Adsorption of inorganic anionic contaminants on surfactant modified minerals

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Abstract: Organo-mineral complexes were obtained by treatment of aluminosilicate minerals (zeolite, bentonite and diatomaceous earth) with a primary amine (oleylamine) and an alkyl ammonium salt (stearyldimethylbenzylammonium chloride). The modification of the zeolite surface was carried out in two steps. The first step was treatment of the zeolite with 2 M HCl. This acid treatment of the zeolite increased its affinity for neutral molecules such as surface-active amines. The second step of the modification was the adsorption of oleylamine on the acid treated zeolite. Four types of organo-mineral complexes were prepared and their anion adsorption properties were compared to those of organo-zeolite. The adsorption of sulphate, dichromate and dihydrogenphosphate anions on the organo-mineral complexes was investigated. The anion adsorption measurements showed that the most efficient adsorbent for anion water pollutants was the primary amine modified H+-form zeolite.

Keywords: zeolite, bentonite, diatomaceous earth, oleylamine, adsorption, anions.

INTRODUCTION

Zeolites possess a negative net charge compensated by the presence of exchangeable cations at the aluminosilicate surfaces. A variety of cations can be adsorbed on zeolites by the cation exchange mechanism. Therefore, natural zeolites are known as efficient adsorbents for cation water pollutants. To increase the ability of zeolites to remove nonpolar and anion water pollutants, it is necessary to modify their surface. The permanent negative charge in the crystal structures of some minerals (zeolite, bentonite, illite, kaolinite etc.), make them suitable for surface modification by long chain organic cations – surfactants.1–5 When the aqueous surfactant concentration is greater than the critical micelle concentration (CMC) and sufficient surfactant is present in the system, the sorbent surfactant molecules primarily form a bilayer on the external surface6 of the zeolite. Three-dimensional framework of zeolites retains the high molecular weight surfactants primarily on their outer surfaces, whereby at sufficient loading the surfactant forms a bilayer. This bilayer forma-

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tion results in a reversal of the charge on the external surface of the zeolite, providing sites where anions will be retained and cations repelled, while neutral species can partition into the hydrophobic core.

On the other hand, surfactant retention occurs in the interlayer space of bentonite and other layer silicates. These modified minerals provide a primarily hydrophobic environment for the retention of organic molecules of low polarity.6

The first aim of this study was to provide an efficient anion adsorbent based on zeolite modified by acid and amine treatment. For comparison of the efficiency of different modification of non-metallic minerals, it was considered to be of interest to examine the possibilities of various organo-mineral complexes based on zeolite, bentonite and diatomaceous earths to remove anion water pollutants.

EXPERIMENTAL

Materials

The purity of all the used chemicals was reagent-grade. Distilled water was used. The surface-active agents used for obtaining the organo-mineral complexes were oleylamine and stearyldimethylbenzyl-aminonium chloride (SDMBA), both supplied by Akzo-Chemie. Oleylamine is a primary, long chained fatty amine with the chemical formula: C18H35 NH2. Oleylamine is insoluble in water but readily soluble in polar and non-polar organic solvents. SDMBA is a quaternary ammonium salt with the chemical formula C9H19(CH2)17(CH3)2NC6H5+ Cl-. It is soluble in water and in organic solvents.

Synthesis of organo-zeolite adsorbents

Natural clinoptilolite from the deposit Zlatokop, Serbia was used as the starting material for the preparation of organo-zeolite adsorbents. The raw material was ground and wet-classified to < 0.063 mm. The purity degree of the clinoptilolite was higher than 90 %, with pyrite, quartz and feldspar as the major impurities. The chemical composition of the mineral (wt%) was: SiO2, 68.90; Al2O3 13.40; Fe2O3 1.84; TiO2 0.25; MnO 0.01; CaO 3.25; MgO 0.92; Na2O 1.20; K2O 1.00 and H2O 9.25. This clinoptilolite is predominantly of the calcium type with a cation exchange capacity (CEC) of 1420 mmol M+/kg, and an external cation exchange capacity (ECEC) of 190 mmol M+/kg. The ECEC value refers to exchangeable cations at the external zeolite surface.7,8 The zeolite was first treated with an aqueous 2 M HCl solution. The zeolite (5 %) was suspended in the acid solution. The suspension was stirred for 2 h at 60 °C and 24 h at room temperature. The centrifuged zeolite sample was repeatedly washed until Cl- free. The sample was dried at 105 °C until constant mass (Sample HZ). The ECEC value of this zeolite was 187 mmol M+/kg.7

The results of a detailed study of the structural property of the natural and acid treated zeolite are given elsewhere.7,9

The surface modified zeolite samples were prepared as follows:

Sample OHZ. Oleylamine was adsorbed onto the H+ form zeolite (HZ). An alcoholic oleylamine solution (190 mmol/kg) was added to a 5 % aqueous zeolite suspension. The mixture was stirred in a turbo-mixer for 30 min at 10 000 rev. min⁻¹. The filteres organo-zeolite was repeatedly washed until it was amine free. The sample was dried at 80 °C until constant mass (OHZ). The free, non-adsorbed, oeylamine was determined in the supernatant by titration with 0.1 M HCl (ASTM D2074-66).10 The sample characterization has been described in a previous papers.7,9,11

Sample OZ. This organo-zeolite sample was prepared by the reaction of SDMBA with natural zeolite: An aqueous solution CDMBA (190 mmol/kg) was added to a 5 % zeolite suspension. The mixture was stirred in a turbo-mixer for 30 min at 10 000 rev. min⁻¹. The filtered organo-zeolite was repeatedly washed until it was amine free. The sample was dried at 80 °C until constant mass. The free, non-adsorbed SDMBA was determined in the supernatant using a method for the determination of quaternary amines (AkzoChemie, WV/2.001-2).
Synthesis of organo-bentonite adsorbents

Bentonite from the deposit Petrovac, Montenegro, was used as the starting material for the preparation of organo-bentonite adsorbents. This bentonite ore consists of montmorillonite as the main component and impurities such as cristobalite and quartz. A montmorillonite concentrate with particle size (< 10 μm) was obtained by centrifugal classification. The chemical composition of the mineral (wt%) was: SiO$_2$ 67.59; Al$_2$O$_3$ 16.70; Fe$_2$O$_3$ 2.83; TiO$_2$ 0.30; CaO 1.62; MgO 4.06; Na$_2$O 0.52, K$_2$O 0.58 and H$_2$O 6.10. The predominant exchangeable cation was calcium with a CEC value of 780 mmol M+/kg. This purified bentonite was used in the further procedures. The modified bentonite samples were prepared as follows:

**Sample OHB:** Montmorillonite concentrate (< 10 μm) was firstly treated with an aqueous 1 M HCl solution. The 5 % montmorillonite was suspended in the acid solution, stirred for 24 h at room temperature. The montmorillonite sample was then centrifuged and repeatedly washed until it was Cl$^-$ free. Sample was dried at 105 °C until constant mass. The oleylamine was adsorbed on such a prepared H$^+$-form bentonite. An alcoholic oleylamine solution (780 mmol/kg) was added to a 5 % aqueous bentonite suspension. The mixture was stirred in a turbo-mixer for 30 min at 10 000 rev. min$^{-1}$. The filtered organo-bentonite was repeatedly washed until it was amine free. The sample was dried at 80 °C until constant mass. The characterization of this complex has already been described.

**Sample OB:** This organo-bentonite sample was prepared by the adsorption of SDMBA on montmorillonite. An aqueous SDMBA solution (780 mmol/kg) was added to a 5 % montmorillonite suspension. The mixture was stirred in a turbo-mixer for 30 min at 10 000 rev. min$^{-1}$. The filtered organo-bentonite was repeatedly washed until it was amine free. The sample was dried at 80 °C until constant mass.

**Sample ODE (diatomaceous earth adsorbent)**

The diatomaceous earth, which is applied as a clarifying agent in the beer industry, was used in this experiment. This amorphous silicate contains large amounts of impurities such as clay, quartz, mica. The sample was ground and used without purification.

The organo-mineral complex was obtained by adding an alcoholic oleylamine solution (190 mmol/kg) to an aqueous 5 % suspension of diatomaceous earth. The mixture was stirred in a turbo-mixer for 30 min at 10 000 rev. min$^{-1}$. The filtered organo-mineral complex was repeatedly washed until it was amine free. The sample was dried at 80 °C until constant mass.

**Anion adsorption tests**

The prepared organo-mineral complexes were tested on the adsorption of Cr$_2$O$_7^{2-}$ (1.4 mmol/dm$^3$), SO$_4^{2-}$ (3.2 mmol/dm$^3$) and H$_2$PO$_4^-$ (3.2 mmol/dm$^3$) anions. The aqueous solution of the anions were mixed with a 5 % organo-mineral suspension for 5 h on a magnetic stirrer, at room temperature. The adsorption mixtures were left standing overnight, filtered, and the concentration of the anions in the supernatant determined. The amount of anion adsorbed on the organo-mineral complex was calculated from the difference between the anion concentration in solution before and after equilibration. The anion adsorption index was calculated as the ratio of the amount of adsorbed anion and the initial amount of anion. Adsorption isotherms of anions were performed on sample OHZ using the batch equilibrium technique.

**Characterization methods**

The CEC and ECEC values were determined by the method of Ming and Dixon. The stability of organo-mineral complexes was estimated in the following manner:

When amine adsorption on a mineral was finished, the amine remaining in the supernatant combined with the wash solution was determined by known methods (oleylamine- ASTM D2074-66), SDMBA AkzoChemie, WV/2.001-2). The percent of amine bound to the mineral surface was calculated from the difference between the added and remaining amount of amine, divided by the amount of amine added.

Bichromate was determined by atomic absorption spectroscopy, sulphate by a turbidimetric method using a spectrophotometer and phosphate by the molybdo-vanadate method using a spectrophotometer.
RESULTS AND DISCUSSION

A few facts must be considered when choosing a mineral that could be a potential base for the creation of anion adsorbents. Zeolites and bentonites are among the most widely used adsorbing minerals. It is known that minerals such as zeolites and bentonites possess a net negative charge owing to isomorphous substitutions in the crystal lattice. This negative charge is compensated by exchangeable cations present at the external and internal mineral surfaces. The first condition for anion adsorption is the neutralization or inversion of a negative charge. Neutralization can be achieved by adsorption of a surface-active amine. The large amine molecules can penetrate in-between the expandable bentonite layers, but in case of zeolite such adsorption can occur only at the external surfaces. So, the cation exchange capacity (CEC) is a relevant values for the adsorption of amines on bentonites, while the external cation exchange capacity (ECEC) is a value of major importance for the adsorption of amines on zeolites. Therefore, the employed amines were adsorbed in amounts equivalent to the CEC value for bentonites and the ECEC values for zeolites. For bentonites, the ECEC value is equal to the CEC value. The results of amounts of SDMBA or oleylamine adsorbed on different forms of zeolite and bentonite are presented in Table I, together with the results of the quantification of amine bonding on a mineral surface.

TABLE I. Results of the adsorption of SDMBA or oleylamine on zeolites and bentonites

<table>
<thead>
<tr>
<th>Samples</th>
<th>ECEC mmol/kg</th>
<th>Amine/(mmol/kg)</th>
<th>Amine bound/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SDMBA</td>
<td>Oleyamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Added Adsorbed</td>
<td>Added Adsorbed</td>
</tr>
<tr>
<td>OZ</td>
<td>190</td>
<td>190 133</td>
<td>– – 70</td>
</tr>
<tr>
<td>OHZ</td>
<td>190</td>
<td>– – –</td>
<td>190 190 100</td>
</tr>
<tr>
<td>OB</td>
<td>1317</td>
<td>1317 1083</td>
<td>– – 97</td>
</tr>
<tr>
<td>OHB</td>
<td>1317</td>
<td>– – –</td>
<td>1317 1222 93</td>
</tr>
<tr>
<td>ODE</td>
<td>–</td>
<td>– – –</td>
<td>– &lt; 4</td>
</tr>
</tbody>
</table>

It can be seen from Table I that a higher oleylamine adsorption was obtained by using acid pretreated zeolite OHZ (100 %). On natural Ca-zeolite, 50 % of oleylamine was adsorbed, which can be explained by the presence of active acid sites at the mineral surface, as a result of the acid treatment of the zeolite. Binding of quaternary (SDMBA) amine on a untreated natural zeolite was 70 %. If amounts of amine bound on these two organo-zeolites are compared, it is obvious that a far better product was obtained by oleylamine chemisorptions on H⁺-zeolite (100 %), than when naturally zeolite with SDMBA (70 %) was used.

Natural (Ca-form) bentonite formed a stable product with the quaternary amine (OB) (binding 97 % of the amine), as was the case with the H⁺-form and the primary amine (HB – 93 %).

The lowest amount of amine was bound on diatomaceous earth, as was to be expected. It cannot be claimed that the formation of an organo-mineral complex occurred in
this case. The diatomaceous earth, known as an adsorbent of colloid particles and not of polar organic species, was chosen in this experiment to prove that acid modification of the zeolite surface is a decisive factor for amine and anion adsorption.

As amount and kind of organic components in the organo-mineral complexes have a great influence on the ability of an organo-mineral to adsorb anions, it was necessary to examine these points.

The comparative results of the anion adsorption tests on the organo-mineral complexes, all samples being prepared under the same conditions, are presented in Table II and Fig. 1. It can be seen that the most efficient anion adsorbent is OHZ, which removes all the bichromate and 95% of the sulphate and dihydrogenphosphate from polluted water. The other organo-mineral complexes showed relatively high affinities for bichromate, which can be attributed to amine-bichromate interaction which was proven by preliminary tests. The affinity of the adsorbents for phosphate is not negligible, and may also be partially due to amine-phosphate interaction, according to preliminary studies. The adsorption of sulphate was weak on these adsorbents.

### Table II. Adsorption of anions on the examined adsorbents (mmol/kg)

<table>
<thead>
<tr>
<th></th>
<th>SO$_4^{2-}$</th>
<th>Cr$_2$O$_7^{2-}$</th>
<th>PO$_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Added</td>
<td>Adsorbed</td>
<td>Added</td>
<td>Adsorbed</td>
</tr>
<tr>
<td>OZ</td>
<td>82</td>
<td>1.5</td>
<td>158</td>
</tr>
<tr>
<td>OHZ</td>
<td>82</td>
<td>78</td>
<td>158</td>
</tr>
<tr>
<td>OB</td>
<td>82</td>
<td>8</td>
<td>158</td>
</tr>
<tr>
<td>OHB</td>
<td>82</td>
<td>2.5</td>
<td>158</td>
</tr>
<tr>
<td>ODE</td>
<td>82</td>
<td>3</td>
<td>158</td>
</tr>
</tbody>
</table>

**Fig. 1. Anion adsorption indexes for the organo-mineral complexes.**
It can be seen, from the Table II and Fig. 1, that the most efficient anion adsorbent was sample OHZ – oleylamine adsorbent on the H+-form zeolite. The adsorption isotherms for the three examined anions were obtained using the batch equilibrium technique (Table III, Figs. 2, 3 and 4).

**TABLE III.** The results of the adsorption of different amount of anions (SO₄²⁻, Cr₂O₇²⁻, PO₄³⁻) on the OHZ-adsorbent

<table>
<thead>
<tr>
<th>Anion</th>
<th>Added/(mmol/kg)</th>
<th>Adsorbed/(mmol/kg)</th>
<th>Equilibrium conc./(mmol/l)</th>
<th>% A</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻</td>
<td>20</td>
<td>18.5</td>
<td>0.20</td>
<td>92.5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>37</td>
<td>0.30</td>
<td>92.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>57</td>
<td>0.30</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>75</td>
<td>0.47</td>
<td>93.7</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>78</td>
<td>2.6</td>
<td>78</td>
</tr>
<tr>
<td>Cr₂O₇²⁻</td>
<td>32</td>
<td>32</td>
<td>&lt; 0.1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>63.5</td>
<td>&lt; 0.1</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>95</td>
<td>&lt; 0.2</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>126</td>
<td>0.3</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>157</td>
<td>0.5</td>
<td>98</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>20</td>
<td>19.7</td>
<td>0.12</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>39.5</td>
<td>0.12</td>
<td>98.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>59</td>
<td>0.18</td>
<td>98.1</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>77</td>
<td>0.30</td>
<td>96.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>92.5</td>
<td>0.55</td>
<td>92.5</td>
</tr>
</tbody>
</table>

The results of SO₄²⁻ adsorption on OHZ are given in Fig. 2: sulphate adsorbed, mmol/kg depending of the added amount, mmol/kg (Fig. 2a) and as a function of equilibrium concentration, mmol/l (Fig. 2b).

Fig. 2. Sulphate adsorbed on organozeolite – OHZ (as a function of the added amount (a) and the equilibrium concentration (b)).
As can be seen from Fig. 2, more than 90% of sulphate anions were adsorbed up to 80 mmol/kg \( \text{SO}_4^{2-} \) and the equilibrium concentration was below 0.5 mmol/l. With the higher sulphate concentrations, the efficacy of adsorption decreased.

Efficient adsorption of \( \text{Cr}_2\text{O}_7^{2-} \) ions, was obtained over the whole examined concentration range (Fig. 3). The equilibrium concentration was below 0.5 mmol/l and more than 98% of the \( \text{Cr}_2\text{O}_7^{2-} \) ions were adsorbed.

Dihydrogenphosphate adsorption on this adsorbent was also high (Fig. 4).

The phenomena of anion adsorption on organo-mineral complexes are probably electrostatic in nature.\(^{11,15}\) The hemimicelles of the organo-mineral complex attract and trap the anions on the mineral surface. The mechanism of anion adsorption, which is still not clearly...
understood, is thought to be surface precipitation on the organo-zeolite. However, the explanation for such a superior anion adsorption on OHZ lies in the acid surface modification, which resulted in the formation of the most stable organo-mineral complex.

CONCLUSION

The obtained results shows efficient anion adsorbents were prepared by appropriate modification of natural zeolite and bentonite. The organo-zeolite obtained by oleylamine modification of the H\(^+\) form of zeolite is an effective adsorbent of SO\(_4\)\(^2^-\), Cr\(_2\)O\(_7\)\(^2^-\) and H\(_2\)PO\(_4\)\(^-\) anions present in water. The protonated amine molecules at the external surface of the H\(^+\) clinoptilolite act as much stronger anions adsorption sites than the quaternary ammonium salt cations on natural clinoptilolite.

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IZVOD

АДСОРПЦИЈА НЕОРГАНСКИХ АНЈОНСКИХ ЗАГАЂИВАЧА НА
МОДИФИКОВАНИМ МИНЕРАЛИМА

АЛЕКСАНДРА ВУЈАКОВИЋ, АЛЕКСАНДРА ДАКОВИЋ, ЈОВАН ЛЕМИЋ, АНА
РАДОСАВЉЕЋ, МИХАЛОВИЋ И МАГДАЛЕНА ТОМАШЕЋ-ЧАНОВИЋ

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Органо минерални комплекси су добијени активацијом основних минерала (зеолита, бентонита и диатомијске земље) са примарним амином (олејламином) и алкил амонијум јоном (стеарили диметил бензил амонијум хлоридом). Ефикасан адсорбент аниона је припремљен модификацијом површине природног зеолита са примарним амином. Полазни зеолит je прво третиран са 2 M HCl, а затим je na H-форми зеолита извршена адсорпција олејламина. Направљена су још четири органо комплекса модификацијом бентонита и диатомијске земље са стеарили диметил бенил амонијум јоном и испитана је адсорпција аниона на њима. Експерименти адсорпције аниона су показали да се најефикаснији адсорбент за пречишћавање вода контаминираним анјонима добија двостепеним (киселински / аминским) третирањем природног зеолита.

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