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Chromium (VI) removal from aqueous solutions using mercaptosilane functionalized sepiolites

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ABSTRACT

Natural and acid-activated sepiolite samples were functionalized with (3-Mercaptopropyl)trimethoxysilane. By X-ray powder diffraction, Fourier transform infrared spectroscopy, and differential thermal analysis it was shown that functionalization of sepiolites by grafting silane reagents occurs mainly on the surface, whereby their crystalline structure remained unchanged. The efficiency of the adsorbents in Cr(VI) removal from aqueous solutions follows the order: functionalized acid-activated sepiolite > functionalized natural sepiolite > acid-activated sepiolite > natural sepiolite. As the number of silanol groups on the sepiolite surface increased during the acid activation, the silane functionalization increased and this led to an increase in Cr(VI) adsorption. The adsorption capacity strongly depended on the pH of the solution from which the adsorption occurred. Maximum Cr(VI) removal was *ca.* 8.0 mg Cr(VI) per g of functionalized acid-activated sepiolite at initial pH 3, when the pH of solution reached 4.7, and *ca.* 2.7 mg Cr(VI) per g of functionalized natural sepiolite at initial pH 2, when the pH of the solution reached 2.5. Cr(VI) removal by the functionalized sepiolites was mainly attributed to electrostatic attraction between the protonated mercapto groups and the negatively charged Cr(VI) species. The sorption isotherms showed that Cr(VI) removal by both functionalized sepiolites for all initial investigated solution pH values is well described using the Dubinin–Radushkevich model. The thermodynamic data suggest spontaneity of the major physical adsorption process at 298 K.

1. Introduction

Hexavalent chromium is a well-known highly toxic metal, causes problems such as skin dermatitis, bronchitis, perforation of the nasal septum, bronchogenic carcinoma, liver damage, ulcer formation, etc. [1]. Major sources of Cr(VI) to environment are effluents from electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection, chromium mining and milling, brass, electrical and electronics' equipments manufactures and catalysis.

Cr(VI) species may be in the form of dichromate ($Cr_2O_7{}^{2-}$), hydrochromate ($HCrO_4{}^{-}$), or chromate ($CrO_4{}^{2-}$), depending on the pH and concentration of the chromium solution [1,2]. Due to repulsive electrostatic interactions, Cr(VI) anionic species are poorly adsorbed by the negatively charged soil particles in the environment, and hence, they can transfer freely into aqueous environments. Therefore, it is necessary to control Cr(VI) content in industrial effluents before their discharge into sewages or rivers in order to prevent the deleterious impact of Cr(VI) on the ecosystem and public health.

Adsorption processes can be a promising and effective techniques for the removal of Cr(VI) from waste water. Clays have been investigate for decreasing the amount of Cr(VI) released into the environment, owing to their high specific surface area with unique swelling, intercalation, and ion-exchange properties, low cost and ubiquitous presence in most soils. The study of the adsorption of Cr(VI) from aqueous solutions by natural or modified clay minerals (kaolinite, bentonite, illite, stevensite, rectorite, etc.) was the subject of several investigations [3–7], but no study to date has considered the adsorption of Cr(VI) onto sepiolite. It was, therefore, the objective of this study to investigate the amenability of removal of Cr(VI) anionic species by sepiolite.

Sepiolite is a non-swelling, lightweight, porous, fibrous natural clay mineral with a large specific surface area. Chemically, sepiolite is a hydrated magnesium silicate with the ideal formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4{\cdot}8H_2O$ belonging to the phyllo-silicate group of clay minerals. The sepiolite structure is constituted by a magnesium octahedral sheet in-between 2 layers of silica tetrahedrons which extend as a continuous layer with an inversion of the apical ends every six units. This inversion produces a dis-

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Nomenclature

c_i	initial concentration of Cr(VI) in solution (mg/dm^3)
c_e	equilibrium concentrations of Cr(VI) in solution (mg/dm^3)
E	adsorption free energy (kJ/mol)
K_L	Langmuir constant (dm^3/mg)
K_f	Freundlich adsorbent capacity (mg/g(dm^3/mg)$^{1/n}$)
K_d	the equilibrium constant
n	Freundlich constant
q_e	equilibrium Cr(VI) concentration on the adsorbent (mg/g)
q_m	maximum adsorption capacity (mg/g)
R	gas constant (8.314 J/mol K)
T	absolute temperature (K)
V	volume of the Cr(VI) solution (dm^3)
w	mass of the sepiolite sample (g)
ΔG^0	standard free energy of adsorption (kJ/mol)
β	D–R constant (mol^2/kJ^2)
ε	Polanyi potential (J/mol)

continuous octahedral sheet which allows for the formation of a rectangular section, tunnel-like pores, parallel to the fiber axis. These tunnels measure approximately 3.6 × 10.6 Å in cross section, and are completely filled with zeolitic water $[H_2O]_{zeol}$ under ambient conditions. The terminal Mg^{2+} cations that are located at the edges of the octahedral sheets complete their coordination with two molecules of structural water, which are in turn hydrogen-bonded to zeolitic water molecules located within the nanopores of the magnesium silicate [8]. A significant number of silanol groups (≡Si–OH) are present at the surface of this mineral. The presence and concentration of surface functional groups plays an important role in the adsorption capacity and the removal mechanism of adsorbates. In addition, the adsorption capacity which is restricted to the external surface may be enhanced by acid activation. Acid treatment has been used to increase the surface area of sepiolite and to obtain a solid with high porosity and a large number of acidic centers from this mineral [9].

Sepiolite is widely used to remove undesired components from household and industrial wastewaters and also in various industrial manufacturing processes, such as, some organic matters from wastewater, heavy metals, chloridazon and phosphorus, color and other undesirable components, Reactive Blue 15 and Acid Red 57 anionic dyes, chlorophyll-*a* and β-carotene [10–17].

Furthermore, through surface functionalization, the properties of sepiolite can be tailored for specific applications [18–21]. Two different functionalization processes are possible: (i) adsorption of quaternary ammonium salts or amines, and (ii) surface modification through reaction of surface silanol groups with organosilane reagents. The very high density (2.2 groups per 100 Å^2) of silanol groups on the sepiolite surface allows an adequate functionalization with silane reagents [8]. Silane coupling agents are a family of organosilicon monomers, which are characterized by the general structure $R–SiX_3$, in which R is an organo-functional group attached to silicon in a hydrolytically stable manner. X designates hydrolysable alkoxy groups (usually methoxy, $–OCH_3$, or ethoxy, $–OC_2H_5$), which are converted to silanol groups by hydrolysis. Most commonly, R is composed of a reactive group R′ separated by a propylene group from silicon, $R'–(CH_2)_3–SiX_3$. The reactive group can, for example, be vinyl ($–HC{=}CH_2$), amino ($–NH_2$), or mercapto (–SH) or can contain several chemical functional groups [20].

The aim of this study was to investigate the adsorption of Cr(VI) onto natural, acid-activated and silane-functionalized sepiolite samples. Natural and acid-activated sepiolite were functionalized with 3-mercaptopropyltrimethoxysilane. Then, the affinity of natural, acid-activated and functionalized sepiolites for Cr(VI) adsorption, the effect of pH on Cr(VI) adsorption by the sepiolite samples and the mechanism of Cr(VI) adsorption on these sepiolite samples and the adsorption isotherms were investigated. Langmuir, Freundlich and Dubinin–Radushkevick adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. Furthermore, some thermodynamic parameters were calculated to interpret the results.

2. Materials and methods

2.1. Starting materials

Sepiolite material obtained from Andrići in Serbia was used in the experiments. Before use, the clay was treated as follows: after cleaning the clay mechanically from visible impurities, it was dried at 110 °C for 2 h, then powdered and sieved. The fraction under 250 μm was used in all the experiments. The physico-chemical properties of the natural sepiolite (SEP) were reported previously [10].

In order to prepare acid-activated sepiolite (ASEP), 10 g of natural sepiolite was suspended in 100 cm^3 of 4 mol/dm^3 HCl solution at room temperature in a stirred reaction flask for 10 h according to a previous study [10]. Then, the mixtures were filtered and the resulting solid was washed with distilled water until no chloride anions could be detected in the washings. The solid was dried at 110 °C for 2 h. The physico-chemical properties of the ASEP were reported previously [10].

A chromium solution was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in demineralized water.

2.2. Functionalization of natural and acid-activated sepiolites by mercaptosilane

(3-Mercaptopropyl)trimethoxysilane ($HS–(CH_2)_3–Si–(OCH_3)_3$) or mercaptosilane (MPTS) (Sigma–Aldrich) was used for treating the sepiolite samples.

The functionalization reactions were performed with 12 g of sepiolite sample and 12 cm^3 of mercaptosilane in the presence 300 cm^3 of toluene as a dispersing medium. The sepiolite samples suspended in toluene were refluxed and mechanically stirred for half an hour under dry nitrogen. To these suspensions, mercaptosilane was added dropwise. The mixtures were refluxed for 24 h, filtered, washed with toluene and ethanol and then dried under dry nitrogen for 24 h [21]. The functionalized natural and acid-activated sepiolites were denoted as MSEP and MASEP, respectively.

2.3. Characterization

X-ray powder diffraction (XRD) analysis of the MSEP and MASEP samples was performed on an ITAL STRUCTURES APD 2000 diffractometer equipped with a back monochromator operating at a tube voltage of 40 kV and a tube current of I = 30 mA using a copper cathode as the X-ray source (λ = 0.15406 nm), in the 2θ angle range from 10° to 80°. A step size of 0.02° and a time per step of 0.5 s were used.

Fourier transform infrared (FT-IR) spectra of the MSEP and MASEP samples were recorded over the wave number range from 400 to 4000 cm^{-1} on a MB Bomem 100 Hartmann & Brown instrument using the KBr pressed disk technique. The samples were prepared with sample/KBr ratio of 1:100.

Differential thermal analysis (DTA) was realized in air using a computer controlled AMINCO instrument. The samples were heated to 1000 °C at a heating rate of 10 °C/min.

The point of zero charge (pH_{pzc}) of MSEP and MASEP samples was determined by a batch equilibration technique [22]. The first set of the measurements included ten samples with 25 cm^3 of KNO_3 solution (concentration 0.1 mol/dm^3) in poly(vinyl chloride) (PVC) vessels. The initial pH values ($pH_{initial}$), in the pH range from 3.5 to 10.0, were adjusted by adding a 0.1 mol/dm^3 solution of HCl or KOH to the electrolyte solution. Then, 0.050 g of functionalized sepiolite was added to each sample. Equilibration was realized by shaking for 24 h at room temperature. The dispersions were then filtered and the final pH of the solutions (pH_{final}) was determined. The point of zero charge was found from a plot of pH_{final} vs. $pH_{initial}$. For the second set of measurements, the former procedure was repeated, only this time the concentration of the KNO_3 solution was 0.01 mol/dm^3.

2.4. Adsorption experiments

The adsorption experiments were conducted using the batch method. All adsorption experiments were performed at 25 °C. A thermostated shaker was used to keep the temperature constant. The sepiolite samples were placed in PVC flasks containing solutions of Cr(VI) and equilibrated for 24 h.

The adsorption of Cr(VI) onto the SEP and ASEP adsorbents was performed using solutions of $K_2Cr_2O_7$ with an initial concentration of 10 mg Cr(VI)/dm^3, at a ratio adsorbent to Cr(VI) solution of 2 g: 100 cm^3. The adsorption experiments were conducted at initial pH values from 5.0 to 3.0 for SEP and from 5.0 to 2.0 for ASEP. According to the literature [10], decreasing the pH value of the solution to below pH = 3 leads to the dissolution of SEP. Considering this, the adsorption of Cr(VI) onto SEP was not performed at an initial pH value below pH = 3.

In order to investigate the specific adsorption of Cr(VI) species on SEP and ASEP, the shift of the pH_{pzc} of these adsorbents was observed by the batch equilibration technique. The experiments were performed using solutions of $K_2Cr_2O_7$ with a concentration 0.001 mol/dm^3, at a ratio sepiolite to Cr(VI) solution of 0.1 g: 25 cm^3.

The adsorption of Cr(VI) onto the MSEP and MASEP was examined at initial pH values of 4.5, 3.0, and 2.0 using solutions of $K_2Cr_2O_7$ with initial concentrations of 5–100 mg Cr(VI)/dm^3 at a ratio functionalized sepiolite to Cr(VI) solution of 0.1 g:25 cm^3.

The initial concentrations of Cr(VI) ions, as well as the concentrations after the adsorption were determined using atomic absorption spectrometer (AAS) (Perkin Elmer 730). All the adsorption studies were repeated twice; the reported value is the average of two measurements.

The amounts of Cr(VI) adsorbed were calculated from the concentrations in solutions before and after adsorption using Eq. (1) [23]:

$$q_e = \frac{c_i - c_e}{w} V \tag{1}$$

3. Results and discussion

3.1. Characterization of the functionalized sepiolite samples

The X-ray diffractograms of the MSEP and MASEP samples are shown in Fig. 1. From the XRD pattern of MSEP, it can be seen that the sepiolite structure had not changed after functionalization [10]. Therefore, the XRD results suggest the maintenance of the ordered structure after functionalization. This is because MPTS functionalization occurs mainly on the surface or by partial replacement of zeolitic water [8], thereby maintaining the structure unmodified.

The characteristic peak positions and the relative peak intensities of the acid-activated sepiolite sample had not changed after functionalization with MPTS. Therefore, the XRD results indicated that the structure and crystallinity of the ASEP sample [10] were maintained in the MASEP sample.

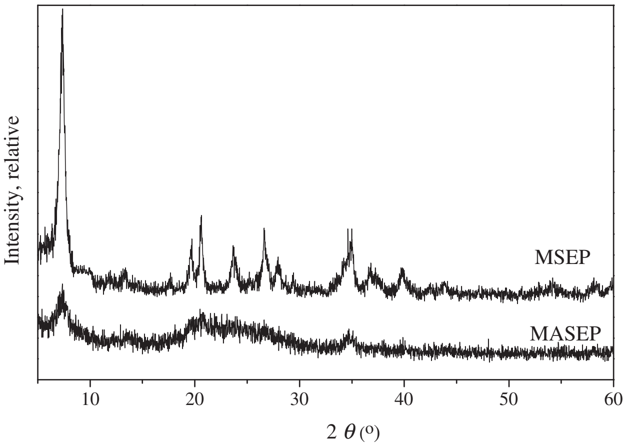

Fig. 1. X-ray diffractograms of the MSEP and MASEP samples.

The FT-IR spectra of the of the functionalized sepiolite samples, MSEP and MASEP, are shown in Fig. 2.

FT-IR spectrum of MSEP is generally similar to that of the SEP sample [10], and the FT-IR spectrum of MASEP is similar to that of the ASEP sample [10]. A difference was observed only in the intensity of the peaks at 2936 and 2857 cm^{-1}, assigned to the C–H stretching vibration, which confirmed that organic matter was attendant in the samples. Thus, the FT-IR spectra of the SEP, ASEP, MSEP and MASEP samples were only considered between 3750 and 2750 cm^{-1} (Fig. 3). From the FT-IR spectra of the SEP and ASEP samples, the intensity of the bands corresponding to the organic matter were decreased after the acid treatment, confirming that the content of organic matter in the sepiolite decreased during the acidic treatment.

After silanization with MPTS, the intensity of the bands at 2936 and 2857 cm^{-1} in the MSEP and MASEP functionalized sepiolite samples were increased in comparison to the corresponding bands in the SEP and ASEP samples. According to the literature [18,19,24,25], C–H stretching vibrations of the methoxy ($O–CH_3$) and chain methylene (CH_2) groups in the modifier silane can be observed at 2839 and 2940 cm^{-1}, respectively. These two peaks were also observed in the FT-IR spectra of the present functionalized samples with small shifts at 2857 and 2936 cm^{-1}, respectively. The peak due to the chain CH_2 groups at 2936 cm^{-1} is clearly seen,

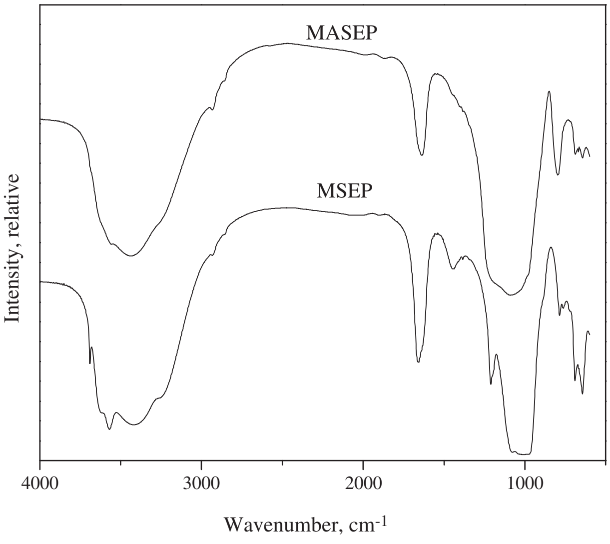

Fig. 2. FT-IR spectra of the MSEP and MASEP samples.

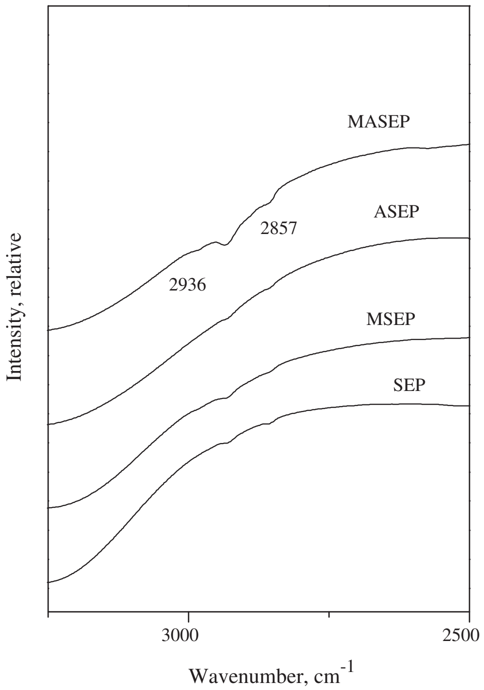

Fig. 3. FT-IR spectra of the sepiolite samples.

while the C–H vibration due to the O–CH_3 at 2857 cm^{-1} is very weak. As seen in Fig. 3, the intensities of these bands in the spectrum of MASEP were higher than those in the MSEP spectrum, confirming that the content of mercaptosilane in MASEP was higher than in MSEP, i.e., the MPTS functionalization of acid-activated sepiolite was better compared to the functionalization of natural sepiolite. The increase in the content of mercaptosilane in MASEP was attributed to the high number of silanol groups on the acid-activated sepiolite surface that can bind to the mercaptosilane.

The results of the DTA analysis of the MASEP and MSEP samples are shown in Fig. 4.

The DTA curves of functionalized sepiolite samples can be divided into three regions (Fig. 4): (i) the dehydration of the clay, (ii) the combustion of the organic matter, and (iii) the dehydroxylation of the clay [19].

By comparing the DTA curves of the samples MSEP and MASEP to those of the samples SEP and ASEP [10], it can be observed that the endothermic peak at 150 °C, corresponding to the loss of zeolite water, was decreased after the addition of the mercaptosilane molecules. This suggests that some molecules of mercaptosilane enter the interior channels and replace the zeolitic water molecules [19]; hence, the removal of zeolitic water from the structure of the MSEP and MASEP samples was weaker than from the SEP and ASEP samples.

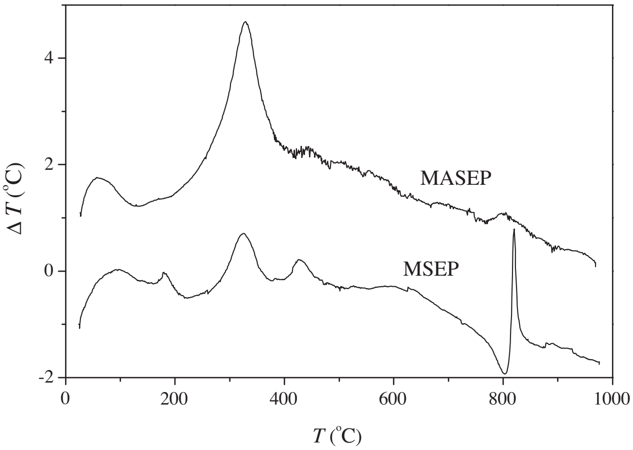

Fig. 4. DTA curves of the MSEP and MASEP sepiolite samples.

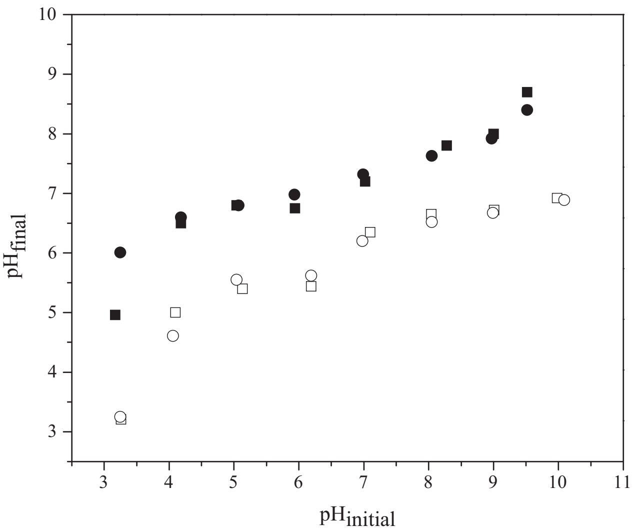

Fig. 5. Dependence of pH_{final} on $pH_{initial}$ during the equilibration of 0.05 g of MSEP with 25 cm^3 solution of (■) 0.1 M KNO_3, (●) 0.01 M KNO_3, and 0.05 g of MASEP with 25 cm^3 solution of (□) 0.1 M KNO_3, (○) 0.01 M KNO_3.

The DTA curves, illustrated in Fig. 4, shown two exothermal peaks. The peaks at around 450 °C correspond to combustion of organic matter present naturally in sepiolite. The low intensity of these peaks for the MASEP sample is the consequence of a decrease in the content of organic matter after the acid treatment. The intensive exothermal peak at 330 °C observed on the DTA curves of the MSEP and MASEP samples clearly indicate the presence mercaptosilane in the functionalized sepiolite samples. The difference between the intensity of the exothermal peak appears because the amount of mercaptosilane in the MSEP sample was less than in the MASEP sample. This result is in accordance with results of the FT-IR analysis. During the acid treatment of the sepiolite, Mg^{2+} ions in the octahedral sheet are driven away from the matrix and the active adsorbent sites have a large number of silanol groups distributed both on the surface and in the structural channels. The very high density of silanol groups on the acid-activated sepiolite allows adequate functionalization with silane reagents. These data support the hypothesis that the binding of mercaptosilane is essentially controlled by interaction with silanol groups on the sepiolite surface.

The results of the determination of the point of zero charge, pH_{pzc}, for the MSEP and MASEP sepiolite samples are presented in Fig. 5. From the dependence pH_{final} vs. $pH_{initial}$, the value of the pH_{pzc} was obtained as the pH value at which the curve plateau, i.e., the curve inflexion, appears. At this pH value, a change in surface charge from positive to negative or *vice verse* occurs. According to Fig. 5, the pH value at the plateau of the pH_{final} vs. $pH_{initial}$ plots remains constant (within the limit of error) with changing concentration of the KNO_3 electrolyte within the studied ranges. In this way, the common plateau obtained at a pH value of 7.4 ± 0.1 for MSEP and 5.4 ± 0.1 for MASEP corresponds to the pH_{pzc} of these functionalized sepiolite powders.

That the point of zero charge for the SEP [10] and MSEP were the same indicates that the acid–base properties of the sepiolite surface did not change after functionalization, but the SEP sample showed a higher buffer capacity than the MSEP sample.

Table 1
The results of the adsorption of Cr(VI) on natural sepiolite (SEP) and acid-activated sepiolite (ASEP).

$pH_{initial}$	SEP		ASEP	
	pH_{final}	q_e (mg/g)	pH_{final}	q_e (mg/g)
5.0	7.28	<0.01	6.39	<0.01
4.5	7.25	<0.01	6.26	<0.01
4.0	7.22	<0.01	6.15	~0.01
3.5	7.18	<0.01	5.83	0.06
3.0	7.08	<0.01	5.22	0.07
2.5	–	–	4.86	0.09
2.0	–	–	3.76	0.10

After functionalization of the acid-activated sepiolite sample with mercaptosilane, the value of the point of zero charge decreased. The decrease in the point of zero charge after MPTS functionalization indicates that the molecules of mercaptosilane bind to the silanol groups on the ASEP surface. This finding confirms that a strong interaction had occurred between the mercaptosilane molecules and the silanol groups of the ASEP surface, whereby a covalent bond was formed [8,19–21,24]. The mercaptosilane molecules behave as non-polar modifying agents reducing the pH_{pzc} to lower pH values [18], i.e., from 6.9 for the ASEP unfunctionalized sample [10] to 5.4 for the MASEP functionalized sample.

3.2. Adsorption of Cr(VI) onto the sepiolite samples

3.2.1. Adsorption of Cr(VI) onto the unfunctionalized sepiolites

The amount of Cr(VI) removed by the SEP and ASEP adsorbents from a 10 mg Cr(VI)/dm^3 solution at adsorbent to Cr(VI) solution ratio of 2 g:100 cm^3 and various initial pH values ($pH_{initial}$) of the solution together with the final pH values (pH_{final}) of the solution are given in Table 1.

The results from Table 1 indicate that practically there was no adsorption of Cr(VI) from aqueous solutions onto SEP regardless of the different initial pH values of the solution. This result is closely related to the surface charge of the SEP and the predominant species of Cr(VI) [1,2] at the final pH of the solution. When the natural sepiolite was dispersed in Cr(VI) solution at initial pH values from 5.0 to 3.0, adsorption of H^+-ions onto the sepiolite surface lowers the number of H^+-ions remain in the solution, which leads to higher final pH values. Since the final pH solution values approach the pH_{pzc} (7.4) of SEP [10], the sepiolite surface remained negatively charged or appeared neutral [12] and the adsorbed amount of Cr(VI) anion species was negligible (<0.01 mg Cr(VI) per g SEP). The slight effect of the initial pH value on the Cr(VI) removal was due to the high final pH value over a wide initial pH range, which was the consequence of the large buffer capacity of sepiolite [10,12].

As seen in Table 1, it was found that the amount of Cr(VI) ions adsorbed onto acid-activated sepiolite increased with decreasing initial and final pH of the solution. As the final pH of the Cr(VI) solutions became lower than the pH_{pzc} (6.9) of the ASEP [10], the more protonated hydroxyl groups (M–OH_2^+) on the ASEP surface would be favorable for the adsorption of $HCrO_4^-$ species, as Coulombic interaction forces can readily exist [3]. But, adsorption capacity is very small in consequence of small surface charge density, which confirmed earlier by potentiometric titration [10].

The dependences of pH_{final} on $pH_{initial}$ during the equilibration of the SEP and ASEP samples with 0.001 mol/dm^3 solutions of $K_2Cr_2O_7$ are shown in Fig. 6. As is known from the literature [10], the specific adsorption of anions on a solid surface shifts the value of pH_{pzc} toward higher pH values. The comparison of the results presented in Fig. 6 with the results of the determination of the pH_{pzc} of the SEP and ASEP samples [10] in indifferent electrolyte indicates that the specific adsorption of $HCrO_4^-$ and CrO_4^{2-} anion species, i.e., the formation of surface complexes did not occur, because there was no shift in the plateau positions.

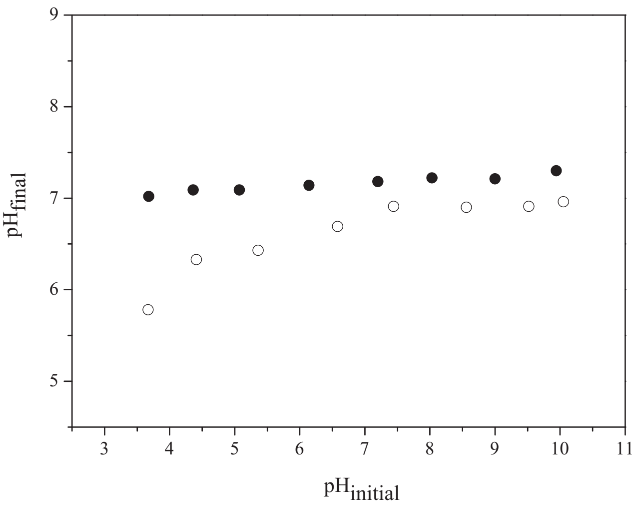

Fig. 6. Dependence of pH_{final} on $pH_{initial}$ during the equilibration 0.05 g SEP (●) and ASEP (○) with 25 cm^3 of a 0.001 mol/dm^3 solution of $K_2Cr_2O_7$.

According to the reported results, the removal of Cr(VI) anion species by both unfunctionalized sepiolites (SEP and ASEP) was negligible because there were only very weak electrostatic interactions between the Cr(VI) anion species and surface of the sepiolites owing to the nature of surface of these minerals and because there was no complex formation of the chromium species with the surface of the minerals.

3.2.2. Adsorption of Cr(VI) onto the functionalized sepiolite samples

The dependence of the final solution pH value (pH_{final}) after equilibration of Cr(VI) solutions with MSEP and MASEP samples on the initial concentration of the Cr(VI) solution is shown in Fig. 7 and the dependence of the adsorbed amount of Cr(VI) on the pH of the final solution is shown in Fig. 8. Within the equilibrium pH range (2.2–7.5), the predominating forms of Cr(VI) are $HCrO_4^-$ and CrO_4^{2-}. As the pH increases, the $HCrO_4^-$ concentration decreases and the CrO_4^{2-} concentration increases [1,2].

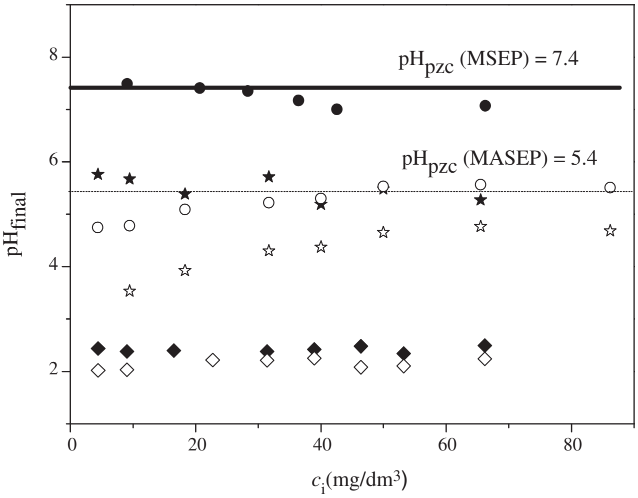

Fig. 7. Dependence of the final solution pH value on the initial Cr(VI) concentration during the equilibration of 25 cm^3 of Cr(VI) solution with 0.1 g of adsorbent: MASEP at initial pH values 2.0 (◊), 3.0 (☆) and 4.5 (○), and MSEP at initial pH values of 2.0 (♦), 3.0 (★) and 4.5 (●).

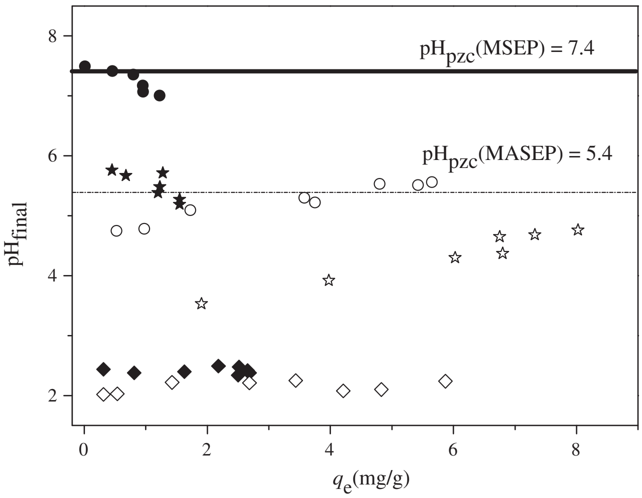

Fig. 8. The effect of pH of the solution on the adsorption of Cr(VI) onto MSEP at initial pH values of 2.0 (◆), 3.0 (★) and 4.5 (●); and on MASEP at initial pH values of 2.0 (◊), 3.0 (☆) and 4.5 (○); the adsorbent to Cr(VI) solution ratio was 0.1 g:25 cm^3.

According to Fig. 7, it was found that with increasing initial concentration of the Cr(VI) solution, the equilibrium pH values stabilized at: around 2.2 for MASEP and 2.5 for MSEP at an initial pH value of 2.0; from 3.5 to 4.7 for MASEP and from 5.7 to 5.2 for MSEP at an initial pH of 3.0; and from 4.8 to 5.5 for MASEP and from 7.5 to 7.0 for MSEP at an initial pH of 4.5. With decreasing initial pH value from 4.5 to 2.0, the equilibrium pH of the solution was decreased for both functionalized sepiolites. In the experiments performed with MSEP, at initial solution pH values of 4.5 and 3.0, the equilibrium solution pH values remained nearly constant with increasing initial Cr(VI) concentration. During experiments with MASEP, at moderate initial solution pH values of 4.5 and 3.0, a remarkable increase in the final pH was observed with increasing initial Cr(VI) concentration. At an initial pH value of 2.0, the significant increase in the final pH value was not observed, due to the highly acidic conditions in the suspensions of both functionalized sepiolites.

It can be seen from Fig. 8 that the removal of Cr(VI) by MSEP increased with decreasing initial solution pH. The amount of Cr(VI) adsorbed on MSEP increased from 1.35 mg per g (at $pH_{initial} = 4.5$) to 1.55 mg per g (at $pH_{initial} = 3.0$) and 2.69 mg per g (at $pH_{initial} = 2.0$). When MASEP was used at initial pH values of 2.0 and 4.5, a similar sorption capacity was observed, 5.65 mg per g (at $pH_{initial} = 4.5$) and 5.90 mg per g (at $pH_{initial} = 2.0$), and a higher sorption capacity was found at an initial pH value of 3.0, i.e., 8.03 mg per g (Fig. 8). According to the results presented in Fig. 8, the optimal pH for Cr(VI) adsorption is about pH 2.5 for MSEP and in the pH range 3.5–4.7 for MASEP.

According to the literature [26–31], anionic species $HCrO_4^-$ and CrO_4^{2-} could be removed from solution owing to electrostatic interaction with positive sites on the surface of MSEP and MASEP at pH values below the value pH_{pzc}. The positive surface charge of the functionalized sepiolites is governed by the following equilibrium, involving the protonation of the surface mercapto groups (–SH):

$$SiOSi(OCH_3)_2–(CH_2)_3–SH \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} SiOSi(OCH_3)_2–(CH_2)_3–SH_2^+ \qquad (2)$$

In addition to this, another possible mechanism for Cr(VI) removal from solution by functionalized sepiolites could be the reduction of Cr(VI) to Cr(III) in the acidic medium [29–36]. At lower solution pH values, the mercapto groups (–SH) can be oxidized by $HCrO_4^-$ into sulfonic groups ($–SO_3H$) [37], following Eq. (3):

$$2HCrO_4^- + (–SH) + 8H^+ 2Cr^{3+} + (–SO_3H) + 5H_2O \qquad (3)$$

Due to highly acidic conditions, as the pH changes from initial pH solution of 2.0 to the equilibrium pH solution values about 2.5 (for MSEP) and about 2.2 (for MASEP), the reduction of Cr(VI) to Cr(III) ions could been the predominating step, but the charge repulsion between resulting Cr^{3+} ions and protonated MSEP and MASEP surfaces were high. Oxidation of the mercapto groups yields sulfonic groups ($–SO_3H$), but in a highly acidic medium, the ionization of these groups to the sulfonate group ($–SO_2O^-$) would be low [37]. Removal of Cr(III) from solution was negligible because a small number of $–SO_2O^-$ groups were available for electrostatic interaction with Cr^{3+} ions. Therefore, the electrostatic attraction between the protonated mercapto group ($–SH_2^+$) on the MSEP and MASEP surface and $HCrO_4^-$ ion was probably the dominant mechanism of Cr(VI) removal from solution at initial pH value of 2.0.

For MASEP, with increasing equilibrium pH value from 3.5 to 4.7 from an initial pH of 3.0, protonation of the mercapto group and Cr(VI) reduction were retarded because both these reactions require protons [34,35]. At an initial pH of 3.0, as the number of protonated mercapto groups on the MASEP surface was lower than at initial pH of 2.0, the electrostatic attraction between $–SH_2^+$ groups and $HCrO_4^-$ ions was lower. On the other hand, the reduction of Cr(VI) to Cr(III) ions was less, but removal of the resulting Cr^{3+} ions from solution was higher than at $pH_{initial} = 2.0$, due to higher ionization of the $–SO_3H$ groups at higher pH values. Therefore, the higher sorption capacity of MASEP at initial pH of 3.0 than at initial pH of 2.0 can be explained by the lower reduction of Cr(VI) to Cr(III) followed by a higher removal of obtained Cr^{3+} ions and the remarkable protonation of the –SH groups. Due to the increase in the equilibrium pH values to 4.8–5.5, for MASEP in Cr(VI) solutions at an initial pH value of 4.5, the Cr(VI) reduction was further decreased but the equilibrium solution pH values approached the point of zero charge of MASEP (5.4) and the mercapto groups on the MASEP surface were less protonated. Thus, amount of $HCrO_4^-$ removed from solution was decreased. According to this consideration, the maximum Cr(VI) removal by MASEP was accomplished at final pH value of 4.7.

When MSEP was used as the adsorbent in Cr(VI) solutions, as the pH changed from the initial pH of the solutions of 3.0 to the equilibrium pH solution values, above 5.0, due to weak acidic conditions, the reduction of Cr(VI) to Cr(III) ions was negligible and the protonation of the surface mercapto groups was also low. At an initial pH value of 4.5, the equilibrium pH values approached the point of zero charge of MSEP (7.4) and protonation of the mercapto groups was lower than at an initial pH of 3.0. Hence, the removal of Cr(VI) by MSEP using an initial pH of 4.5 was lower than the initial pH value was 3.0.

Hence, electrostatic attraction of anionic Cr(VI) species by protonated mercapto groups and reduction of Cr(VI) to Cr(III) followed by electrostatic attraction between Cr^{3+} ions and the oxidized mercapto groups were possible mechanisms of Cr(VI) removal by the MSEP and MASEP functionalized sepiolites. These mechanisms were strongly related to the solution pH.

The MASEP sample showed a higher maximum adsorption capacity for Cr(VI) than the MSEP sample at all the studied initial pH values. These results could been expected due to better MPTS functionalization of the acid-activated sepiolite compared to natural sepiolite and, as a consequence, the higher content of mercapto groups in MASEP compared to MSEP. Very little chromium was adsorbed on the unfunctionalized ASEP sepiolite despite the fact that it had a large surface area [10], which supports the idea that the adsorption occurs on the mercapto groups, which are not present on the unfunctionalized ASEP sepiolite [26].

3.2.3. *Adsorption isotherms*

The isotherms for Cr(VI) adsorption on the MSEP and MASEP samples at various initial pH values are illustrated in Figs. 9 and 10,

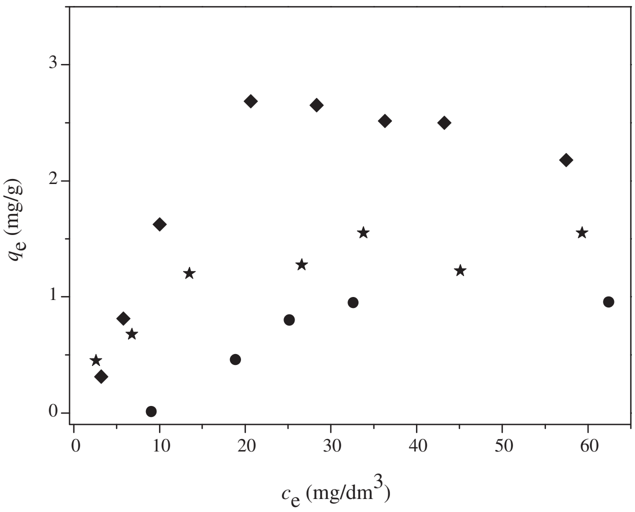

Fig. 9. The adsorption isotherms of Cr(VI) onto MSEP at different initial pH values: 2.0 (♦), 3.0 (★) and 4.5 (●) (the MSEP to Cr(VI) solution ratio was 0.1 g:25 cm^3).

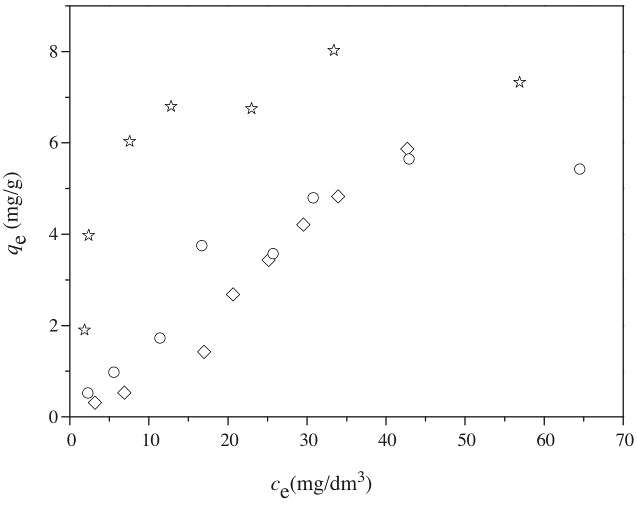

Fig. 10. The adsorption isotherms of Cr(VI) onto MASEP at different initial pH values: 2.0 (◊), 3.0 (☆) and 4.5 (○) (the MASEP to Cr(VI) solution ratio was 0.1 g:25 cm^3).

respectively. The Langmuir, Freundlich and Dubinin–Radushkevick (D–R) isotherms were used to describe the sorption of Cr(VI) species from solution onto the surface of the functionalized sepiolites. Adsorption parameters and the statistical fits of the sorption data to these equations are given in Table 2.

According to results presented in Table 2, the experimental data for an initial solution pH of 3.0, for both samples, were best fitted with the Langmuir isotherm. However, the correlation of these data with the D–R model was also good.

In order to gain insight into the possible mechanisms involved in the removal process, the standard free energy of adsorption, ΔG^0, for Cr(VI) adsorption by MSEP and MASEP at initial solution pH of 3.0 was calculated using Eq. (4) [28,38,39]:

$$\Delta G^0 = -RT \ln K_d \tag{4}$$

In the literature [14,15,38], it was reported that a ΔG^0 value between −20 and 0 kJ/mol is consistent with physical adsorption, while ΔG^0 values in the range from −80 to −400 kJ/mol reflect chemisorption. The obtained value of ΔG^0 for MSEP and MASEP at 25 °C was −9.482 kJ/mol and −13.588 kJ/mol, respectively. These results suggested that the interaction between functionalized sepiolites (MSEP and MASEP) and the Cr(VI) at initial pH of 3.0 was likely due to physisorption. The negative values of ΔG^0 indicate that the adsorption process is spontaneous.

The equilibrium adsorption data for Cr(VI) adsorption by MASEP at an initial solution pH of 2.0 were best fitted with the Freundlich model, but these data can also be well-fitted by the D–R model ($R^2 = 0.997$). The Freundlich parameters, K_f and n, indicate whether the nature of adsorption is favorable or unfavorable. The small value of the K_f (0.083) indicates a modest adsorption capacity [12]. The value of Freundlich constant, n (0.871) indicates that the adsorption intensity was good [12].

The results of Cr(VI) adsorption by MSEP at initial pH values of 2.0 and 4.5 and MASEP at an initial pH value of 4.5 were best fitted with the D–R isotherm. However, it is interesting that all results for both samples and for all initial pH values could be well-fitted with D–R model ($R^2 > 0.99$). A good fitting of adsorption data with the D–R model shows that the sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same sorption potential.

The mean free energy E (kJ/mol) of adsorption per mole of adsorbate when it is transferred to the surface of a solid from infinity in the solution, which is equal to $1/(2\beta)^{0.5}$, gives information about adsorption mechanism [38]. When the value of E is between 8 and 16 kJ/mol, the adsorption process is by ion-exchange, while for a value of $E < 8$ kJ/mol, physical adsorption prevails [40].

The values of the mean free energy of adsorption were: 0.460 kJ/mol for MSEP at an initial pH of 2.0; 0.118 kJ/mol for MSEP at an initial pH of 4.5 and 0.585 kJ/mol for MASEP at an initial pH of 4.5. These values indicate that adsorption of Cr(VI) onto MSEP at initial pH values of 2.0 and 4.5 as well as onto MASEP at an initial pH of 4.5 were of a physical nature [38,40].

3.3. *Comparison of chromate adsorption onto the functionalized sepiolites and onto other adsorbents*

The highest adsorption capacities for Cr(VI) obtained in this study was approximately 2.70 mg/g (at $\text{pH}_{\text{initial}} = 2.0$) for MSEP

Table 2

Langmuir, Freundlich and D–R parameters and correlation coefficients (R^2) for the adsorption of Cr(VI) onto the functionalized sepiolite samples.

Adsorbent	$\text{pH}_{\text{initial}}$	Langmuir isotherm $\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m}$			Freundlich isotherm $\ln q_e = \ln K_f + \frac{1}{n} \ln c_e$			Dubinin–Radushkevick (D–R) isotherm $\ln q_e = \ln q_m - \beta\varepsilon^2$ $\varepsilon = RT \cdot \ln\left(1 + \frac{1}{c_e}\right)$		
		q_m (mg/g)	K_L (dm^3/mg)	R^2	K_f mg/g(dm^3/mg)$^{1/n}$	n	R^2	q_m (mg/g)	β (mol^2/J^2)	R^2
MSEP	2.0	2.850	0.098	0.911	0.235	1.506	0.793	2.675	4.727×10^{-6}	0.997
	3.0	1.767	0.115	0.993	0.318	2.504	0.944	1.466	1.817×10^{-6}	0.978
	4.5	1.502	0.039	0.597	0.047	0.955	0.887	1.406	7.145×10^{-5}	0.993
MASEP	2.0	57.504	0.002	0.286	0.083	0.871	0.999	5.468	6.307×10^{-6}	0.997
	3.0	7.732	0.617	0.994	0.270	5.013	0.840	7.496	1.226×10^{-6}	0.993
	4.5	8.253	0.037	0.899	0.243	1.192	0.994	5.336	2.922×10^{-6}	0.997

Table 3
Comparison of adsorption capacity of Cr(VI) on the functionalized sepiolites with that of other adsorbents.

Samples	Adsorption capacity (mg/g)	Optimum pH	References
Dodecylbenzyldimethylammoniumchloride rectorite (OREC1)	0.97	6.0	[7]
Wollastonite	0.826	2.5	[41]
Spent activated clay	1.42	2.0	[3]
Cetyltrimethylammoniumbromide sepiolite (CTA-sepiolite)	1.77	–	[6]
Hexadecyltrimethylammoniumbromide rectorite (OREC2)	2.39	6.0	[7]
(3-Mercaptopropyl)trimethoxysilane functionalized natural sepiolite (MSEP)	2.68	2.5	This study
Octadecyltrimethylammoniumbromide rectorite (OREC3)	3.57	6.0	[7]
Al-stevensite	3.93	3.5–6.0	[6]
Mercaptopropil-silica	5.2	6.0	[42]
Activated alumina	7.44	4.0	[43]
(3-Mercaptopropyl)trimethoxysilane functionalized acid-activated sepiolite (MASEP)	7.73	4.7	This study
Cetyltrimethylammoniumbromide stevensite (CTA-stevensite)	10.27	2.0–6.0	[6]
Benzyldimethyloctadecylammoniumchloride bentonite (BDMODA-bentonite)	13	2.5–7.0	[5]

functionalized sepiolite and 8.00 mg/g (at $\mathrm{pH_{initial}} = 3.0$) for MASEP functionalized sepiolite sample containing the highest concentration of mercapto groups. This shows a significant increase of the Cr(VI) adsorption capacity onto functionalized sepiolite samples containing the highest concentration of mercapto groups.

Table 3 gives a comparison between the affinity of sepiolite samples prepared in this study and various other adsorbents for the adsorption of Cr(VI). While the adsorption capacity of MSEP functionalized sepiolite is comparable to those of CTA-sepiolite [6] and organo-modified rectorite samples [7], the adsorption capacity of MASEP functionalized sepiolite is comparable to those of mercaptopropyl-silica [42], activated alumina [43] and CTA-stevensite [6]. As Table 3 shows, the functionalized sepiolite samples may be considered as effective adsorbents for the removal of Cr(VI) from aqueous solutions.

4. Conclusions

The removal of Cr(VI) from aqueous solutions using sepiolite samples as adsorbents was studied. The retention of Cr(VI) on natural and acid-activated sepiolites was negligible. By surface functionalization with mercaptosilane, the adsorption capacity of these adsorbents for Cr(VI) was greatly enhanced. The better functionalization of the acid-activated sepiolite, due to its higher content of silanol groups, resulted in a higher adsorption capacity of this sample in comparison to that of functionalized natural sepiolite.

The adsorption efficiency of the functionalized sepiolites was greatly affected by the solution pH value. The optimum pH values for the maximum adsorption of Cr(VI) onto functionalized acid-activated sepiolite was in the range of 3.5–4.7 (at an initial pH of 3.0) and at around 2.5 (at an initial pH of 2.0) for the functionalized natural sepiolite. Removal of Cr(VI) occurs dominantly by electrostatic attraction of anionic Cr(VI) species by protonated mercapto groups of the functionalized sepiolites surface. Another possible mechanism could be the reduction of Cr(VI) to $\mathrm{Cr^{3+}}$ ions by mercapto groups, followed by their electrostatic interaction with the sulfonate group ($-\mathrm{SO_2O^-}$), obtained by oxidation of the mercapto groups. These mechanisms are strongly related to the solution pH.

The adsorption isotherms showed that Cr(VI) removal by both functionalized sepiolites for all initial solution pH values was well described using the Dubinin–Radushkevich model. The fitting by a Dubinin–Radushkevich isotherm showed that the adsorption capacities of the functionalized natural sepiolite varied from 1.41 to 2.68 mg/g and from 5.37 to 7.50 mg/g for the functionalized acid-activated sepiolite, depending on the solution pH value. The obtained thermodynamic data suggest that physical adsorption was the major mechanism of Cr(VI) removal by the functionalized sepiolites.

The results of this study show that functionalized sepiolite samples can be used effectively in the removal of anion Cr(VI) species from aqueous solutions by adsorption.

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