Functionalization of thermo-acid activated sepiolite by amine-silane and mercapto-silane for chromium(VI) adsorption from aqueous solutions

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Abstract

Chromium(VI) adsorption from aqueous solutions onto thermo-acid activated sepiolite functionalized with (3-mercaptopropyl)trimethoxy-silane and [3-(2-aminoethylamino)propyl]trimethoxy-silane was investigated. Scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric and differential thermal analysis, nitrogen adsorption-desorption, and determination of the point of zero charge were used to characterize the obtained adsorbents. It has been established that the silanes were successfully grafted on the thermo-acid activated sepiolite surfaces and that the structure of parent material was preserved during the functionalization. The adsorption of Cr(VI) onto functionalized thermo-acid activated sepiolite was tested as a function of initial pH values at 298 K. The amine functionalized thermo-acid activated sepiolite showed a higher adsorption capacity than the mercapto functionalized thermo-acid activated sepiolite at all studied initial pH values, especially at the initial pH 2.

Keywords: thermo-acid activated sepiolite, functionalization, (3-mercaptopropyl)trimethoxy-silane, [3-(2-aminoethylamino)propyl]trimethoxy-silane, adsorption, chromium(VI).

In the environment, chromium originates from geochemical and anthropogenic sources (industry, energy, mines and smelters). The most stable forms of chromium in the environment are trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), whereas Cr(VI) is more toxic, carcinogenic and mutagenic to the living organisms [1]. In aqueous solutions, Cr(VI) occurs in several stable forms, such as: Cr₂O₇²⁻, H₂CrO₄, HCrO₄⁻ and CrO₄²⁻. The relative abundance of those forms mainly depends on the pH value of the solution and Cr(VI) concentration. H₂CrO₄ generally exists at pH less than about 1.0; HCrO₄⁻ predominates at pH values between 2.0 and 6.0; and when pH increases to above 6.8, CrO₄²⁻ is the primary form. The dichromate, Cr₂O₇²⁻, forms when the concentration of chromium exceeds approximately 1 g/dm³ [1].

A simple, effective and inexpensive method for the Cr(VI) removal from aqueous solutions, like polluted water, is the adsorption, where the key factor is the selection of a proper adsorbent. The adsorption of Cr(VI) oxyanions from aqueous solutions by natural clay minerals was not given much attention, mainly due to the fact that clays are negatively charged and moreover minerals for the adsorption of anionic species of Cr(VI) from aqueous solutions, it is necessary to change the character of their surface, which can be achieved via functionalization processes by adsorption of quaternary ammonium salts or amines and by organosilane grafting, through reaction with surface silanol groups. The study of Cr(VI) adsorption from aqueous solutions by functionalized clay minerals (kaolinite, montmorillonite, stevensite, rectorite, etc.) was the object of several researches [3–12]. To the best of our knowledge, there are no studies about Cr(VI) removal from aqueous solutions by functionalized sepiolite, except our previous studies, where natural and acid activated sepiolites were functionalized by using (3-mercaptopropyl)trimethoxy-silane [13] and [3-(2-aminoethylamino)propyl]trimethoxy-silane [14]. It was shown that functionalized partially acid activated sepiolite has a higher degree of functionalization and a higher adsorption capacity for anionic species of Cr(VI) compared to functionalized natural sepiolite [13,14].

Our further studies were directed to the investigation of the removal of Cr(VI) by using fully-acid activated sepiolite functionalized with both (3-mercaptopropyl)trimethoxy-silane and [3-(2-aminoethylamino)propyl]trimethoxy-silane. It was shown [15–19] that during acid treatments of sepiolite, variable amounts of structural Mg²⁺ were removed, depending on the intensity of the acid treatment. If the treatment is aggressive enough, as during acid activation at elevated temperature, the octahedral cations are completely dissolved,
10 g of sepiolite was suspended in 100 cm$^3$ of 4 N HCl solution and heated at 65±1 °C in a stirred reaction flask for 10 h. Then, the mixture was filtered, washed with hot distilled water until it became Cl$^-$ free and dried at 110 °C for 2 h. Hereinafter, sepiolite activated by acid at elevated temperature was marked as TASEP.

With the determination of the chemical composition of TASEP by AAS, Perkin Elmer 730 (89.6 wt.% SiO$_2$, 0.12 wt.% MgO, < 0.03 wt.% Al$_2$O$_3$, 0.08 wt.% Fe$_2$O$_3$, < 0.05 wt.% CaO and 8.66 wt.% LOI) it was shown that there was almost complete magnesium leaching from sepiolite structure during applied thermo-acid activation.

**Functionnalization of the thermo-acid activated sepiolite by organosilane**

The TASEP sample was functionalyzed with organosilane, 99.99% purity, manufactured by Sigma-Aldrich: i) (3-Mercaptopropyl)trimethoxysilane (HS–(CH$_2$)$_3$–Si–(OCH$_3$)$_3$) or shortly named mercapto-silane and ii) [3-(2-aminoethylamino)propyl]trimethoxysilane or amine-silane, with the chemical formula (CH$_3$O)$_3$Si–(CH$_2$)$_3$–NH–(CH$_2$)$_2$–NH$_2$. The functionalization reactions were performed according to previous studies [13,14]. The mercapto and amine functionalized samples were denoted as MTASEP and APT-TASEP, respectively.

**Characterization**

The morphology of the TASEP, MTASEP and APT-TASEP powders was analysed by scanning electron microscopy (SEM) on a TESCAN MIRA 3 XMU microscope operating at 20 kV.

The phase compositions of TASEP, MTASEP and APT-TASEP were determined using a conventional powder diffractometer (Ital Structures APD 2000) with Bragg-Brentano geometry and CuK$_{α1,2}$ radiation (Ni filter) with a 0.02° 2θ step and a 2 s counting time per data point.

FT-IR analyses of the samples were performed on a 100 MB Boman Hartmann & Brown instrument in the wave number range from 400 to 4000 cm$^{-1}$. The samples were prepared by the KBr method, at a ratio of the sample:KBr = 1:100.

Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) of the samples (approximately 5 mg) were performed in a flowing air atmosphere using a TA thermogravimetric analyzer (TA Instruments, New Castle, USA), model SDT Q600. The samples were heated up to 1000 °C at a heating rate of 20 °C/min.

The specific surface area, pore volume and pore size distribution of the samples were determined on the basis of nitrogen adsorption-desorption isotherms, using a Micromeritics ASAP 2020 instrument for measurements. Before the sorption measurement, the samples were degassed at 150 °C for 12 h, in vacuum. Then, adsorption of nitrogen (purity 99.9%) on the free surfaces of the samples was performed at a temperature of liquid nitrogen (−196 °C). Desorption of nitrogen was carried out at liquid nitrogen temperature. The specific surface area of each sample was calculated according to the Brunauer–Emmett–Teller (BET) method from the linear part of the nitrogen adsorption isotherm. The volume of the mesopores and pore size distribution were calculated according to the Barrett, Joyner and Halenda method [21] from the desorption branch of isotherm. The Dubinin–Radushkevich method [22] was used for analyzing of micropores.

The point of zero charge of the samples was determined using previously described batch equilibration technique [13–15,23] in KNO$_3$ solution (concentration 0.1 or 0.01 mol/dm$^3$). In all experiments, a series of samples of 25 cm$^3$ KNO$_3$ solution, with the concentration of 0.1 and 0.01 mol/dm$^3$ and the preset adjusted pH values (pH$_{initial}$) of approximately 2.0 to approximately 11.0, were equilibrated with 0.05 g of sepiolite sample, during 24 h at 25 °C with constant shaking. In the case of TASEP and MTASEP samples, equilibration was performed for the two ratios of solid/liquid (0.05 and 0.10 g/25 cm$^3$). After achieving equilibrium, the suspensions were filtered through filter paper, and the

**Materials and Methods**

**Starting Material**

A fraction < 250 µm of natural sepiolite (SEP) from Andrić, Čačak (Serbia), was used as the starting material [15]. An acid treatment was performed at elevated temperature (thermo-acid activation) as follows [20]: 10 g of sepiolite was suspended in 100 cm$^3$ of 4 mol/dm$^3$ HCl solution and heated at 65±1 °C in a stirred reaction flask for 10 h. Then, the mixture was filtered, washed with hot distilled water until it became Cl$^-$ free and dried at 110 °C for 2 h. Hereinafter, sepiolite activated by acid at elevated temperature was marked as TASEP.

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pH value of the filtrate (pHfinal) was measured. The point of zero charge (pHZC) was determined from the dependence of the pHfinal vs. pHinitial as the pH value of plateau or as the pH value of the curve inflexion [13–15,23].

Adsortion experiments

The aqueous solutions of Cr(VI) anions were prepared by dissolving K2Cr2O7, in demineralized water.

The Cr(VI) adsorption was investigated at batch conditions at a constant temperature in a thermostat with a shaker (MEMMERT), where the temperature was maintained at 25±0.01 °C. The measured mass quantities of MTASEP or APT-TASEP were mixed with solutions of Cr(VI), at the preset pH values (pHinitial) in PVC vessels. Upon expiration of the required mixing time in the thermostat, the suspensions were filtered and further, the concentrations of Cr(VI) in solution and the final pH value of the solution (pHfinal) were determined.

In order to determine the concentration of Cr(VI) in the solution, atomic absorption spectroscopy (AAS) was performed using a Perkin Elmer 730 instrument, while the pH value of the solution was measured by a pH meter (Inolab WTW series pH 720). To adjust the initial pH values of solutions, solutions of HCl or KOH of 0.1 mol/dm3 concentration were used.

The adsorption of Cr(VI) on MTASEP or APT-TASEP was investigated at different initial concentrations of Cr(VI) solution of 5 to 205 mg/dm3 and at different initial pH values: 4.5, 3.0 and 2.0±0.1. The ratio of adsorbent/solution was 0.10 g/25 cm3 for MTASEP and 0.05 g/25 cm3 for APT-TASEP.

The amounts of Cr(VI) ions adsorbed per unit mass of functionalized sepiolite were calculated using Eq. (1):

\[ q_e = \frac{c_i - c_e}{w} V \]

where: \( c_i \) – initial concentration of Cr(VI) in solution (mg/dm3); \( c_e \) – the equilibrium concentration of Cr(VI) in solution (mg/dm3) \( w \) – mass of adsorbent (g), \( V \) – volume of Cr(VI) solution (dm3).

All adsorption experiments were repeated twice. The presented results represent the mean of two measurements.

RESULTS AND DISCUSSION

Characterization of the unfunctionalized and functionalized thermo-acid activated sepiolites

Figure 1 shows micrographs of TASEP (a), MTASEP (b) and APT-TASEP (c). It can be seen that the thermo-acid activated sepiolite (TASEP) has a fibrous structure (Figure 1a) like a natural sepiolite [24], but the difference is that TASEP fibres are shorter (Figure 1a). What is more, the fibre structure of MTASEP and APT-TASEP samples was preserved during functionalization (Figure 1b and c), whereby the fibres were more connected comparing to the parent material (Figure 1a).

The diffraction patterns of TASEP, MTASEP and APT-TASEP are given in Figure 2. The X-ray diffractogram of the TASEP sample shows almost completely amorphous structure. The appearance of the broad diffraction peak at 2θ = 23° indicates the formation of amorphous structure. There are no differences between diffractograms of functionalized (MTASEP and APT-TASEP) and parent sample (TASEP), which indicates that functionalized samples retained the structure of unfunctionalized one.

FT-IR spectra of the TASEP, MTASEP and APT-TASEP samples are shown in Figure 3. The spectrum of MTASEP is very similar to the spectrum of TASEP, but there is the difference in the intensity of the bands in the 2950–2840 cm−1 range, which can be assigned to vibration of C–H bonds in mercapto-silane [13,14,25–27].

Also, FT-IR spectrum of APT-TASEP is generally similar to FT-IR spectrum of TASEP, but the intensity of the bands in the 2950–2840 cm−1 range in the spectrum of APT-TASEP is higher than in the spectrum of TASEP. In addition, there is a band at around 1500 cm−1, which is characteristic of amine groups in amine-silane [25,28–34].

In order to assess the differences between the functionalized and unfunctionalized samples, the results of FT-IR spectroscopy of TASEP, MTASEP and APT-TASEP were presented in the range between 3200 and 2500 cm−1 (Figure 4).

From the Figure 4, it can be seen that there are the bands at about 2936 and 2857 cm−1 which can be assigned to the C–H vibration of methoxy (OCH3) and methylene (CH2) groups, respectively [13,14,25–27]. These bands cannot be observed in the FT-IR spectrum of TASEP. The presence of methoxy groups in the functionalized samples indicates that the silanes do not bind to the surface by reaction of all (three) methoxy groups, but probably by reaction of one OCH3 with one silanol group at the surface of TASEP [26,35]. The intensities of the both bands are higher for APT-TASEP than for MTASEP, which indicates that the content of CH2 and OCH3 groups is higher in APT-TASEP than in MTASEP, supposing it is due to the fact that the amine-silane contains five CH2 groups, while mercapto-silane contains only three. However, higher content of OCH3 groups in APT-TASEP is an indicator of better functionalization of TASEP by amine-silane than by mercapto-silane.

Figure 5 shows TG/DTA curves of the TASEP, MTASEP and APT-TASEP sepiolite samples. It should be noted that there is no exothermic peak at about 820 °C [15] on DTA curves, which would correspond to the phase transformation of sepiolite to enstatite. This is indica-
Figure 1. SEM Micrographs of TASEP (a), MTASEP (b) and APT-TASEP (c).

Figure 2. X-Ray diffractograms of the TASEP, MTASEP, and APT-TASEP samples.
tion of destruction of sepiolite structure during thermal-acid activation.

According to DTA curves in Figure 5, the two characteristic regions can be noticed: endothermic, from room temperature to \( \sim 200 \) °C, and exothermic, from \( \sim 200 \) to approximately \( \sim 700 \) °C. The weight loss in the first region, due to dehydratation \([26,36]\), is approximately the same for all samples, but slightly lower for APT-TASEP (3.5 wt.%) than for TASEP (4.2 wt.%) and MTASEP (5.6 wt.%). On the other hand, the weight loss in the second region is much higher for APT-TASEP (16.6 wt.%) than for TASEP (4.0 wt.%) and MTASEP (5.3 wt.%). The weight loss in the second region is primarily due to combustion of the organic matter, \( i.e. \), amine-silane or mercapto-silane \([28,33,37]\). Bearing in mind the molar mass of amine-silane, 209 g/mol, and mercapto-silane, 185 g/mol, it can be said that higher weight loss of APT-TASEP in the second region compared to MTASEP is primarily the result of much better functionalization of TASEP by amine-silane than by mercapto-silane.

Table 1 shows the textural properties of the TASEP, MTASEP and APT-TASEP samples. The results show that mercapto functionalization of TASEP leads to slight decreases in specific surface area, mesopore volume and micropore volume, while amine functionalization leads to significant decrease of these parameters.

Such changes of the textural parameters of TASEP by functionalization, especially micropore volume, can be explained by the size of organosilane molecules, \( i.e. \), the possibility of organosilane molecule to enter into the pores of TASEP. In the case of APT-TASEP, it can be assumed that the large molecules of amine-silane entered and closed micropores \([28,37–39]\) of TASEP during amine functionalization which caused a decrease of porosity, mainly microporosity, and consequently specific surface area. The decrease of microporosity of APT-TASEP compared to the TASEP causes the increase of the maximum and mean pore diameter of the APT-TASEP compared to the TASEP. Due to micropore closing, the content of pore water in APT-TASEP is lower than in TASEP and MTASEP, and consequently weight loss is lower due to dehydration (Figure 5). According to the textural parameters of the MTASEP and TASEP (Table 1), a slight decrease of porosity of MTASEP compared to TASEP can be seen, so it could be
Figure 5. TG/DTA curves of the a) TASEP, b) MTASEP and c) APT-TASEP samples.
assumed that the entry of relatively small molecules mercapto-silane in pores of TASEP did not cause a significant reduction in volume of micropores and mesopores. The maximum and mean pore diameters of MTASEP are similar to those of TASEP indicating that micropores of the TASEP were not closed during the mercapto functionalization of TASEP.

The results of determination of the point of zero charge, pH\(_{pzc}\) for the samples TASEP, MTASEP and APT-TASEP are shown in Figure 6. The pH\(_{pzc}\) of APT-SEP (Figure 6c) was determined as the pH value of the plateau of pH\(_{\text{final}}\) vs. pH\(_{\text{initial}}\) dependence, while the pH\(_{pzc}\) of TASEP and MTASEP was obtained as pH\(_{\text{final}}\) vs. pH\(_{\text{initial}}\) curves inflection (Figure 6a and b, respectively). To precisely define the curve inflection, the pH\(_{pzc}\) of TASEP and MTASEP were determined for two solid/liquid ratio.

From Figure 6 it is obvious that the pH value of the plateau or inflexion of the pH\(_{\text{final}}\) vs. pH\(_{\text{initial}}\) dependence remains constant with changing concentration of KNO\(_3\) solution, which means that KNO\(_3\) is an indifferent electrolyte. In that way, the common plateau obtained at a pH value of 9.5±0.1 for APT-TASEP corresponds to the pH\(_{pzc}\) of the APT-TASEP. In addition, in the case of pH\(_{pzc}\) of TASEP and MTASEP determination, the position of curve inflection was independent of solid/liquid ratio and values of pH\(_{pzc}\) of TASEP and MTASEP were determined as 5.0±0.1 and 4.7±0.1, respectively.

The results of determination of the point of zero charge showed that acid-base properties of functionalized sepiolite were very much depended on the type of organosilane used for functionalization. The value of the point of zero charge of APT-TASEP was much higher than that of MTASEP, because amine-silane contains more basic groups (–NH\(_2\) and –NH–) than mercapto-silane (–SH). The acid-base properties of MTASEP are very similar to that of TASEP, because (–SH) group has similar acidity as (–OH) group. In addition, the buffer capacity APT-TASEP is much higher than that of MTASEP and TASEP. In the wide range of pH\(_{\text{initial}}\) the final pH values were constant and equal to pH\(_{pzc}\) of APT-TASEP. Just in the range below the initial pH ~ 4.0, the final pH values were less than pH\(_{pzc}\) for APT-TASEP and the surface charge of APT-TASEP could become positive.

The adsorption of Cr(VI) onto mercapto-silane and amine-silane functionalized thermo-acid activated sepiolite samples

The results of preliminary experiments showed that adsorption capacity of TASEP for Cr(VI) is very low, as in the case of natural and acid-activated sepiolite [13]. Therefore, adsorption onto functionalized samples MTASEP and APT-TASEP was investigated and presented in this study.

The adsorption experiments were done at different initial pH values. During equilibration of adsorbent with ion solution, the pH value of solution can be changed due to: protonation/deprotonation of surface functional groups of adsorbent, interaction of H\(^+/\)OH\(^–\) with ions in the solution, specific adsorption of adsorbent, etc. Therefore, in order to assess the influence of pH on adsorption, it is not enough to adjust initial pH value, but it is necessary to follow the changes of pH during adsorption.

The dependence of the final solution pH value (pH\(_{\text{final}}\)), during equilibration of the Cr(VI) solution with MTASEP and APT-TASEP samples on the initial concentration of Cr(VI) solution is shown in Figure 7a and b, respectively. The dependence of the adsorbed amount of Cr(VI), q\(_e\), on the equilibrium concentration of Cr(VI) solution, c\(_e\), is shown on Figure 8a for MTASEP and 8b for APT-TASEP.

During equilibration of the Cr(VI) solutions with MTASEP and APT-TASEP at pH\(_{\text{initial}}\) 2.0 (Figure 7), the pH\(_{\text{final}}\) remained nearly constant with an increase in initial Cr(VI) concentration and approximately equal to pH\(_{\text{initial}}\) due to high acid conditions in the suspension of both samples. The similar dependence of pH\(_{\text{final}}\) on Cr(VI) concentration was obtained for MTASEP for pH\(_{\text{initial}}\) 3.0. But, in the case of APT-TASEP at pH\(_{\text{initial}}\) 3.0, as well as at pH\(_{\text{initial}}\) 4.5, pH\(_{\text{final}}\) was much higher due to high buffer capacity of APT-TASEP. At low Cr(VI) concentration, pH\(_{\text{final}}\) was equal to pH\(_{pzc}\) of APT-TASEP, but with the increase of Cr(VI) concentration pH\(_{\text{final}}\) decreased, which can be explained by deprotonation of HCrO\(_4\)\(^–\) ions at pH > 6.8 (HCrO\(_4\)\(^–\) ⇌ H\(^+\) + CrO\(_2\)\(^{2–}\)) [1].

During Cr(VI) adsorption on MTASEP at pH\(_{\text{initial}}\) 4.5, final pH values were not much higher than the initial pH, because of low buffer capacity of the adsorbent. A slight increase of pH\(_{\text{final}}\) with the increase of Cr(VI) con-

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**Table 1. The textural parameters of the TASEP, MTASEP, and APT-TASEP samples**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TASEP</th>
<th>MTASEP</th>
<th>APT-TASEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area, S(_{BET}) / m(^2) g(^{-1})</td>
<td>449</td>
<td>403</td>
<td>33</td>
</tr>
<tr>
<td>Micropore volume, V(_{micropore}) / cm(^3) g(^{-1})</td>
<td>0.415</td>
<td>0.349</td>
<td>0.058</td>
</tr>
<tr>
<td>Mesopore volume, V(_{mesopore}) / cm(^3) g(^{-1})</td>
<td>0.571</td>
<td>0.396</td>
<td>0.133</td>
</tr>
<tr>
<td>Maximum pore diameter, D(_{max}) / nm</td>
<td>3</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Mean pore diameter, D(_{mean}) / nm</td>
<td>7</td>
<td>6</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 6. Dependence of $pH_{\text{final}}$ on $pH_{\text{initial}}$ during the equilibration: a) of 0.1 g of TASEP with 25 cm$^3$ solution of (■) 0.1 M KNO$_3$, (●) 0.01 M KNO$_3$ and 0.05 g of TASEP with 25 cm$^3$ solution of (□) 0.1 M KNO$_3$, (○) 0.01 M KNO$_3$; b) of 0.1 g of MTASEP with 25 cm$^3$ solution of (■) 0.1 M KNO$_3$, (●) 0.01 M KNO$_3$ and 0.05 g of MTASEP with 25 cm$^3$ solution of (□) 0.1 M KNO$_3$, (○) 0.01 M KNO$_3$; c) of 0.05 g of APT-TASEP with 25 cm$^3$ solution of (□) 0.1 M KNO$_3$, (○) 0.01 M KNO$_3$. 
The adsorption of Cr(VI) on functionalized sepiolites is dependent on the pH of the solution which affects the surface charge of the adsorbent and the predominant species of Cr(VI) in solution.

It was found (Figure 8) that the amount of Cr(VI) ions adsorbed onto MTASEP slightly increased with pHfinal decreasing from 5.2 (at pHinitial 4.5) to 3.1 (at pHinitial 3.0) and 2.1 (at pHinitial 2.0). Thus, the amount of adsorbed Cr(VI) was higher at lower pHs (around 3.0 and 2.0) than at higher pHs (around 5.0), but the sorption capacity of MTASEP was a bit higher at pHs ~ 3.0 than at pHs ~ 2.0.

The results, shown in Figure 7a, indicate that at pHinitial of 2.0 and 3.0, pHfinal were lower than pHpzc of MTASEP (4.7), which means that the surface of MTASEP was positively charged due to protonation of the surface mercapto (−SH) groups. As the pHfinal was lower than the pHpzc of MTASEP, the surface was more positively charged, due to the large number of protonated mercapto groups (−SH2+). A higher positive charge of the surface of MTASEP caused higher electrostatic attraction between MTASEP surface [13,40–44] and HCrO4−, which is predominant form of Cr(VI) in the solution of examined pH range [1].

It was shown [13,45–47] that in very acidic conditions, at pH < 3, mercapto groups can reduce Cr(VI) to Cr(III), whereby the mercapto groups are oxidized into sulfonic groups (−SO3H) of high acidity. It can be supposed that at pHinitial 2.0, due to very acidic conditions, sulfonic groups were weakly ionized, and Cr3+, formed...
by reduction of Cr(VI), were weakly adsorbed on the surface MTASEP, due to a very small number of –SO₂O– groups, that could bind the Cr³⁺ through electrostatic attraction. According to that, it was assumed that the predominant mechanism of removal of Cr(VI) from aqueous solutions, at initial pH value of 2.0, was the electrostatic attraction between HCrO₄⁻ from the solution and protonated mercapto (–SH₂⁺) groups on the surface of the MTASEP.

On the other hand, at pH initial 3.0, the reduction of Cr(VI) to Cr³⁺ was lower than at pH initial 2.0, but due to a higher number of –SO₂O– groups, formed by ionization of the –SO₃H groups at higher pH value, it can be suppose that Cr³⁺ were better adsorbed on the surface MTASEP due to the electrostatic attraction between the Cr³⁺ and –SO₂O⁻ groups. Thus, it was assumed that the reduction of Cr(VI) to Cr(III) followed by removal of resulted Cr³⁺ gave the contribution to adsorption of chromium onto MTASEP at pH initial 3.0. Therefore, the electrostatic attraction between HCrO₄⁻ and the protonated –SH₂⁺ groups on the MTASEP surface, as well as reduction of Cr(VI) to Cr(III) followed by electrostatic attraction between Cr³⁺ and –SO₂O⁻ groups were possible mechanisms of Cr(VI) removal from solution at initial pH initial 3.0.

It can be seen from Figure 8b that Cr(VI) adsorption onto APT-TASEP significantly increased with initial and final pH value decreasing to pH ≈ 2 and ≈ 2.2, respectively. During the equilibration of APT-TASEP with Cr(VI) solution at pH initial 2.0, the final pH values were much lower than pH_pzc of APT-TASEP, which means that the surface of APT-TASEP had high positive charge, due to
protonation of the surface amine groups (–NH– and –NH2) [29,30,34,39,40,48–50]. The presence of a large number of protonated amine groups on the surfaces of the APT-TASEP favoured HCrO4− adsorption by electrostatic attraction [8,13,29,40,48–50]. At higher pH_initial, 3.0 and 4.5, the pH_final of solutions were near the pH_pzc of the APT-TASEP and the surface of APT-TASEP was less positively charged. Thus, electrostatic attractions between the surface and Cr(VI) anions were lower than at pH_initial 2.0 and the amount of Cr(VI) removed from solution was also lower. The possible mechanism of Cr(VI) removal at those pH values is also the formation of hydrogen bonding between oxygen atoms of CrO4^{2−} (which is a predominant form of Cr(VI)) at pHs approximately equal to pH_pzc for APT-TASEP and hydrogen atoms of non-protonated amine groups [29,40].

According to the reported results, the amine functionalized thermo-acid activated sepiolite is a more effective adsorbent than mercapto functionalized thermo-acid activated sepiolite for Cr(VI), at all investigated initial solution pH values, especially at lower pHs. Although TASEP mercapto functionalization leads to a slight decrease in the specific surface area and porosity, while the amino functionalization leads to a significant reduction in these parameters, the APT-TASEP showed a higher adsorption capacity than the MTASEP. It is obvious that the type of silane used for modification, e.g., its chain length and basicity of groups in silane that could be protonated, has a pronounced influence on adsorption capacity for Cr(VI). Similar results were obtained in our previous studies for the functionalised natural and acid-activated sepiolites [13,14]: adsorption capacities of amine-functionalized sepiolites were much higher than of mercapto functionalized sepiolites. The maximum adsorption capacities of the functionalized thermo-acid activated sepiolites are higher than those of the functionalized natural sepiolites [13,14], but lower than those of the functionalized acid activated sepiolite, at the same conditions (pH and temperature). In this study, it was assumed that by thermo-acid activation of sepiolite, silica with high content of silanol groups at the surface could be obtained, which could enable higher degree of functionalization by covalent grafting of silane and consequently higher adsorption capacity for anionic species of chromium (VI) compared to functionalized acid activated and natural sepiolite. However, this was not the case. The lower adsorption capacities of functionalized thermo-acid activated sepiolites compared to functionalized acid activated sepiolites can be explained by the higher degree of condensation of surface silanol groups of thermo-acid activated sepiolites, which caused a decrease in the number of silanol groups at the surface for silane grafting.

CONCLUSION

The removal of Cr(VI) from aqueous solution using adsorbents obtained by covalent grafting of mercapto-silane and amine-silane onto thermo-acid activated sepiolite was studied. Based on the presented results, it was concluded that the structure as well as fibre morphology of the thermo-acid activated sepiolite were preserved during organosilane functionalization. FT−IR and DTA/TG results showed much better functionalization of thermo-acid activated sepiolite by amine-silane than by mercapto-silane.

According to the value of the point of zero charge, pH_pzc, it was shown that amine-silane gave a basic character to the surface and caused the pH_pzc shift from 5.0 (pH_pzc of unfunctionalized sample) to 9.5 (pH_pzc of amine-functionalized sample), while the pH_pzc of mercapto-silane functionalized sample (4.7) is slightly lower than pH_pzc of unfunctionalized sample, due to similar acidity of their surface groups (−SH and −OH).

In addition, the specific surface area, pore volume, maximum and mean pore diameters of amine functionalized sample were reduced, while these textural parameters of the mercapto functionalized sample were similar to those of parent sample.

The amine functionalized thermo-acid activated sepiolite showed a higher adsorption capacity for Cr(VI) than the mercapto functionalized sample at all the studied initial pH values, especially at lower initial pH values. The electrostatic attraction of anionic Cr(VI) species with protonated amine/mercapto groups of functionalized samples is a possible mechanism of Cr(VI) removal, at pH values of solution below the point of zero charge of adsorbent. The formation of hydrogen bonds between oxygen atoms of oxyanion species of Cr(VI) and hydrogen atoms of amine groups, at pH values of solution close to the pH_pzc of amine functionalized sample could be another possible mechanisms of Cr(VI) removal by amine-silane functionalised sample. In the case of mercapto-functionalized sample, the reduction of Cr(VI) by mercapto groups to Cr^{3+}, followed by their electrostatic interaction with the sulfonate group, obtained by oxidation of the mercapto groups, is a possible mechanism at lower solution pH values.

Acknowledgements

The authors wish to acknowledge the financial support for this research from the Ministry of Education, Science and Technological Development of the Republic of Serbia through the project III45019.

REFERENCES


IZVOD

ADSORPCIJA HROMA(VI) IZ VODENIH RASTVORA NA TERMO-KISELINSKI AKTIVIRANOM SEPIOLITU FUNKCIONALIZOVANOM AMINO-SILANOM I MERKAPTO-SILANOM

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Predmet ovog rada je funkcionalizacija termo-kiselinski aktiviranog sepiolita primenom (3-merkaptopropil)trimetoksi silana ili merkapto-silana i [3-(2-amino-etilamino)propil]trimetoksi silana ili amino-silana, određivanje fizičko-hemijskih svojstava i proučavanje adsorpcije Cr(VI) iz vodenih rastvora na funkcionalizovanim materijalima pri različitim početnim pH vrednostima (2,0, 3,0 i 4,5). Za karakterizaciju funkcionalizovanih adsorbenata korišćene su: rendgenska difrakciona analiza (XRD), infracrvena spektroskopska analiza (FT-IR), termogravimetrijska i diferencijalno-termijska analiza (TG/DTA), skenirajuća elektronska mikroskopija (SEM), dok su adsorpciono–desorpcione izoterme azota korišćene za određivanje specifične površine, zapreminе i raspodele veličina porа. Tačka nultog naleza adsorbenata je određena metodom uravnotežavanja posebnih proba. Rezultati karakterizacije su pokazali da je bolja funkcionalizacija termo-kiselinski aktiviranog sepiolita postignuta primenom amino-silana. Tokom funkcionalizacije organsilanim sačuvana je struktura i vlaknasta morfologija termo-kiselinski aktiviranog sepiolita. Kovalentnim vezivanjem amino-silana za površinu termo-kiselinski aktiviranog sepiolita povećava se bazni karakter površine, dok se u slučaju vezivanja merkapto-silana kiselobazna svojstva ne menjaju značajno. Specifična površina, zapremina i prečnici pora amino-silaniziranog uzorka su značajno manji u odnosu na nefunkcionalizovan uzorak, dok su kod merkapto-silaniziranog sepiolita približno isti kao kod polaznog materijala. Kapacitet adsorpcije Cr(VI) amino-silikaniziranog adsorbenta je veći od kapaciteta merkapto-silaniziranog uzorka na svim ispitivanim početnim pH vrednostima Cr(VI) rastvora i naročito pri veoma niskoj početnoj pH vrednosti (2,0). Dominantan mehanizam adsorpcije Cr(VI) pri početnoj pH rastvora 2,0 na amino-silikaniziranom adsorbentu je elektrostatičko privlačenje između Cr(VI) anjona i protonovanih amino grupa, a pri višim početnim pH rastvora moguće je obrazovanje vodoničnih veza između CrO42– i amino grupa. Adsorpcija Cr(VI) na merkapto-silaniziranom adsorbentu se zasniva na elektrostatičkim interakcijama između Cr(VI) anjona i protonovanih merkapto grupa, kao i redukciji Cr(VI) do Cr3+ merkapto grupama, uz elektro-statičko privlačenje redukcijom nastalih Cr3+ i sulfonatnih grupa dobijenih oksi-dacijom merkapto grupa.

Ključne reči: Termo-kiselinski aktiviran sepiolit • Funkcionalizacija • (3-Merkaptopropil)trimetoksilsilan • [3-(2-Aminooetilamino)propil]trimetoksilsilan • Adsorpcija • Hrom(VI)