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Preparation and application of organo-modified zeolitic material in the removal of chromates and iodides

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Abstract

The removal of chromates and iodides from aqueous solutions by organo-modified tuffs from the Pentolofos area (Thrace, Greece) was investigated using ^{51}Cr- and ^{131}I-labelled solutions and gamma-ray spectroscopy. The zeolitic material was modified by hexadecyltrimethyl-ammonium bromide (HDTMA-Br) and octadecyltrimethyl-ammonium bromide (ODTMA-Br) and characterized by scanning electron microscopy, FT-IR spectrometry and zeta potential measurements.

Both experimental study and modelling indicated that both organo-zeolitic sorbents have a bigger affinity for iodide than for chromate. The chromium uptake did not seem to be influenced by the type of modifier but showed, as expected, a dependence on the solution pH. The maximum sorption capacity (2.27 mg/g) of Cr(VI) was achieved for the solution of initial pH 4. On the other hand, the HDTMA-modified tuff showed a lower sorption affinity for iodides than did the ODTMA-modified one (3.37 and 4.02 mg/g, respectively).
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1. Introduction

Chromium and iodine are rated among elements absolutely necessary for the living organisms. However, despite chromium's relatively high abundance in nature (average concentration in the earth's crust: ca. 100 mg/kg), it is considered as a high-priority environmental pollutant. Its concentration in industrial effluents (e.g., from the leather tanning, metallurgy and plating industries) reaches up to 50 000 mg/L, with an average concentration of 50 mg/L. The toxicity of chromium strongly depends on its oxidation state. The trivalent chromium Cr(III) is an essential dietary nutrient but can be toxic at high doses. On the other hand, Cr(VI) has been associated with increased incidence of lung cancers. The different bioavailability and bioactivity between the trivalent and hexavalent species might account for the differences in toxicity [1].

As regards iodine, 90% of this element is concentrated in the thyroid gland of the human body. Iodine isotopes ^{131}I ($T_{1/2} = 8.02$ days) and ^{129}I ($T_{1/2} = 1.57 \times 10^7$ years) are produced with high yield during ^{235}U-fission and are liberated during the normal operation of nuclear reactors and reprocessing facilities as well as in the cases of nuclear accidents [2,3].

Both chromium and iodine are present in aqueous solutions in various anionic forms (CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$, I^- and IO_3^-) which can be toxic to living beings even at μg/L concentrations. Among the different techniques proposed for their removal (e.g., reduction/precipitation [4,5], biosorption [6–8], and nano- and ultrafiltration [9–11]), adsorption on natural and synthetic sorbents still seems to be quite attractive [12–14]. Bailey et al. [15] and Dakiky et al. [16] already presented the application of a number of low-cost sorbents to the removal of heavy metals from aqueous solutions, whereas Haggerty and Bowman [17], Nikashina et al. [18] and Zamboulis et al. [19] presented the sorption of chromates on organo-modified natural tuffs.

The natural zeolites are microporous aluminosilicate materials that can occur as mm- or greater-sized particles in many parts

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of the world and are free of shrink/swell behavior. This can result in superior hydraulic characteristics and make them suitable for use in filtration systems and in permeable barriers slowing or preventing the migration of dissolved hazardous metals in the biosphere [20]. Due to the isomorphic substitution of silicon by aluminium atoms in their crystal lattice that is compensated by exchangable cations (e.g., H^+, Na^+, K^+, Ca^{2+}), natural zeolitic materials possess a negatively charged surface and therefore mainly cation exchange properties. However, recent investigations have shown that chemical treatment and modification of the zeolite surface can also provide them with an affinity for inorganic anions and non-polar organic species, while retaining much of their sorption capacity for metal cations [21]. Moreover, modified zeolitic materials can protect drinking water from viruses and bacteria [22]. Since anion and pathogen contamination of drinking water is a worldwide problem, research into the process of removal of these species by surface-modified zeolite sorption is of significant practical importance. Therefore, the objective of this work was to prepare, characterize and investigate the sorption properties of surface modified forms of the Pentalofos zeolitic materials. Chromates and iodides were selected as test anions for the evaluation of sorption capacity of the materials.

2. Experimental

2.1. Materials

A natural clinoptilolite-rich tuff from the Pentalofos area, Thrace, Greece was used for the investigations. The mineral content of the zeolitic material from quarry face, based on the XDR technique, was clinoptilolite 93 wt.% accompanied by small amounts of accessory minerals such as feldspars (plagioclase and sanidine) 2 wt.%, micas and clays 4 wt.%, quartz 1 wt.%. Water content ranged between 13.4% and 14.4% [23]. Cation exchange capacity calculated from the sum of the exchangeable cations ranged from 1.19 to 1.52 meq/g [24]. The grain size of the material used for the experimental work was 0.5–1.0 mm.

2.2. Surface modification

The Na-form of the zeolitic material was prepared prior to modification. For this purpose the zeolitic material was agitated for 48 h in a 1 M NaCl solution at 25 °C, washed using distilled water until free of chloride ions (AgNO$_3$ test) and dried at 105 °C to constant weight.

The chemical modification was performed according to Li and Bowman [26], by physical immobilization of the bromide salts of hexadecyl-trimethyl-ammonium (HDTMA, $CH_3(CH_2)_{15}N(CH_3)_3^+$) and octadecyl-trimethyl-ammonium (ODTMA, $CH_3(CH_2)_{17}N(CH_3)_3^+$). For this purpose 1–2 g of the zeolite in Na-form were mixed for 12 h with 10 mL of surfactant solution in 15-mL centrifuge tubes placed in the rotary evaporator and shaken at 150 rpm. Solutions of HDTMA-Br concentrations 10, 60 and 120 mg/L and ODTMA-Br concentration 60 mg/L were utilized for the modification (modification temperature: 33 °C). Following modification the materials were

thoroughly washed using distilled water and dried at 25 °C for 12 h.

2.3. Characterization of the zeolitic material

The raw as well as the Na- and surface-modified forms of the zeolitic material were characterized by:

(1) Scanning electron microscopy (JEOL 840A SEM equipped with an OXFORD ISIS 300 SEM-EDS analyzer). To avoid charging effects during observations an ion sputtering device (JOEl JFC 1100) was used for fine gold coating of the single crystals.
(2) FT-IR spectroscopy (Perkin-Elmer Spectrum One FT-IR). The FT-IR spectra in the wave number range from 200 to 4000/cm were obtained with the use of the Kbr pellet technique. The pellets were obtained from a mixture of the zeolite and dried at 45 °C Kbr (ratio about 1:200) and were then subjected to a pressure of about 10 tons/cm^2.
(3) ζ-potential measurements as a function of solution pH (Rank Brothers, Particle Microelectrophoresis Mark II). 10 mg of the zeolite in different forms were mixed for 24 h with 10 mL of deionized water in 15-mL centrifuge tubes placed in the rotary evaporator. The pH range of deionized water for the Na-form zeolite was 3.0–7.1; for the HDTMA-form zeolite, 4.2–9.2; and for the ODTMA-form zeolite, 4.2–9.9. After that, samples were placed in a glass cell and treated by applying a voltage which makes the particles move to towards the anode or cathode. The ζ-potential value was estimated as an average value of 10 measurements.

2.4. The sorption experiments

The iodide sorption experiments were conducted using solutions of initial concentration between 10 and 500 mg/L prepared by dissolution of the appropriate amount of NaI (Merck, analytical grade) in doubly distilled water. The solutions were labelled with a small amount of radioactive Na ^{131}I solution. The iodine-131 has a decay time of 8 days and emits γ-radiation of 364 keV energy. The initial pH of the solutions was adjusted to 4 using CH$_3$COOH.

The Cr(VI) sorption experiments were performed using solutions of initial chromium concentration between 20 and 500 mg/L prepared by the dissolution of an appropriate amount of K$_2$CrO$_4$ (Merck, analytical grade) in doubly distilled water. The solutions were labelled with a small amount of radioactive K$_2$^{51}CrO$_4$ solution. Chromium-51 has a decay time of 27.7 days and emits γ-radiation of 321 keV energy. The initial pH of the solutions was adjusted to 4 and 7 using CH$_3$COOH.

For the individual experiments 0.1 g of organo-modified zeolitic materials were shaken for 24 h with 10 mL of the individual solutions in polycarbonate centrifuge tubes at ambient temperature. Preliminary experiments indicated that the contact time of 24 h was sufficient for the establishment of equilibrium. The pH of the solutions was checked before beginning and at the end of the sorption experiments. Duplicate samples were prepared for all experimental conditions.

Table 1
Analysis of the zeolitic material utilized (all data expressed as oxides, % w/w)

Element	Raw	Na-form	Modified 10 mg/L HDTMA
SiO_2	58.47	63.76	59.95
Al_2O_3	12.25	15.43	14.75
CaO	1.52	0.79	0.64
K_2O	3.22	2.15	2.12
Na_2O	0.46	3.47	2.83
Fe_2O_3	2.77	1.17	1.57
MgO	1.42	1.11	1.12

Following sorption, the liquid phase was separated from the solid by centrifugation. Chromium and iodine concentration was determined in 2 mL of sample of the solutions by high resolution γ-ray spectroscopy using a high purity Ge-detector (Canberra REGe-detector, efficiency 20% relative to $3 \times 3''$ NaI(T1) detector; energy resolution 2.1 keV for 1.332 MeV ^{60}Co γ-radiaton) connected to a standard γ-ray spectrometry set-up (computer-based Oxford PCA3 data acquisition and analysis card).

The equilibrium concentration of the solutions was calculated taking into account the activity of the solutions before and after the sorption, whereas the chromium and iodine uptake q (mg/g) was calculated from the difference between the initial c_0 (mg/L) and final c (mg/L) concentrations of the anions of the solutions:

$$q = \frac{V}{W}(c_0 - c) \tag{1}$$

where V is the volume of the solution (L) and W is the mass of the dry zeolite (g).

3. Results and discussion

3.1. Characterization of zeolitic material

The analysis of the raw zeolitic material used for the experimental work obtained by SEM/EDS is given in Table 1. The Si/Al ratio of the material is 4.22 corresponding to a classical HEU-type zeolite (range: 4.0–5.2).

The treatment of the zeolite with NaCl caused an almost seven-fold increase of its sodium content at the expense of Ca^{2+}, Mg^{2+}, Fe^{2+}, and K^+. On the other hand, the treatment of the Na-form of the zeolite by the quaternary amine solutions leads only
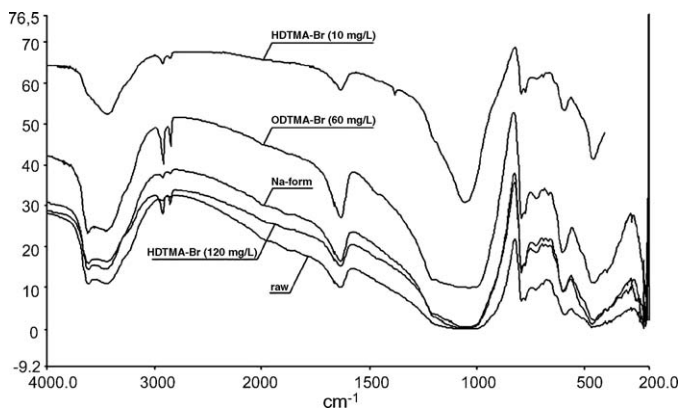

Fig. 2. IR spectra of the raw zeolitic material, its Na-form and zeolite samples treated by 10 and 120 mg/L of HDTMA-Br as well as by 60 mg/L of ODTMA-Br.

to partial removal of Na, suggesting that the organic amino-groups containing cations are sorbed via ion-exchange but only to places easily accessible to molecules of big dimensions. Thus, this process is limited to the external surface of the zeolite grains.

However, according to Li and Bowman, the sorption of a cationic surfactant onto a negatively charged zeolite surface is a complex process involving both cation exchange and hydrophobic bonding [25].

The modification of the zeolitic material after treatment with the HDTMA-Br solution was verified by the FT-IR spectra and the SEM/EDS examination of the material.

Fig. 1 presents a SEM microphotograph of the raw Pantalofos tuff (A) and a sample modified by 10 mg/L HDTMA-Br (B). Field observation and macroscopic study of the samples revealed that raw zeolitic material occurs predominantly as well-formed crystals (Fig. 1A). However, the crystal structure of zeolite is indiscernible when its surface is covered with an organic layer (Fig. 1B). The formation of an organic layer on the zeolitic material is obvious, whereas a few naked HEU-type zeolite crystals can be seen only in the upper left part of the Fig. 1B.

The FT-IR spectra of the raw tuff and its Na-form are given in Fig. 2. The spectra of the zeolitic material modified by 10 and 120 mg/L HDTMA-Br as well as by 60 mg/L of ODTMA-Br
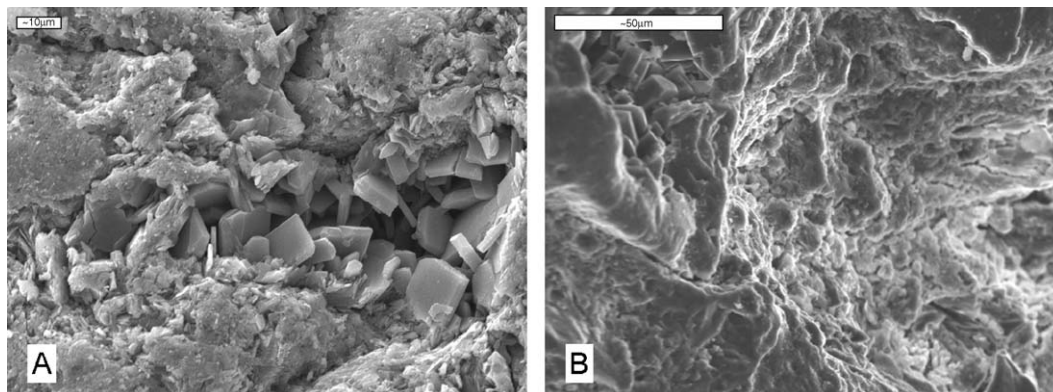

Fig. 1. Scanning electron microphotograph of the Pentalofos tuff (A) raw, (B) modified by 10 mg/L HDTMA-Br.

are also shown in the same picture. The spectra contain bands due to

(1) Si–O–Si and Si–O–Al vibrations (1200–950 cm^{-1}),
(2) the presence of zeolitic water (3619, 3440 and 1640 cm^{-1}) and
(3) pseudo-lattice vibrations (800–500 cm^{-1}). The peak at 602 cm^{-1} is a special characteristic of the HEU-type zeolites [24].

The spectra of the organo-modified materials had additionally two intense bands in the region 3000–2800 cm^{-1} assigned to the asymmetric and symmetric stretching of the C–CH$_2$ group of the alkyl chain. As can be seen, their intensity increases with the increasing of HDTMA-Br concentration from 10 to 120 mg/L. However, the bands obtained for zeolite modified by 60 mg/L of ODTMA-Br are more intensive than this observed for 120 mg/L of HDTMA-Br. This indicates that the amount of organic material on the zeolite surface is more strongly affected by the length of aliphatic chain of the organic modifier than by its concentration. On the other hand, the expected scissoring oscillations due to the methylene groups of the aliphatic chain (1460 cm^{-1}) were not observed. These bands could be covered by the wide band due to Si–O or shifted according to the structural order of the methylene chain group [26]. Similarly, the vibrations associated with the symmetric and asymmetric CH$_3$–N stretching were not observed in the FT-IR spectra of organo-zeolitic material. According to Sullivan et al. this behavior indicates lower hydration of the sorbed head-groups (quaternary ammonium) than of those in solution [27].

The results of the ζ-potential measurements (Fig. 3) show that the negative surface charge of Na-form of the zeolite changed to positive after modification. The charge reversal indicated that the ionic surfactants form an organic layer coating the charged surface. It is supposed that surfactant was initially sorbed by cation exchange, and later by hydrophobic forces. These additional molecules were bonded to the surface via non-electrostatic

mechanisms to form admicelles or a bilayer [28]. Admicelles were bound by weak bonding and probably do not cover a significant surface area of organo-zeolite, regardless of the amount of surfactants initially sorbed [29].

As can be seen in Fig. 3, the positive charge measured on the zeolite surface modified by 60 mg/L ODTMA-Br is almost two times higher than that of the material treated by 120 mg/L HDTMA-Br. This confirms that the amount absorbed depended on the number of CH$_2$ groups in the organic modifier. Bowman et al. found that ζ-potential do vary with surfactant loading, but not with solution form of the surfactant [21]. The explanation of the difference in HDTMA and ODTMA adsorption could be that at 120 mg/L HDTMA-Br concentration, the surfactant solution may be cloudy because of the low solubility of the surfactant. Moreover, some part of HDTMA-Br could also crystallize on the zeolitic material surface.

3.2. Sorption study of iodide and chromate anions

The isotherms for sorption of iodides and chromates by the Pentalofos zeolite modified by 60 mg/L ODTMA-Br and 120 mg/L HDTMA-Br solutions are respectively given in Figs. 4 and 5. The possibility of using the surfactant-modified clinoptilolite for chromate and iodide adsorption results from the replacement of weakly held anions (Br$^-$), balanced by positively charged surfactant head groups, by more strongly held counterions such as I$^-$. This reaction can be written as [30]:

$$(\text{HDTMA-zeolite–Br}) + \text{I}^- \rightleftarrows \text{HDTMA-zeolite–I} + \text{Br}^-$$
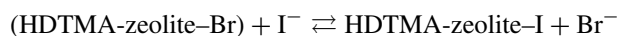
For sorption experiments, the iodide solution with pH$_{init}$ 7 was used. The equilibrium pH of the iodide solutions was slightly different from the initial one depending on the initial concentration of iodides. In the case of HDTMA-modifier, the equilibrium pH$_{eq}$ ranged from 6.9 to 6.5, whilst for ODTMA from 7.1 to 6.8. The iodide sorption capacity of the ODTMA-modified material (4.02 mg/g) was higher than the corresponding one of the HDTMA-modified zeolite (3.37 mg/g).
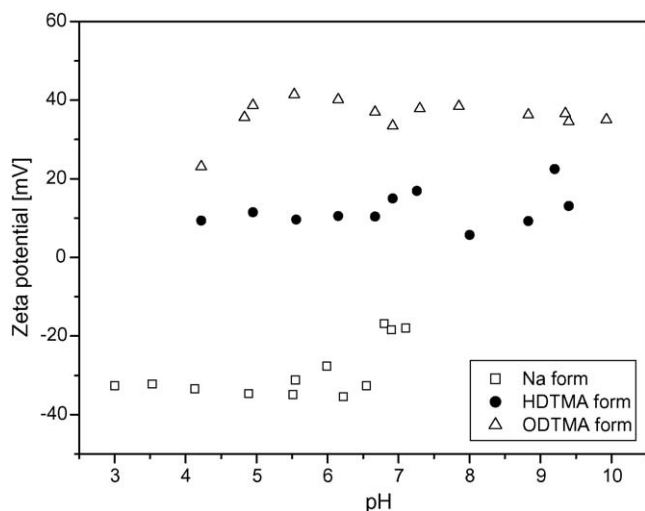

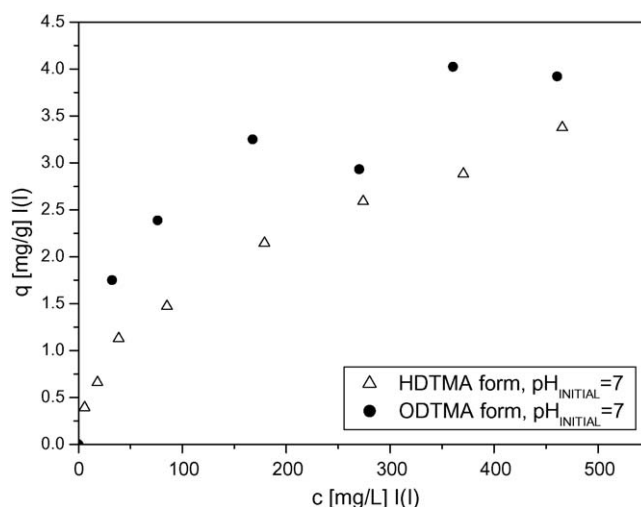Fig. 3. ζ-potential of the Pentalofos tuff in the Na-form, modified by 120 mg/L HDTMA and modified by 60 mg/L ODTMA.

Fig. 4. Sorption isotherms for the removal of iodide from aqueous solutions of pH$_{init}$ 7 by the HDTMA- and ODTMA-modified zeolitic material.
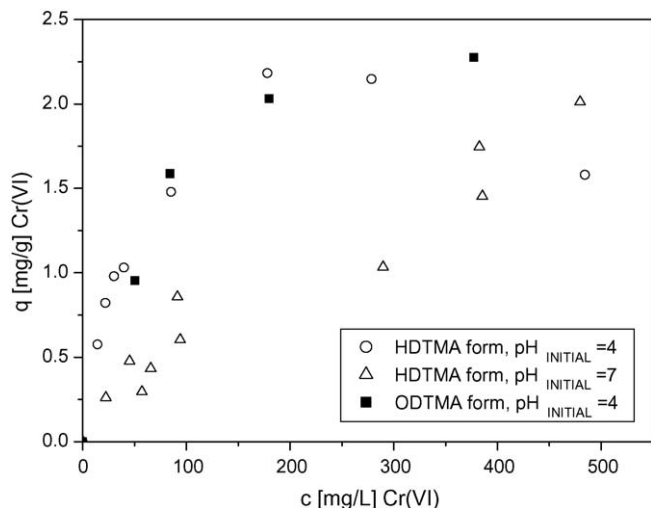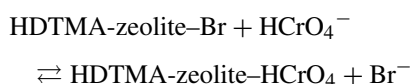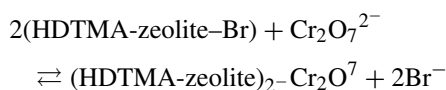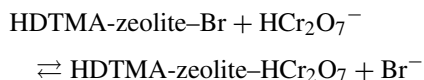
Fig. 5. Sorption isotherms for the removal of chromates from aqueous solutions by the HDTMA- and ODTMA-modified zeolitic material.

Chromate ions exist in an aqueous solution in different ionic forms. The pH and concentrations dictate which particular chromate species will predominate. The bichromate ions ($Cr_2O_7^{2-}$) dominate in acidic environments for chromium concentrations higher than 500 mg/L, while the $HCrO_4^-$ and CrO_4^{2-} oxyanions dominate at concentrations below 500 mg/L. The ratio of $HCrO_4^-$ to CrO_4^{2-} depends on the pH of the solution [31]. $HCr_2O_7^-$ is present at low pH values (pH < 1). At slightly acidic pH (below 7) $Cr_2O_7^{2-}$ is the most predominant Cr(VI) species with small quantities of $HCrO_4^-$, the share of which decreases as pH increases. At neutral and slightly alkaline pH, CrO_4^{2-} is the predominant chromate species in the aqueous phase. Beyond pH 8 the removal of CrO_4^{2-} by organo-modified zeolite is not favored. This results from the competition between the chromate and hydroxide ion and the formation of hydroxyl complexes of chromium [32].

The results obtained for the sorption of Cr(VI) by the HDTMA- and ODTMA-modified Pentalofos zeolite investigated in this research were similar to those found during the study of polyhexamethylene–guanidine-modified Metaxades and Tedzami zeolitic materials [19].

Two Cr(VI) solutions with pH_{init} 4 and 7 were used for the sorption experiments. Acidification of aqueous solution of chromate initiates formation of a few Cr(VI) anionic species ($HCr_2O_7^-$, $Cr_2O_7^{2-}$ and $HCrO_4^-$) which can interact with the organo-modified zeolitic sorbent as follows [32]:

$$HDTMA\text{-zeolite–Br} + HCr_2O_7^-$$
$$\rightleftarrows HDTMA\text{-zeolite–}HCr_2O_7 + Br^-$$

$$2(HDTMA\text{-zeolite–Br}) + Cr_2O_7^{2-}$$
$$\rightleftarrows (HDTMA\text{-zeolite})_2\text{–}Cr_2O^7 + 2Br^-$$

$$HDTMA\text{-zeolite–Br} + HCrO_4^-$$
$$\rightleftarrows HDTMA\text{-zeolite–}HCrO_4 + Br^-$$

Equilibrium solution pH values were between 4.5 at low chromate concentrations and 4.2 at high chromate concentrations.

The maximum sorption capacities gained for the ODTMA- and HDTMA-modified zeolites were 2.27 and 2.18 mg/g, respectively. The lowest efficiency of chromium uptake (2.01 mg/g) was obtained for the solution at pH_{init} 7. In this case, the equilibrium pH increased with chromium concentration and ranged from 7.0 to 7.2. The principal species present in the solution is CrO_4^{2-} anion and its removal can be expressed by the following reaction [33]:

$$2(HDTMA\text{-zeolite–Br}) + CrO_4^{2-}$$
$$\rightleftarrows (HDTMA\text{-zeolite})_2\text{–}CrO_4 + 2Br^-$$
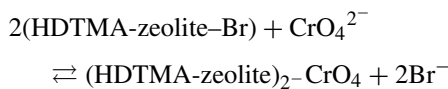
However, according to Krishna et al., the formation of HDTMA-$HCrO_4$ salt is more favored than the other chromate complexes. This results from the fact that the organic coat on the zeolite surface holds chromate ions in the salt forms that possess lower-solubility products in acidic pH [32].

The obtained experimental data for chromium uptake by ODTMA-modified zeolite at pH_{init} 4 and the iodine uptake by HDTMA-modified zeolite at pH_{init} 7 were used for sorption equilibrium calculations. For fitting the data the Freundlich and Langmuir sorption equations were selected:

- Freundlich equation:

$$q = K_{eq} c^{1/n} \tag{2}$$

where K_{eq} is equilibrium constant. The $1/n$ characterizes the heterogeneity of the organo-zeolite surface.
- Langmuir equation:

$$q = \frac{\Gamma K_{eq} c}{1 + K_{eq} c} \tag{3}$$

where Γ is the sorption capacity (mg/g).

The average deviation from the experimental data was calculated from the difference between the experimental concentrations of anionic species in the solution and that predicted using the above-mentioned equations, according to the following formula:

$$R = \sum_{i=1}^{N} \left(\frac{c_{exp.} - c_{cal.}}{c_{exp.}} \right)^2 \tag{4}$$

The isotherms for the sorption of iodides and chromates on the investigated organo-zeolites are presented in Figs. 6 and 7 respectively, while the parameters obtained by fitting of the experimental data are listed in Table 2.

The simulation of the iodide sorption behavior of the HDTMA-modified zeolite in solutions of pH_{init} 7 using the Freundlich equation showed a better agreement with the experimental data than using the Langmuir one (Fig. 6). This could result from the fact that the shape of the Langmuir isotherm is more suitable for the description of a sorption equilibrium involving a range of maximum sorption capacities. It is possible that the initial concentration of iodine employed in the experimental work did not allow the achievement of sorption plateau.
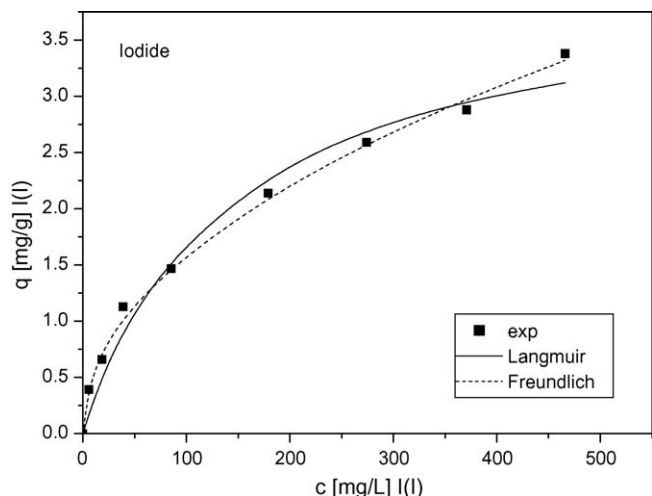
Fig. 6. Simulation of the iodide sorption behavior of HDTMA-modified zeolite in solutions of pH$_{init}$ 7 using the Freundlich and Langmuir equations.
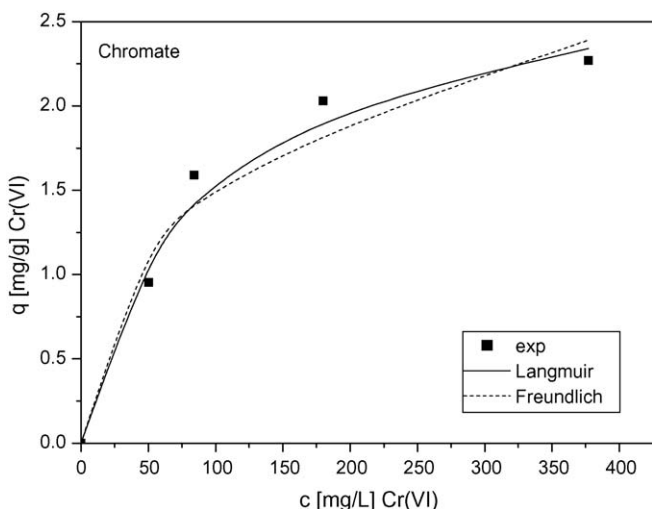

Fig. 7. Simulation of the chromates sorption behavior of ODTMA-modified zeolite in solutions of pH$_{init}$ 4 using the Freundlich and Langmuir equations.

In the case of chromate sorption, the approximation to the experimental data is rather poor for both equations used for calculation of the equilibrium data (Fig. 7). This could result from not having enough experimental data for proper modelling of a non-linear process equilibrium. Table 2 presents the fitted isotherm parameters for the Langmuir and Freundlich isotherms. The values of K_{eq} in the Langmuir equation indicate stronger interaction of

Table 2
Freundlich and Langmuir parameters obtained by fitting experimental data for the sorption of chromate and iodide by ODTMA- and HDTMA-modified Pentalofos tuffs

Estimated parameters	Iodide		Chromate	
	Freundlich	Langmuir	Freundlich	Langmuir
K_{eq}	0.184	0.008	0.313	0.013
Γ (mg/g)	–	3.99	–	2.82
n	2.12	–	2.92	–
Mean error (%)	4.45	16.1	12.4	7.52

chromate with the surface of modified zeolite in comparison to the iodide. On the other hand, the values of n, calculated from the Freundlich model which is directly related to the size of the adsorbate molecule, confirm the lower sorption capacity for chromate in comparison to iodide.

4. Conclusions

The surface modification of the Pentalofos tuff by long-chain quaternary amines resulted in an organo-zeolitic material possessing anionic sorption properties. The number of methylene groups as well as the value of the positive charge on the organic part on the zeolite surface were more affected by the length of the aliphatic chain of the organic modificator than by its concentration.

ODTMA-treated clinoptilolite tuff showed greater chromate and iodide sorption than the zeolitic material modified by HDTMA. Moreover, experimental as well as modelled equilibrium studies indicated that both organo-zeolitic sorbents have a bigger affinity for iodide than for chromate. Although the sorption of chromate in the pH range employed (4–7) was not significantly affected by pH value, the variation in adsorption can be attributed to the presence of deferent hexavalent chromium anionic species. Regardless of the somewhat low sorption capacity of surface-modified zeolite, that cannot be compared with synthetic materials, the organo-zeolitic sorbents investigated in these experiments can find interesting and important applications in environmental technology.

Acknowledgements

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