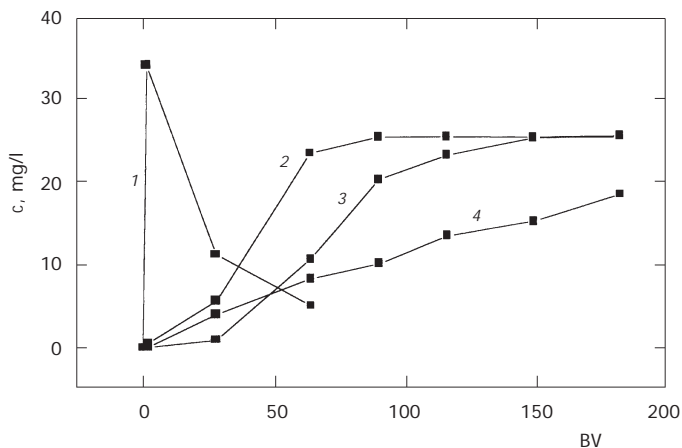

FIG. 10
Regeneration of arsenate-loaded ODA-clinoptilolite column with 2% NaCl aqueous solution (*1*) and breakthrough curves for ODA clinoptilolite with arsenate solution of 25 mg/l initial concentration (*2*); repeated cycle after regeneration (*3*); breakthrough curve for Pb-clinoptilolite (*4*)

While the clinoptilolite-rich tuff as natural cation exchanger does not or negligibly adsorb chromate or arsenate on the external surface, an enhanced adsorption was recorded with inorganically substituted (Ag, Pb)-monoforms, probably due to chemically bound precipitates of Ag(Pb)-arsenate or chromate on the zeolite surface.

Considerable higher increase of adsorption characteristics than with cation-exchanged forms was observed with surfactant-modified clinoptilolite, however, lower than with compared natural montmorillonite. As expected, the large interplanar dimensions of montmorillonite structure allowed the most extensive adsorption of both oxyanions. The values around 12.5 Å are typical of montmorillonite with only one water layer in the interlamellar space, whereas stable 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 into the voids range only from 2.6 to 7.6 Å [16].

Regarding the intensity of surface-attached anions, the desorption experiments performed with the increasing ionic strength media, favoured the ODA-modified clinoptilolite. Sufficiently strong surface-attached oxyanions and superior hydraulic properties of grain-sized natural zeolite prefered ODA-modified clinoptilolite for the further column experiments.

As shown by plotted breakthrough curves, the ODA-clinoptilolite columns quantitatively removed chromate or arsenate species from aqueous model solutions and reproducible repeated breakthrough curves were recorded after regeneration with 2% NaCl (Na_2SO_4) regenerant solutions.

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