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The adsorption of sulphate, hydrogenchromate and dihydrogenphosphate anions on surfactant-modified clinoptilolite

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Abstract

The adsorption of sulphate, hydrogenchromate and dihydrogenphosphate anions on surfactant-modified clinoptilolite (SMC) was investigated. The SMCs were prepared by the adsorption of *cis*-1-aminooctadecen-9 (oleylamine) on both modified and unmodified natural clinoptilolite tuff. The properties of the modified clinoptilolite samples, such as cation type, structure of the zeolite framework and ECEC value, determined the mechanism of oleylamine adsorption, and consequently anion adsorption on the external clinoptilolite surface. According to the strength of the anion adsorption, two groups of SMCs could be distinguished: strong and weak anion adsorbents. Strong anion adsorbents were obtained by oleylamine adsorption on H⁺-clinoptilolites by protonation of the –NH₂ groups. This mechanism of oleylamine adsorption resulted in the surface precipitation mechanism of anion adsorption being the dominant mechanism. The oleylamine derivatives of Ca- and Na-clinoptilolite were weak anion adsorbents. Oleylamine is adsorbed on Ca- and Na-clinoptilolite by hydrogen bonding, thus yielding insufficient adsorption sites for anions. Hydrogenchromate and dihydrogenphosphate anions were nevertheless adsorbed on these SMCs by interaction with oleylamine. The experiments of anion adsorption on various oleylamine loaded SMCs confirmed the existence of two types of anion adsorption sites and showed that excess oleylamine did not significantly influence the anion adsorption in the investigated

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concentration range. The kinetic results showed that SO_4^{2-} and H_2PO_4^- adsorptions were slow processes while HCrO_4^- adsorption was completed in a few minutes. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Numerous applications of natural zeolites arise from their properties of molecular sieves and cation exchanges. The availability and low cost of natural zeolites has stimulated further research for new applications. A new field is anion adsorption. Natural zeolites do not show any affinity for anions without previous modification. A few papers have been published on zeolite modification by the adsorption of quaternary ammonium salts (Sullivan et al., 1998). Such modified zeolites adsorb organic contaminants (Popovici et al., 1995) and, to some extent, inorganic anions (Bowman et al., 1995). Another more common way of natural zeolite modification is their transformation into the H^+ -form. This modification method is widely used for various purposes (Dyer and Keir, 1989). Many papers have been published on the preparation of the H^+ -form of zeolites either by acid treatment or by deammonization of the NH_4^+ -form of natural zeolites (Barrer, 1978; Acroya et al., 1994). These treatments modify the acidity and chemical composition of zeolite as well as its texture and structure (Tsitsishvili, 1988). The formation of strong acid sites on the zeolite surface can increase the amine adsorption in processes of preparing organo-zeolites. The strong organo-zeolite complex obtained by amine adsorption on H^+ zeolite may exhibit a high adsorption of anions from aqueous solutions.

In this study, an alternative method for preparing clinoptilolite-based anion adsorbent is proposed. Instead of ion exchange with a quaternary ammonium salt, the adsorption of the long-chained primary amine, *cis*-1-aminooctadecen-9 (oleylamine), was performed on various cation forms of clinoptilolite. The anion adsorption properties of such prepared surfactant-modified clinoptilolite (SMC) and the influence of zeolite pretreatment on the anion adsorption were investigated.

2. Materials and methods

2.1. Preparation and characterization of clinoptilolite samples

The starting material for the preparation of SMC was the clinoptilolite-rich tuff from the deposit Zlatokop (Vranje), Yugoslavia. The content of clinoptilolite is 85% (w/w) with pyrite, quartz and feldspar as major impurities, based on

quantitative X-ray diffraction analysis (Tomazović et al., 1996). The raw material was ground and wet-classified to < 0.063 mm. This clinoptilolite tuff is predominantly of the calcium type with a cation exchange capacity (CEC) of $1420 \text{ mmol M}^+/\text{kg}$. The modified clinoptilolite samples were prepared from the starting one (Z) as follows.

Sample HZ-1. The clinoptilolite tuff was successively treated five times with 0.005 M HCl , with a solid content of 0.5% (w/w) at room temperature. The solution was changed daily. The purpose of this clinoptilolite treatment with dilute acid solution was to obtain partially H^+ -exchanged clinoptilolite having a preserved zeolite framework.

Sample HZ-2. In order to attain a high degree of H^+ -exchange and a partially destructed zeolite framework, the clinoptilolite was treated with a strong acid solution. The clinoptilolite tuff was treated once with 1 M HCl , with a solid content of 5% (w/w), for 2 h at 60°C and then left in contact with the acid for 24 h at room temperature.

Sample HZ-3. The clinoptilolite tuff was treated three times with $0.5 \text{ M NH}_4\text{Cl}$, with a solid content of 5% (w/w), for 2 h at room temperature and then left in contact with the solution for 24 h. The washed and dried sample was calcined at 400°C for 3 h, in order to obtain H^+ -clinoptilolite with a high degree of H^+ -exchange with a preserved zeolite framework.

Sample NaZ. A partially Na-exchanged clinoptilolite sample was prepared as follows. The clinoptilolite tuff was treated three times with 0.5 M NaCl , with a solid content of 5% (w/w), for 2 h at room temperature and then left in contact with the solution for 24 h.

All samples were repeatedly washed with distilled water until Cl-free and then dried at 105°C to constant mass.

Sample MCZ. The natural clinoptilolite tuff was mechanochemically treated in a vibro mill with rings. The clinoptilolite sample (100 g) was put in a vibro mill and then milled with three hardened steel rings for 1 h, in order to obtain a sample with a damaged zeolite framework.

The Si/Al framework ratios of the clinoptilolite samples were calculated from chemical analysis data (Table 1).

The CEC and ECEC values of the clinoptilolite samples were determined by the method of Ming and Dixon (1987). The principles of the method will be briefly described. The samples were washed five times with a buffered sodium acetate solution (pH 5) to ensure complete Na-saturation of the exchangeable sites. The external exchangeable Na^+ was displaced by three washings with *tert*-butyl ammonium bromide solution. The Na^+ on the internal exchangeable sites was removed by washing three times with ammonium acetate. Since native Ca^{2+} , Mg^{2+} and K^+ were not fully displaced even after five washes with sodium acetate, all these exchangeable cations along with Na^+ were analyzed by atomic absorption spectrophotometry. The sum of the cation equivalent released by washing with *tert*-butyl ammonium bromide represents the ECEC and the

Table 1
Properties of clinoptilolite and SMC samples

Clinoptilolite					SMC		
Sample name	Cation form (% of CEC)	Si/Al (mol/mol)	BET surface (m ² /g)	ECEC (mmol/kg)	Sample name	Oleylamine added (mmol/kg)	% of ECEC occupied by oleylamine
Z	67% Ca	4.37	37.0	191	OZ	190	78
HZ-1	23% H ⁺	4.31	43.5	190	OHZ-1	190	95
HZ-2	70% H ⁺	8.21	199.2	187	OHZ-2/1	95	50
					OHZ-2/2	190	99
					OHZ-2/3	285	147
					OHZ-2/4	380	192
HZ-3	95% H ⁺	4.63	52.0	182	OHZ-3	190	95
NaZ	50% Na	4.34	42.9	189	ONaZ	190	71
MCZ	67% Ca	4.50	40.3	198	OMCZ	190	76

ones released by washing with ammonium acetate represent the internal CEC. The total CEC is the sum of the external and internal CEC. The ECEC is relevant for the preparation of SMC since the large oleylamine molecules are excluded from the internal exchange sites of clinoptilolite. The cation form (% of CEC) which is presented in Table 1 was calculated as the cation concentration divided by CEC and multiplied by 100.

The determination of the specific surface area of the clinoptilolite samples was based on the BET method (Brunauer et al., 1938). The N₂ adsorption was performed on a Strohleim Area Meter. The samples were outgassed at 300°C. It should be mentioned that the N₂ adsorption method reveals only the external surface area of clinoptilolites, with the exception of partially dealuminated sample HZ-2 which has enlarged micropores (Table 1).

2.2. Preparation of SMC samples

For the batch anion adsorption isotherm experiments described in the following section, the adsorbents were prepared by oleylamine adsorption on the series of clinoptilolite samples.

The oleylamine supplied by AkzoChemie was used as received without further purification. The SMC samples OZ, OHZ-1, OHZ-2/2, OHZ-3, ONaZ and OMCZ were prepared by oleylamine adsorption on the clinoptilolite samples Z, HZ-1, HZ-2, HZ-3, NaZ and MCZ, respectively. The oleylamine was added in amounts equal to the ECEC values of the clinoptilolite. The SMC samples OHZ-2/1, OHZ-2/2, OHZ-2/3 and OHZ-2/4 were prepared by oleylamine adsorption on HZ-2 in amounts equal to 50%, 100%, 150% and 200% of the ECEC value. The first series of SMCs was prepared with the purpose of analyzing the effect of different clinoptilolite forms on the adsorption of anions. The second series of SMCs was prepared to analyze the effect of

surface coverage on the adsorption of anions. The SMC preparation experiments were carried out as follows. Clinoptilolite (15 g) and 300 ml of distilled water were placed in a plastic beaker. For the first series of SMCs, 7.7 ml of a 10% (w/w) alcoholic solution of oleylamine were added to the suspension, while 3.9, 7.7, 11.6 or 15.4 ml were added to the others. The adsorption mixtures were vigorously mixed using a turbo mixer at $10\,000\text{ min}^{-1}$ at room temperature. The equilibrium was reached in 30 min. After filtration, the SMC samples were rinsed with distilled water until free of amine and then dried at 60°C to constant mass.

The free oleylamine in the supernatants after the adsorption on the clinoptilolite samples was determined by a titration method, ASTM D2074-66. The principle of the method is the neutralisation of the amine base dissolved in ethanol with an HCl propanol solution in the presence of bromphenol blue as indicator.

The amounts of oleylamine adsorbed were calculated from the differences between the amount of oleylamine added and that remaining in the final equilibrium solution. The amounts of oleylamine adsorbed were divided by the clinoptilolite ECEC to obtain the percents of ECEC occupied by oleylamine (Table 1).

2.3. Anion adsorption

Adsorption isotherms of anions on the SMCs were obtained using the batch equilibration technique. Aqueous solutions of Na_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KH_2PO_4 were prepared for anion adsorption on the SMC-samples: OZ, OHZ-1, OHZ-2/1, OHZ-2/2, OHZ-2/3, OHZ-2/4, OHZ-3, ONaZ and OMCZ. The initial anion concentrations ranged from 1 to 5.2 mmol/l for SO_4^{2-} and H_2PO_4^- , and from 1.6 to 7.9 mmol/l for HCrO_4^- . The pH values of the equilibrium solutions ranged from 4.0 to 5.1, 3.6 to 4.0 and 3.9 to 4.9 for SO_4^{2-} , HCrO_4^- and H_2PO_4^- , respectively. The solid content was 5% (w/w) SMC. The suspensions were mixed for 8 h, on a magnetic stirrer at 25°C , then occasionally mixed overnight and filtered after a 24 h contact time. The equilibrium anion concentrations were measured in the supernatants. Appropriate solution and SMC blanks were included in each batch. The SO_4^{2-} , HCrO_4^- and H_2PO_4^- adsorption experiments on OHZ-2 were done in duplicate for each anion concentration. The difference between two measurements did not exceed 10%. In order to test the interactions of the anions with free oleylamine, the following blank test was done. A 10% (w/w) alcoholic solution of oleylamine (7.7 ml) was mixed with aqueous solutions of medium anion concentrations: 3.1 mmol/l SO_4^{2-} , 4.8 mmol/l HCrO_4^- and 3.1 mmol/l H_2PO_4^- for 8 h on a magnetic stirrer at 25°C . After 24 h, the anion concentrations remaining in the solution were determined.

The anion concentrations were determined as follows: hydrogenchromate by atomic absorption, sulphate by turbidimetry (Spectrophotometer, ASTM D516,

1982) and dihydrogenphosphate by molybdatovanadophosphate (Spectrophotometer, ASTM D515, 1982).

The amounts of the anions adsorbed on the SMCs were calculated from the differences between the anion concentration in solution before and after equilibration. The adsorption curves were obtained by plotting the amounts adsorbed (mmol/kg) against the equilibrium anion concentrations in solution (mmol/l).

It was observed that the kinetics of the adsorption of an anion on a SMC differed significantly for SO_4^{2-} and H_2PO_4^- on the one hand and HCrO_4^- on the other. The sample OHZ-2/2 and medium anion concentrations of 3.1 mmol/l SO_4^{2-} , 4.8 mmol/l HCrO_4^- and 3.1 mmol/l H_2PO_4^- were chosen for the kinetic study which was carried out as follows: 5% (w/w) SMC suspensions in aqueous anion solutions were mixed for 48 h on a magnetic stirrer, at 25°C. Aliquots were taken by syringe at chosen periods of adsorption times and filtered. The anion concentrations were determined in the supernatants and were plotted against the time.

3. Results

3.1. Properties of the SMC anion adsorbents

The results of a detailed study of the clinoptilolite and SMC properties are given elsewhere (Vujaković et al., 1999). Table 1 shows only the clinoptilolite and SMC properties that are essential for anion adsorption.

The cation exchange treatments of clinoptilolite tuff resulted in the preparation of three H^+ -forms of clinoptilolite with various degree of exchange, and one Na-form. The Si/Al ratios and BET surface areas remained essentially unchanged in all samples except for the sample HZ-2, pointing to its partial dealumination. The ECEC values were not significantly affected by ion exchange and mechanochemical treatment of the clinoptilolite tuff. Oleylamine was added to the modified clinoptilolite samples in amounts equal to ECEC and at 50%, 150% and 200% of the ECEC to obtain the series of SMC samples. The oleylamine coverage of the external zeolite surface, expressed as percent of ECEC, is also given in Table 1. It can be seen that the most quantitative oleylamine adsorption was achieved on the H^+ forms of clinoptilolite. The oleylamine adsorption on the clinoptilolite samples can be described by type I isotherms (Vujaković et al., 1999), indicating a monolayer coverage of the clinoptilolite surface. Partial bilayer surface coverage was obtained only for the SMC samples with excess oleylamine (OHZ-2/3 and OHZ-2/4).

3.2. Anion adsorption

The strongest sulphate adsorption occurred on the H^+ -form of SMC after oleylamine adsorption. The highest adsorption was obtained on the OHZ-2/2

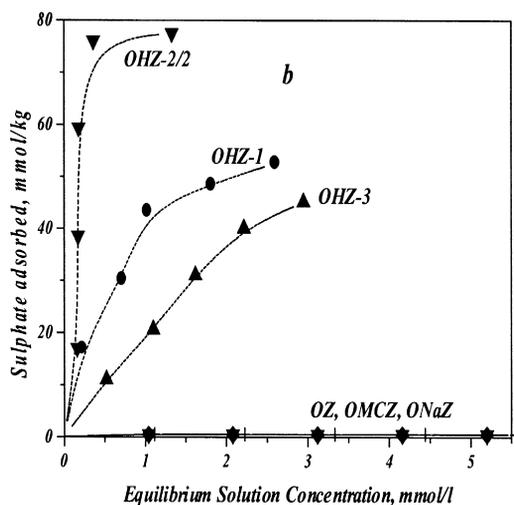


Fig. 1. Sulphate adsorption on the series of SMCs.

sample (Fig. 1). At equilibrium concentrations below 0.5 mmol/l, over 90% of the sulphate anions were removed by the OHZ-2/2 sample. At higher anion concentrations, the adsorption efficiency was lower. For the OHZ-1 sample, a high adsorption efficiency was observed in a lower range of equilibrium concentrations. The OHZ-3 sample was a weaker adsorbent of SO_4^{2-} anions. The OZ, ONaZ and OMCZ samples showed no adsorption affinity for SO_4^{2-} .

The strongest adsorption of hydrogenchromate anions was also observed with the H^+ -forms of SMC after oleylamine adsorption (Fig. 2). The adsorption on these three SMCs exceeds 99% of the initial HCrO_4^- concentration up to 0.5 mmol/l. Lower HCrO_4^- adsorption was observed for the oleylamine derivatives

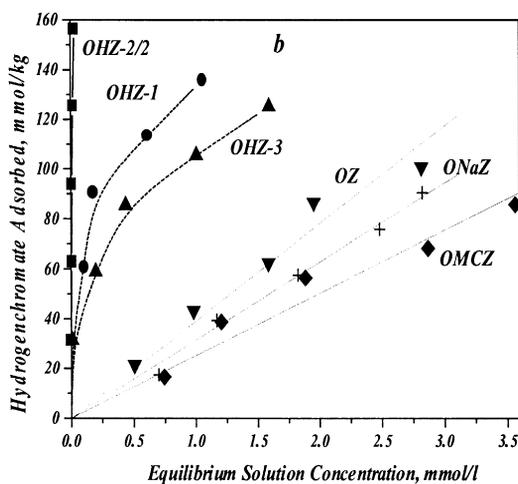


Fig. 2. Hydrogenchromate adsorption on the series of SMCs.

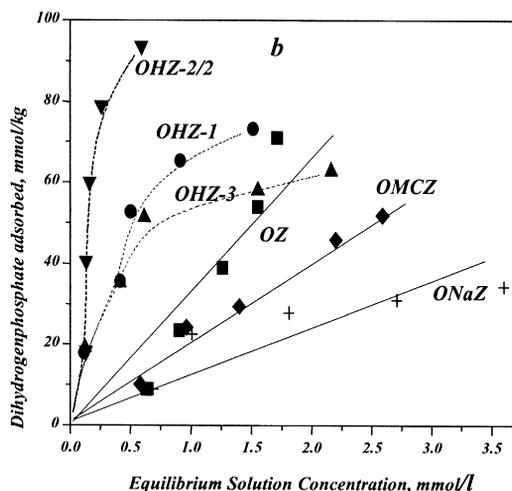


Fig. 3. Dihydrogenphosphate adsorption on the series of SMCs.

of natural, sodium-exchanged and mechanochemically treated tuff. Nevertheless, the HCrO_4^- adsorption on these samples was significant.

A different adsorption behavior was observed for the adsorption of dihydrogenphosphate anions (Fig. 3). The strongest adsorption was obtained on the H^+ -forms of SMC, but significant adsorption was also observed on the oleylamine derivatives of the natural and mechanochemically treated samples.

The most efficient anion adsorbent was OHZ-2/2. Therefore, this sample was used to study the influence of oleylamine loading. Samples OHZ-2/1, OHZ-2/3 and OHZ-2/4 were prepared with oleylamine additions of 50%,

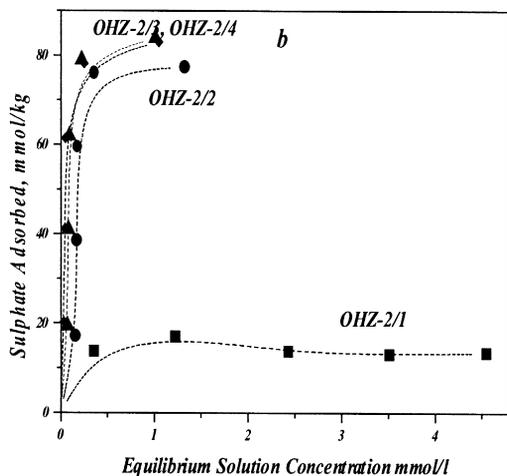


Fig. 4. Sulphate adsorption on variously oleylamine loaded SMCs.

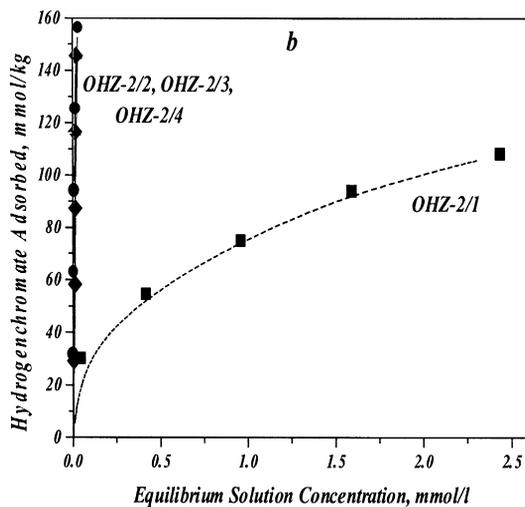


Fig. 5. Hydrogenchromate adsorption on variously oleylamine loaded SMCs.

150% and 200% related to the ECEC of the tuff, respectively. Excellent adsorption of SO_4^{2-} was obtained with oleylamine loadings from 100% to 200% of the ECEC (Fig. 4). Namely, the adsorption exceeds 90% up to an equilibrium sulphate concentration of 0.3 mmol/l. Practically all the hydrogenchromate anions were adsorbed on OHZ-2/2, OHZ-2/3 and OHZ-2/4 (Fig. 5). The SMC with oleylamine at 50% of the ECEC also showed almost complete HCrO_4^- adsorption up to 0.1 mmol/l, but its efficiency became lower at higher HCrO_4^- concentrations.

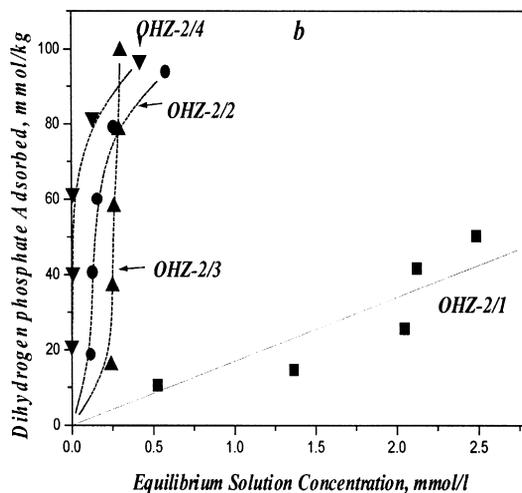


Fig. 6. Dihydrogenphosphate adsorption on variously oleylamine loaded SMCs.

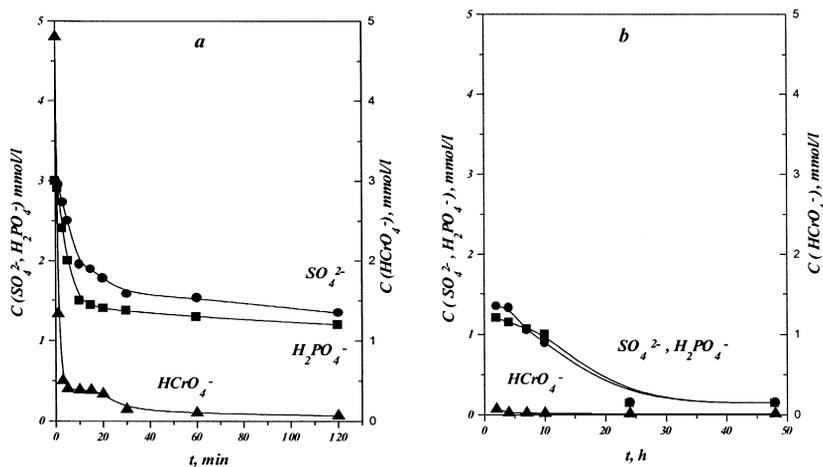


Fig. 7. The anion concentrations in solution as a function of adsorption time (a — in first 2 h, b — in 48 h).

The H_2PO_4^- adsorption was also almost complete at oleylamine loadings of 100%, 150% and 200% of the ECEC (Fig. 6). In the investigated H_2PO_4^- concentration range, about half the amount of hydrogenphosphate was adsorbed at an oleylamine loading of 50% of the ECEC.

During the experiments, it was observed that the adsorption is greatly influenced by the contact time (Fig. 7). More than 99% of HCrO_4^- was adsorbed in the first 2 h while the residual amount was slowly adsorbed during 48 h. In contrast, the SO_4^{2-} and H_2PO_4^- concentrations decreased to half in the first 10 min and then changed slowly.

4. Discussion

The adsorption of anions is greatly affected by the oleylamine–zeolite interaction. In terms of their anion adsorption ability, the examined adsorbents may be divided in two groups: (a) strong anion adsorbents based on the H^+ -forms of the oleylamine derivatives (OHZ-1, OHZ-2/2 and OHZ-3), and (b) weak anion adsorbents based on the Ca- and Na-forms of the oleylamine derivatives (OZ, NaZ and OMCZ). Consistent with this, two different anion adsorption mechanisms are proposed.

The first proposed anion adsorption mechanism is surface precipitation on the strong anion adsorbents prepared by oleylamine adsorption on H^+ -clinoptilolite. Among the three H^+ clinoptilolites, the strongest anion adsorbent was obtained from the HZ-2 sample (Figs. 1–3). This acid treated clinoptilolite tuff was also partially dealuminated and possessed the largest number and highest strength of acid sites (Benashvili et al., 1988). The oleylamine was strongly bound with the

hydronium ions on the external surface of the H^+ -clinoptilolite by protonation of the oleylamine $-NH_2$ “heads”, thus yielding positive ions $-NH_3^+$ (Yariv, 1992). These positive ions that cover the clinoptilolite external surface attract anions from the solution which results in the precipitation of an organic salt. The anion adsorption isotherms (Figs. 1–3) for OHZ-1, OHZ-2/2 and OHZ-3 are of the Langmuir type (type I), indicating a monolayer coverage. The Langmuir type isotherms are consistent with the formation of an oleylamine-anion precipitate because it has been demonstrated by Veith and Sposito (1977) that a precipitation mechanism yields Langmuir adsorption isotherms. The anion adsorption by surface precipitation is dominant but not the only possible mechanism of anion adsorption on oleylamine derivatives of H^+ -clinoptilolite (OHZ-1, OHZ-2/2 and OHZ-3). Another probable mechanism that can apply to both strong and weak anion adsorbents is described below.

The second proposed anion adsorption mechanism is anion interaction with the oleylamine weakly bound on Ca- and Na-clinoptilolite. The oleylamine is adsorbed on Z, NaZ and MCZ by hydrogen bonding with Ca- and Na-hydrating water (Yariv, 1992). The oleylamine is long-chained aliphatic amine and it acts as a proton acceptor (base). The interaction occurs between nitrogen from oleylamine $-NH_2$ group and proton from hydrating water. Since the polarization of water molecules from Ca- and Na-hydrating shell is low, a weak adsorption complex was formed that did not show appreciable anion adsorption. It is evident (Fig. 1) that SO_4^{2-} adsorption did not occur on OZ, ONaZ and OMCZ and was only possible on OHZ-1, OHZ-2/2 and OHZ-3 by the previously described mechanism. However, strong evidence of an alternative anion adsorption mechanism was observed from the $HCrO_4^-$ and $H_2PO_4^-$ adsorption isotherms (Figs. 2 and 3). Unlike sulphate, hydrogenchromate and even more dihydrogenphosphate anions were adsorbed on OZ, ONaZ and OMCZ. It is most likely that these anions were bound by interaction with weakly bound oleylamine. The results of blank tests of anion interaction with oleylamine support this conclusion. The equilibrium sulphate concentration remained unchanged, while the hydrogenchromate and dihydrogenphosphate concentrations decreased to 74% and 47% of the initial concentrations, respectively. This indicates the formation of complexes of $HCrO_4^-$ and $H_2PO_4^-$ with oleylamine. It can be seen (Figs. 2b and 3b) that the $HCrO_4^-$ and $H_2PO_4^-$ isotherms for adsorption on the OZ, ONaZ and OMCZ samples are mainly of the C-type in the investigated concentration range. The linear C-type isotherms point to continuous bonding of $HCrO_4^-$ and $H_2PO_4^-$ with oleylamine, regardless of the degree of saturation of the clinoptilolite surface. This means that anion-oleylamine interactions are responsible for the adsorption of $HCrO_4^-$ and $H_2PO_4^-$ on the OZ, ONaZ and OMCZ samples, the clinoptilolite-oleylamine interactions being of minor importance.

The experiments of anion adsorption on variously oleylamine loaded SMCs confirmed the existence of two types of adsorption sites. The different shape of

the SO_4^{2-} , HCrO_4^- and H_2PO_4^- adsorption isotherms for the OHZ-2/1 sample with an oleylamine coverage equivalent to 50% of the ECEC points to the existence of both types of active sites on the H^+ -forms of oleylamine derivatives. It is evident from the shape of the SO_4^{2-} adsorption isotherms for OHZ-2/1 (Fig. 4b) that the SO_4^{2-} adsorption was terminated after the oleylamine cationic “heads” on the SMC surface were saturated. Unlike the SO_4^{2-} adsorption isotherm, the HCrO_4^- adsorption isotherm for OHZ-2/1 (Fig. 5b) showed a slight increase in the anion adsorption over the whole equilibrium concentration range, which might indicate that the adsorption continued to a small extent after the saturation of the oleylamine cationic “heads”. Similarly, the H_2PO_4^- adsorption isotherms for OHZ-2/1 (Fig. 6b) show a continuous increase in H_2PO_4^- adsorption, regardless of the saturation of the oleylamine cationic “heads” on the SMC surface. Oleylamine loading in excess of the ECEC probably led to the formation of ammonium–amine associations on the external clinoptilolite surface (Yariv, 1975). However, this did not significantly influence the anion adsorption in the investigated anion concentration range. It can be seen from Fig. 4 that SO_4^{2-} adsorption was slightly increased on the OHZ-2/3 and OHZ-2/4 samples. Complete HCrO_4^- adsorption occurred on the OHZ-2/2, OHZ-2/3 and OHZ-2/4 samples in the investigated concentration range so that the influence of excess oleylamine was not visible. Small differences in the H_2PO_4^- adsorption on the OHZ-2/2, OHZ-2/3 and OHZ-2/4 samples were observed (Fig. 6), but no definite conclusions on the influence of excess oleylamine can be drawn.

To the best of the authors knowledge, the anion adsorption data presented in this work are one order of magnitude higher compared to data published until now (Haggerty and Bowman, 1994; Li and Bowman, 1997; Sullivan et al., 1998). An explanation of such big differences in the results of anion adsorption should be searched for in the preparation of the adsorbents. Obviously, the protonated amine molecules at the external surface of H^+ -clinoptilolite act as much stronger anion adsorption sites than the quaternary ammonium salt cations on natural clinoptilolite.

5. Conclusions

The obtained results showed that efficient anion adsorbents were prepared by appropriate modification of clinoptilolite tuff. Simultaneously, such anion adsorbents may also adsorb certain nonpolar organic compounds. The availability of zeolite tuffs, their low cost and simple preparation make this material suitable for the production of large quantities of adsorbents for a wide range of applications in packed-bed water treatment processes and as permeable barriers. Considering all this, SMCs as anion adsorbents provide promising material for the removal of all major classes of soil and water contaminants.

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