



Short Communication

Application of natural and modified hectorite clays as adsorbents to removal of Cr(VI) from aqueous solution—Thermodynamic and equilibrium study

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ABSTRACT

A hectorite (H) clay sample has been modified with 2-mercaptobenzimidazole (MBI) using homogeneous and heterogeneous routes. Both modification methodologies resulted in similar products, named H_{HOM} and H_{HET}, respectively. These materials were characterized by CO₂ gas adsorption, elemental analysis, nuclear magnetic nuclei of carbon-13 and silicon-29. The effect of two variables (contact time and metal concentration) has been studied using batch technique at room temperature and pH 2.0. After achieving the best conditions for Cr(VI) adsorption, isotherms of this adsorbate on using the chosen adsorbents were obtained, which were fitted to non-linear Sips isotherm model. The maximum number of moles adsorbed was determined to be 11.63, 12.85 and 14.11 mmol g⁻¹ for H, H_{HOM} and H_{HET}, respectively, reflecting the maximum adsorption order of H_{HET} > H_{HOM} > H. The energetic effects ($\Delta_{\text{int}}H^\circ$, $\Delta_{\text{int}}G^\circ$ and $\Delta_{\text{int}}S^\circ$) caused by chromium ion adsorption were determined through calorimetric titrations.

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1. Introduction

The contamination of aquatic environment by toxic metals, such as chromium is of great concern due to its trends to accumulate on vital organs of humans and animals causing several health problems. Chromium compounds, mostly hexavalent chromium (Cr(VI)), produced by the chemical industry are used for the manufacture of dyes and pigments, leather tanning etc. [1]. These industries discharge Cr(VI) in large amounts into waterways, requiring an efficient treatment of effluents before being released to the environment [1]. The usual methods to remove Cr(VI) from aqueous effluents include chemical reduction [2–6], ion exchange [7], nanofiltration [8], adsorption on silica composites [9] and on activated carbon [10]. However, these approaches are not cost-effective or difficult to implement in developing countries.

When toxic metals are present in aquatic system, the abatement of pollutant to an acceptable level is necessary. Adsorption and ion exchange processes with high efficiency for industrial treatment of effluents [7]. Activated carbon is the most employed adsorbent from aqueous solution. However, the extensive use of activated carbon for metal removal from industrial effluents is expensive, limiting its large application for waste treatment. In this context, a large number of different adsorbent materials containing a variety of attached chemical functional groups has been reported for this purpose. In the last years, special attention has been focused on the use

of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view. In order to overcome high cost problems, an increasing interest in producing new alternative adsorbent materials to replace activated carbon has been explored, taking also into account the local availability, since frequently these new materials are constituted of residues from agricultural activity or mineral extraction [11–13].

Hectorite clay is generated from soils and sedimentary deposits through weathering, diagenesis and hydrothermal effects, the chemical composition of hectorite included: sodium, lithium, magnesium, silicon, hydrogen and oxygen. Some hectorite samples can be found naturally in the Amazon region. However, this hectorite occurrence is rare due to the fact that the Amazon climate is normally warm-humid, causing acidic lixiviation in soils, conditions that are unfavorable for lamellar structure formation [14–16].

This investigation reports the use of natural and modified hectorite as alternative adsorbents for extraction of toxic metal, which is commonly present in waters from a variety of sources and industrial effluents. For this propose, the adsorption isotherms of chromium(VI) from aqueous solution at room temperature were explored, bearing in mind the influence of different parameters such as metal concentration and contact time. The chemical modification process was developed with attaching of 2-mercaptobenzimidazole (MBI) in homogeneous and heterogeneous routes. The quick adsorption process reached the equilibrium before 10, 15 and 20 min for H, H_{HOM} and H_{HET}, respectively. The kinetic of adsorption was studied through the Lagergren pseudo-second-order model. The energetic effect caused by Cr(VI)/basic

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centers on silicate interaction at the solid/liquid interface was determined through a calorimetric titration procedure.

2. Materials and methods

2.1. Materials

The natural hectorite sample (H) was sampled in the Amazon region, in the northern Brazil. Size fractions of less than $2\ \mu\text{m}$ were separated by sedimentation. The cation-exchange capacity was measured in order to evaluate the potential use of clay for chemical modification, following the ammonium acetate method with concentration of $2.0\ \text{mol dm}^{-3}$ at pH 8.0 (CEC). The result obtained was $120.0\ \text{meq } 100\ \text{g}^{-1}$ of clay (H) on an air-dried basis.

The 2-mercaptobenzimidazole, MBI (Aldrich) and 3-chloropropyltrimethoxysilane, CTS (Aldrich) were used without purification. Deionised water was used throughout the experiments.

2.2. Homogeneous route

A sample of approximately 35 g (175 mmol) of silylating agent CTS reacted with 5.50 g (34 mmol) of MBI compound in the presence of 8.70 g (85 mmol) of triethylamine, which was used as a deprotonating agent in order to increase the efficiency of the reaction, were dissolved in $40.0\ \text{cm}^3$ of dimethyl formamide [17]. The mixture was mechanically stirred for 24 h at $423 \pm 1\ \text{K}$. The formed product, named MBICTS, was placed in suspension with approximately 36 g of natural hectorite and $50.0\ \text{cm}^3$ of dimethyl formamide. This sus-

pension was mechanically stirred in a reflux for 72 h at $423 \pm 1\ \text{K}$. The resulting product was filtrated, washed with water, and named H_{HOM} (Scheme 1) [17].

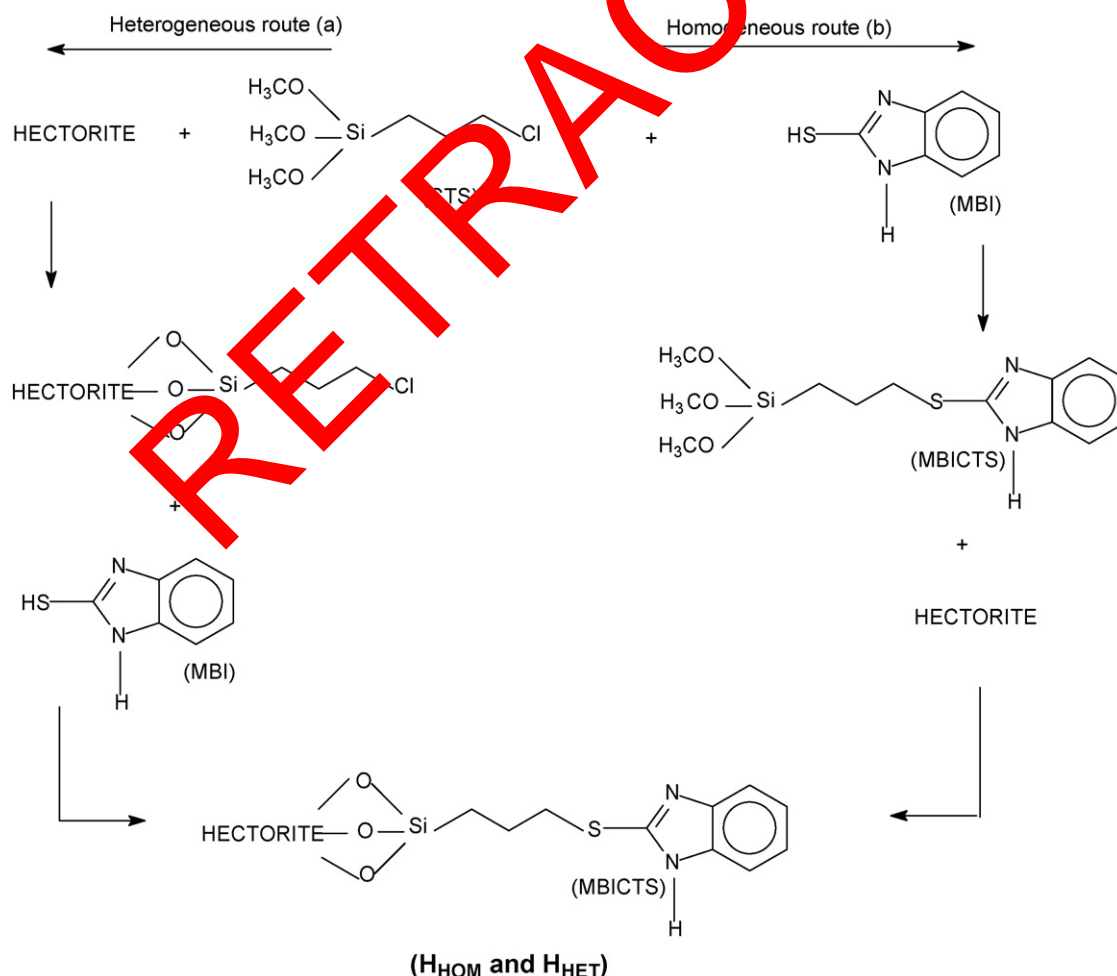
2.3. Heterogeneous route

A sample of approximately 35.0 g of natural hectorite was suspended in $100.0\ \text{cm}^3$ of dry xylene and 45.5 g (220 mmol) of 3-chloropropyltrimethoxysilane (CTS) was added to this suspension. The mixture reacted for 72 h in a reflux system at $410 \pm 1\ \text{K}$. The suspension was filtered and washed; the final product was named H_{CL} .

A sample of 34.5 g of H_{CL} reacted with 10.0 g (66.0 mmol) of compound MBI and 15.6 g (154 mmol) of deprotonating agent (triethylamine) in $100.0\ \text{cm}^3$ of dimethyl formamide. The suspension was kept in a reflux and mechanically stirred for 72 h at $423 \pm 1\ \text{K}$. The final product was filtered off and washed with ethanol and water and named H_{HET} (Scheme 1) [17].

2.4. Characterization of the adsorbents

The natural clay was analyzed by Induced Coupled Plasma-Optical Emission Spectrometry (ICP-OES), using an ARL 34000 instrument. Oven-dried powdered sample weighing exactly 0.231, was placed separately on glass weighing dishes and transferred quantitatively to pre-cleaned nitric acid digestion bottles. The sample was then digested with 7.0 cm^3 of 1 and 3 parts of nitric and hydrochloric acids with fifteen parts of hydrofluoric acid, and



Scheme 1. Incorporation of MBI onto natural hectorite surface by heterogeneous (a) and homogeneous process (b).

allowed to stand for 5 days. The sample was cooled in an ice-bath and 25.0 cm³ of boric acid was added with stirring, followed by 50.0 cm³ of deionized water. The solution was then diluted to 100.0 cm³. A blank and a set of elemental standards were run to calibrate the instrument.

The loss on ignition (LOI) analysis was carried out in a Nabertherm Controller C6 muffle furnace with digital temperature display and thermostatic temperature control. The hectorite sample was heated in a muffle furnace at 950 K for 4 h after being dried at 360 K overnight.

Brunauer–Emmett–Teller (BET) surface, pore diameter and pore volume were obtained from CO₂ adsorption/desorption in a Micromeritics ASAP 2000 BET surface analyzer system, the mesopore size distribution was obtained by applying the Barret–Joyner–Halenda (BJH) method to the adsorption branch of the isotherm.

The nuclear magnetic resonance spectra of solid materials were obtained on an AC 300 P⁻¹ Bruker spectrometer at 298 ± 1 K at 59.6 and 75.47 MHz, for silicon and carbon, respectively. ²⁹Si and ¹³C NMR spectra were obtained with pulse repetitions of 3 s for both nuclei and contact time of 1 and 3 ms, respectively.

The amount of organic pendant chains attached onto the hectorite formed were calculated based on sulfur and carbon percentages, determined through elemental analysis on a PerkinElmer Model 2400 elemental analyzer.

The thermal effects from chromium cation interacting on natural and modified hectorite samples were followed by calorimetric titration using an isothermal calorimeter, Model LKB 2277, from thermometric. In this titration, the metal solution is added to a suspension of about 20 mg of natural and modified hectorite sample in 2.0 cm³ of water, under stirring at 298.15 ± 0.20 K.

The thermodynamic, Lagergren pseudo-second-order and Freundlich models were fitted employing the non-linear fitting method using the non-linear fitting facilities of the software Microcal Origin 7.0. The correlation coefficient (*R*²) and a probability value (*p*) represent the “goodness of fit”. In addition, the model was also evaluated by average relative error function (Eq. (1)), which measures the difference of the amount of the metallic cation uptaken by the adsorbent predicted by the models and the actual *N_f* measured experimentally [15].

$$F_{\text{ERROR}} = \sqrt{\frac{\sum_i^p (N_{f, \text{model}} - N_{f, \text{experimental}} / N_{f, \text{experimental}})^2}{p}} \quad (1)$$

3. Results and discussion

3.1. Characterization

Elemental analysis from ICP-OES technique for the original clay sample, H, gave results consistent with hectorite, with silicon being the major component. The total mineralogical composition is given by 52.80, 27.40, 3.21, 2.40, 1.45, 1.24, and 1.22% of SiO₂, MgO, Na₂O, Fe₂O₃, TiO₂, Li₂O, and Al₂O₃, respectively, and 10.28% of mass was loss in the ignition process.

The CO₂ adsorption values for natural and modified hectorite are listed in Table 1. The specific surface areas were calculated by CO₂ BET method mainly for comparative purposes. The BET surface

areas of the natural and modified hectorite samples demonstrated that chemical modification caused the formation of mesopores in the solid particles, resulting in a higher surface area, revealing 767.8 m² g⁻¹ for H_{HET}, relative to the natural H sample with 48.0 m² g⁻¹. The pore size distribution in the mesopore region was obtained by applying the BJH method from CO₂ isotherms at 77 ± 1 K [15]. A change in pore size distribution was observed by comparing by considering natural and modified hectorite samples. The modified samples presented a unimodal distribution of pore sizes while H showed a bimodal distribution (Fig. 1a). The adsorption–desorption isotherms of gaseous CO₂ on natural and modified hectorite fitted the type IV curve behaviors, as illustrated in Fig. 1b, in concordance with previous results [16].

Nuclear magnetic resonance in solid-state is a technique to give valuable information about the bonding of the pendant chains anchored on an inorganic backbone. For this purpose carbon and silicon nuclei were examined in order to better characterize the synthetic compounds.

The ²⁹Si NMR spectra in the solid state for modified hectorite samples H_{CL}, H_{HOM} and H_{HET} confirm the covalent bond formed between silanol groups and alcohol groups dispersed onto the hectorite structure, as presented in Fig. 2a–c, respectively. These spectra presented four peaks located at –50, –59, –95 and –106 ppm. The first one is assigned to the silicon atom of the silylant agent bonded to the OH group and forming two siloxane bonds with the silicon of the hectorite structure, usually named as the T³ signal. The peak –61 ppm is assigned to three siloxane bonds with silicon and one with carbon, the T⁴ signal. Both signals confirm that the organic groups were covalently bonded on the hectorite surface. The other two peaks are attributed to pure surface signals, described as silicon forming four siloxane groups, Q⁴ at –106 ppm, and silicon forming three siloxane groups and one silanol group, Q³ at –95 ppm [17].

For carbon, the spectrum shown in Fig. 3 provides information about the polysiloxane framework such as various local environments of the atoms involved and the attachment of pendant groups, and the present case the assignments were based on previously studied analogous systems [17]. Thus, spectra for modified clays H_{CL}, H_{HOM} and H_{HET} are shown in Fig. 3a–c, respectively. In the spectra were observed three carbon atom related to the ligand ring, numbered 1, 2, and 3, give signals at 15, 19 and 23 ppm, respectively. For the H_{HET} and H_{HOM} spectra, five well-formed peaks, at 112, 115, 119, 121 and 129 ppm, are observed. These peaks are assigned to five carbons of pendant groups, which are numbered elements in the spectra, as representative feature structures shows in Fig. 3a and b. All these appearances in the spectra are consistent with a more rigid micro-environment created upon the modification processes, confirming the success of the preparation of these materials; these results in concordance with previous results [17].

It is possible to calculate the amount of attached molecules onto the hectorite samples surface (*L*₀) from the percentage of sulfur in the functionalized hectorite samples, calculated by elemental analysis, using the following expression (Eq. (2)) [18,19]:

$$L_0 = \frac{\%S}{\text{sulfur atomic weight}} \times 10 \quad (2)$$

Comparing the amount of attached molecules on the original clay surface (Table 1), it can be concluded that the degree of func-

Table 1
Textural proprieties and quantification of organic molecules of the modified clay samples.

Sample	Surface area-SA _{BET} (m ² g ⁻¹)	Micropore area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (cm ³ g ⁻¹)	<i>L</i> ₀ (mmol g ⁻¹)	<i>d</i> (molecules nm ⁻²)	<i>l</i> (nm)
H _{HOM}	723.0 ± 0.10	32.0 ± 0.13	2.3 ± 0.10	0.31 ± 0.11	0.43 ± 0.11	0.64 ± 0.11	1.32 ± 0.11
H _{HET}	767.8 ± 0.13	36.1 ± 0.10	2.5 ± 0.12	0.32 ± 0.10	0.77 ± 0.11	0.99 ± 0.11	1.00 ± 0.12

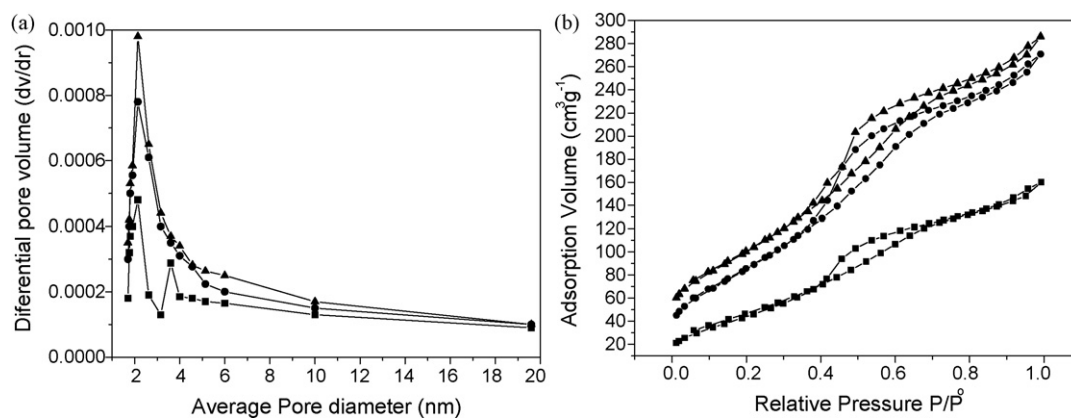


Fig. 1. Pore distribution of natural and modified hectorite samples obtained by BJH method (a) and nitrogen adsorption–desorption isotherms of natural and modified hectorite samples obtained BET method (b) (H ■, H_{HOM} ● and H_{HET} ▲).

functionalization obtained with H_{HOM} and H_{HET} was similar. However, as it can be observed, the quantity of anchored molecules is always superior via the homogeneous functionalization method.

The C/S molar ratio calculated from the elemental analysis of H_{HOM} and H_{HET} indicates a 1:1 stoichiometry, between the silanol groups on the clay surface and the ligand. Taking into account L_0 and specific area (SA_{BET}) of the modified clays, the average surface density, d , of the attached molecules and average intermolecular distance, I , can be calculated by applying the following Eqs. (3) and (4) [18,19]:

$$d = N_A \frac{L_0}{SA_{BET}} \quad (3)$$

$$I = \left(\frac{1}{d}\right)^{1/2} \quad (4)$$

where N_A is Avogadro's number. As expected (Table 1) in hectorite functionalized by heterogeneous method d is higher and I is lower than in hectorite functionalized by the homogeneous method, due to the better degree of functionalization obtained with the heterogeneous method. Also we observed that values of d and I for the modified hectorites are higher and lower, respectively. These results confirm a high efficiency in the functionalization of the hectorite sample. Thus, the high functionalization degree obtained in the H_{HOM} and H_{HET} can be explained as a consequence of its high surface area (Table 1).

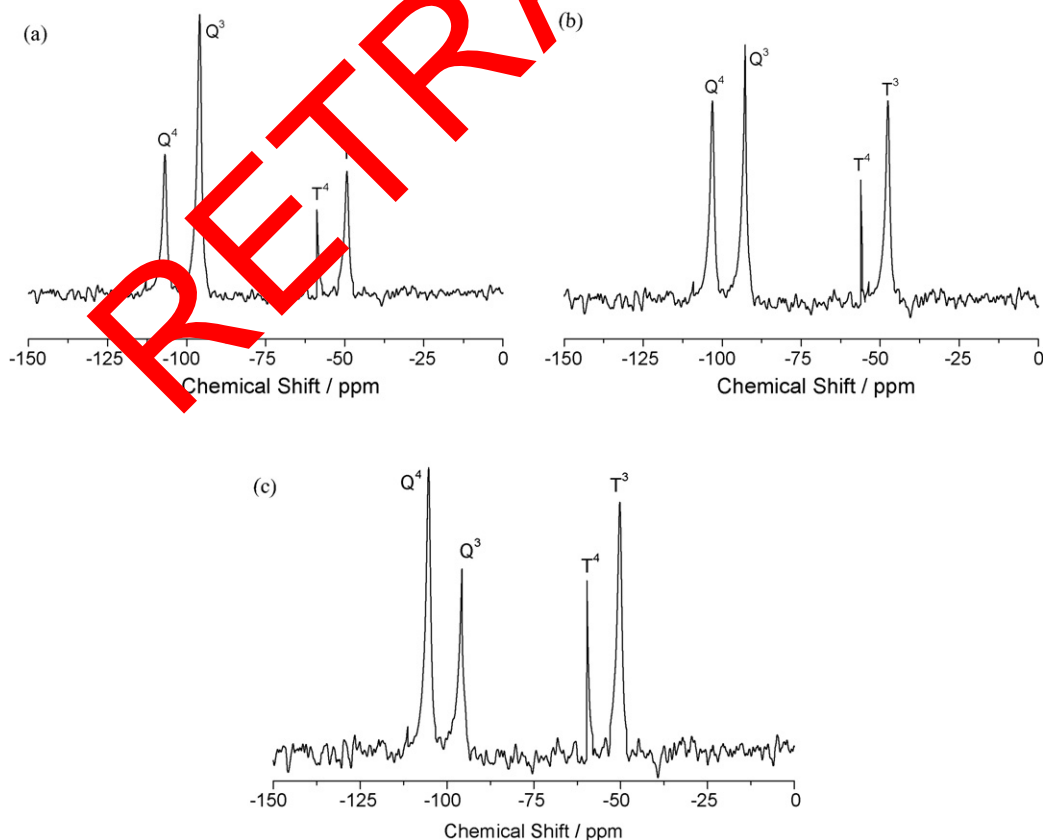


Fig. 2. ²⁹Si MAS NMR spectra of modified hectorite samples: H_{CL} (a), H_{HOM} (b) and H_{HET} (c).

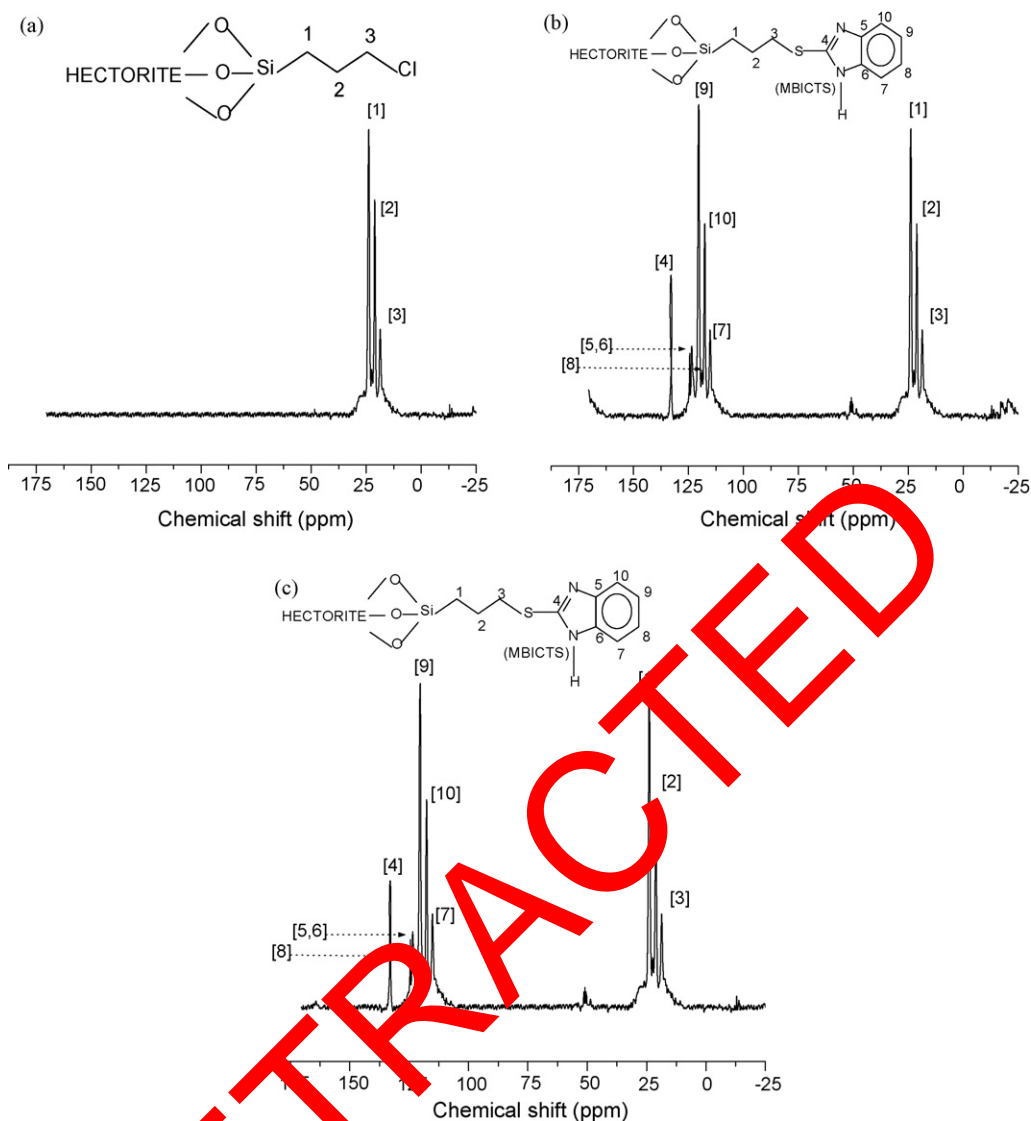


Fig. 3. ^{13}C MAS NMR spectra of modified hectorite samples: H_{Cl} (a), H_{HOM} (b) and H_{HET} (c).

3.2. Adsorption data

The adsorption experiments were performed through the batch-wise method. For such determination, a series of polyethylene flasks containing approximately 20 mg samples of the solid, in 20.0 cm^3 aqueous solutions of cations at concentrations varying from 1.25 to 2.5 mmol dm^{-3} , under orbital stirring for 360 min at $298 \pm 1\text{ K}$. Profiles of the obtained adsorption isotherms represented by the number of moles adsorbed (N_f), versus the number of moles at equilibrium per volume of solution (C_S), for series of isotherms, the data reveal that the adsorption process conforms to the Sips model (Eq. (5)) [20]:

$$N_f = \frac{N_S K_S C_S^{1/n}}{1 + K_S C_S^{1/n}} \quad (5)$$

Where C_S is the concentration of solution at equilibrium (mol dm^{-3}), N_f and N_S are of concentration of chromium adsorbed and the maximum amount of chromium adsorbed per gram of material (mol g^{-1}), respectively, which depend on the number of available adsorption reactive sites, K_S is the equilibrium constant and n is the Freundlich exponent [20].

The main purpose in this study is to establish the ideal conditions of the adsorption capacity, by considering the contact time of the solution at the solid/liquid interface. Adsorption kinetic study is important in treatment of aqueous effluents as it provides valuable information on the reaction pathways and in the mechanism of adsorption reactions [21]. The adsorption data for metal uptake versus contact time for a fixed adsorbent amount is shown in the Fig. 4a, giving identical abrupt increases in adsorption at low times before reaching the plateaus. According to these data, equilibrium is achieved at around 10, 15 and 20 min for H, H_{HOM} and H_{HET} , respectively. However, to be sure of the best adsorption conditions at higher concentrations levels, to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 1 h of contact time in aqueous solution of chromium cation at constant concentration of 2.5 mmol dm^{-3} . This short time period required to attain equilibrium suggests an excellent affinity of the adsorbent for Cr(VI) from aqueous solution. In order to study the specific rate constant of Cr(VI)–H, Cr(VI)– H_{HOM} and Cr(VI)– H_{HET} systems, we used a Lagergren pseudo-second-order rate equation to simulate the kinetic adsorption of Cr(VI) on the phyllosilicates. When the rate of reaction of an adsorption reaction is controlled by chemical exchange, then a pseudo-second-order model can be better

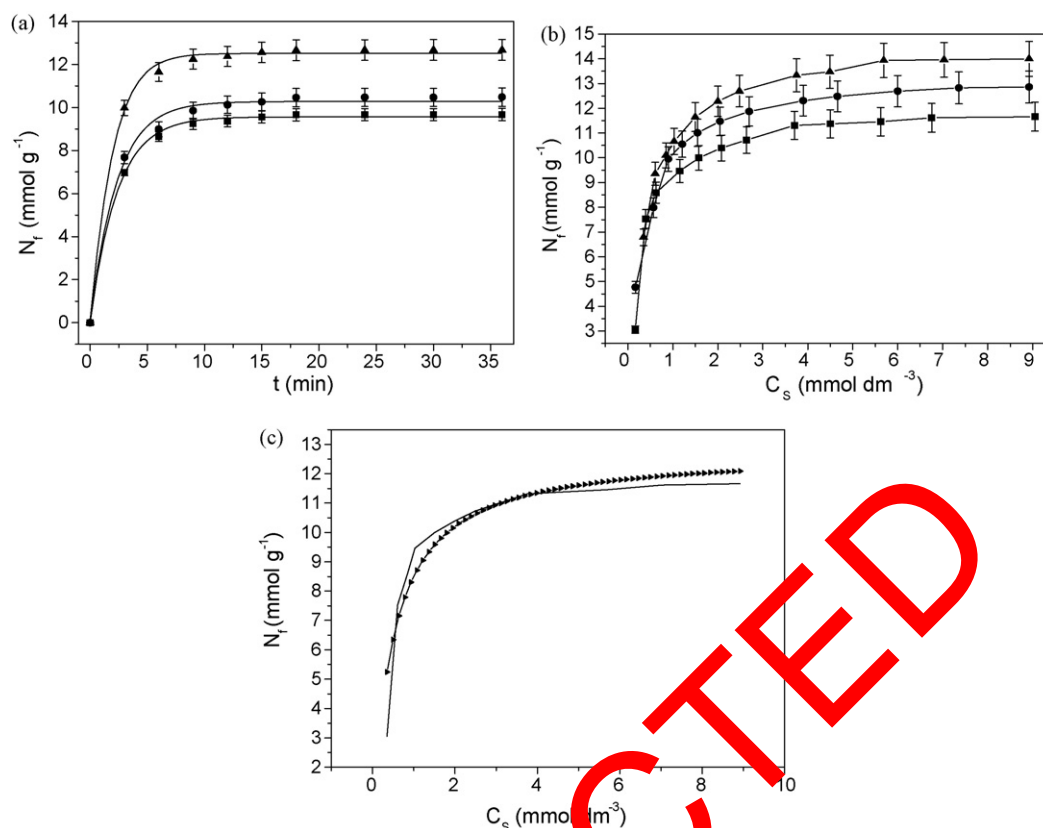


Fig. 4. Chromium cation adsorption onto modified hectorite samples: Contact time (a) and C_s (b) concentration variation (b) (H_{CL} ■, H_{HOM} ● and H_{HET} ▲) and experimental adjusted data with Sips non-linear model (c) (— H_{CL}/Cr(VI) and ► non-linear adjusted) C_s by 1.0 g dm⁻³, pH 2.0, time 360 min and controlled temperature in 298 ± 1 K).

adjusted to the experimental kinetic data [21], as expressed by Eq. (6).

$$\frac{t}{N_f} = \left(\frac{1}{k_2 N_{fEQ}^2} \right) + \left(\frac{1}{N_{fEQ}} \right) t \quad (6)$$

where k_2 is the pseudo-second-order rate (mmol g⁻¹ min⁻¹). The values of k_2 can be obtained from the non-linear regression plot of N_f versus t . Carrying out a set of experiments at constant temperature and monitoring the amount adsorbed with time, the kinetics of the adsorption process should be known. The values of k_2 are 19.2×10^{-3} , 20.8×10^{-3} and 21.7×10^{-3} mmol g⁻¹ min⁻¹ and the values obtained for N_{fEQ} are 9.5×10^{-2} , 9.7×10^{-2} and 11.6×10^{-2} mmol g⁻¹ for H_{CL}, H_{HOM} and H_{HET}, respectively. The correlation coefficients (R^2) of the pseudo-second-order rate equation for all adsorption kinetic experiments were 0.999, which suggest that the kinetic adsorption can be described by the pseudo-second-order rate equation very well.

Adsorption processes involve an array of phenomena that can alter the distribution of undesirable agents on the constituent phases and interfaces of a given systems. Thus, adsorption at a surface or interface is mainly a result of binding forces between the individual atoms, molecules or ions of the adsorbate to the surface [21]. The H_{HOM} and H_{HET} have been used to evaluate the maximum adsorption capacity for up taking chromium from aqueous solutions. In fact, this cation act as acidic Lewis centers that interact with the basic Lewis center attached to the pendant molecules covalently bonded to the modified clay surface. Such processes occurring at the solid/liquid interface give the isotherms that demonstrate the saturation of the modified clay samples with a definite number of moles of chromium cations, as clearly shown in Fig. 4b with the highest pronounced adsorption for chromium onto H_{HOM} and H_{HET}, respectively. Based on such ability of the pendant groups attached

to the inorganic backbone in coordinating the chromium cation, the quantity can be related N_f^{\max} , which presented the values for system Cr(VI)/hectorite 11.63, 12.85 and 14.01 mmol g⁻¹ for H_{CL}, H_{HOM} and H_{HET}, respectively. The exemplification of calculus by Sips non-linear method is shown in Fig. 4c.

3.3. Thermodynamic study

A series of increments of 10 μ L of chromium solutions was added to the Cr(VI)-modified hectorite to obtain the thermal effect interaction (Q_{tit}). Two other titrations are needed to complete the full experiment: (i) the thermal effect due hydration of the modified hectorite (Q_{hyd}), which normally gives a null value and (ii) the dilution effect of chromium solution in water, without sample in the vessel (Q_{dil}) [22–25]. The resulting thermal effect is given by following equation: $\Sigma Q_r = \Sigma Q_{tit} - \Sigma Q_{dil}$ [23]. The molar enthalpy ($\Delta_{int}H^\circ$) of the process can be calculated by the expression $\Delta_{int}H^\circ = \Delta_{int}h^\circ N_S$. The Gibbs free energy can be calculated by the equation $\Delta_{int}G^\circ = -RT \ln K_S$ equation, the entropy is finally calculated from $\Delta_{int}G^\circ = \Delta_{int}H^\circ - T\Delta_{int}S^\circ$ [22–25].

The thermodynamic cycles for this series of functionalizations involving a suspension (sup) of clay samples (H_x) in aqueous (aq) solution with metallic cation (M^{6+}) can be represented by the following calorimetric reactions (Eqs. (7)–(10)):

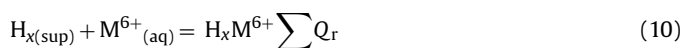
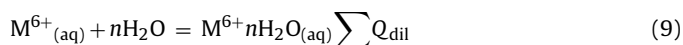


Table 2

Experimental and calculated adsorption data and thermodynamic data for chromium adsorption onto natural and modified clay samples (clay 1.0 g dm⁻³, pH 2.0, time 360 min and temperature of 298 ± 1 K).

Sample	N_f^{\max} (mmol g ⁻¹)	N_s^* (mmol g ⁻¹)	$-\Delta_{\text{int}}h^\circ$ (J g ⁻¹)	$-\Delta_{\text{int}}H^\circ$ (kJ mol ⁻¹)	n^*	$K_S \times 10^{-3}$	$-\Delta_{\text{int}}G^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{int}}S^\circ$ (J K ⁻¹ mol ⁻¹)
H	11.63 ± 0.11	12.09 ± 0.10	96.60 ± 0.10	7.99 ± 0.10	0.74	6.4 ± 0.1	21.7 ± 0.1	46 ± 1
H _{HOM}	12.85 ± 0.10	13.76 ± 0.11	97.70 ± 0.10	7.10 ± 0.10	0.87	7.9 ± 0.1	22.2 ± 0.1	51 ± 1
H _{HOM}	14.00 ± 0.12	14.67 ± 0.10	103.32 ± 0.10	7.00 ± 0.10	0.98	10.2 ± 0.1	22.9 ± 0.1	53 ± 1

* Sips model data, non-linear adjusted.

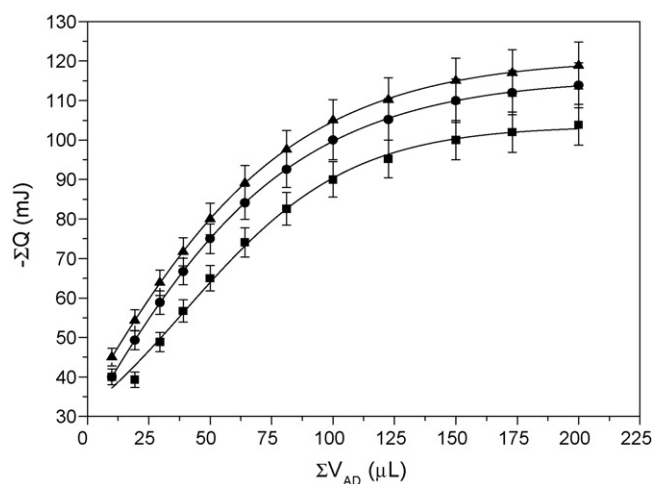


Fig. 5. The resulting thermal effects of the adsorption isotherms for the chromium cation: (H ■, H_{HOM} ● and H_{HET} ▲).

From calorimetric titration data, the net thermal effects resulted in corresponding well-behaved isotherms that were fitted to the Sips model, as shown in Fig. 5 [26,27]. Complete sets of thermodynamic data for each system studied are listed in Table 2. These values suggest that, during complex formation, desolvation disturbs the structure of the reaction medium to promote the disorganization of the system and, consequently, leads to an increase in entropy [24–27]. The thermodynamic values obtained with this study were in concordance with the values obtained by Alcântara et al. [17] with silica gel modified by 2-mercaptobenzimidazole adsorbing Hg(II) in aqueous solution. The spontaneity of this adsorption process is indicated by negative values of $\Delta_{\text{int}}G^\circ$ and $\Delta_{\text{int}}H^\circ$. The highest entropic values were observed for cation with the largest hydration volumes and illustrate the principle that the loss of water of hydration leads to a disorganization of the final systems [24–27]. In conclusion, all thermodynamic values are favorable, with exothermic enthalpy, negative Gibbs energy, and positive entropy, and corroborate Cr(VI)/natural and modified hectorite adsorption and the solid/liquid interface.

4. Conclusion

The modified Amazon hectorite is an excellent alternative adsorbent for removal of Cr(VI) from aqueous solutions. The immobilization of the 2-mercaptobenzimidazole molecules onto a natural hectorite surface was obtained with success through the homogeneous and heterogeneous routes, producing similar materials in all aspects. The series of thermodynamic data reflect the favorable cation/basic center interaction at the solid/liquid interface. These thermodynamic data suggest the application of this series of synthetic, natural and modified layer materials to improve the environment as cation extraction agents. The obtained data suggested the possible industrial application of such materials in concentration and heavy elements removal from nature as well as wastewater systems. The structural features of the new synthesized

materials with long designed chain suggested that it could suitably be modified further by several other synthetic approaches, to yield higher stage pendant chains, for a wide variety of chemical applications.

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