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Mercaptopropyl-grafted magadiite for lead and cadmium sorption and calorimetric determination

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Abstract Sodium magadiite anchored with 3-mercaptopropyltrimethoxysilane was synthesized through direct functionalization. After this reaction, it was observed a decrease in crystallinity, with a slight increase in basal distance to 1.57 nm, when compared to the precursor value of 1.53 nm. This organofunctionalization was evidenced through infrared spectroscopy, indicating by the presence of C–H stretching vibration in the 2900–2800 cm^{-1} region and mainly from the appearance of *T* species at the ^{29}Si NMR spectrum, centered at −65 and −55 ppm. The pendant chains covalently bonded to magadiite layers have the ability to sorb lead and cadmium cations, through a batchwise method at 298 ± 1 K, to give the maximum sorption capacity values of 1.54 and 2.72 mmol g^{-1}, respectively. The energetic effects caused by both cation/sulfur basic center interactions at the solid/liquid interface were determined through calorimetric titration, to give the enthalpies −13.48 ± 0.05 and −0.83 ± 0.053 kJ mol^{-1} for lead and cadmium, respectively. The sulfur basic centers attached to the pendant chains reflect in spontaneous process with negative Gibbs energies of −26.8 ± 0.1 and −24.5 ± 0.1 kJ mol^{-1}, resulting also in positive entropies of 44 ± 1 and 79 ± 1 J K^{-1} mol^{-1}, respectively. This set of favorable thermodynamic data is more pronounced for the softer cation in interacting with the basic atom.

Keywords Magadiite · Organofunctionalization · Sorption · Calorimetry · Thermodynamic

Introduction

Structured layered compounds with planes comprising tightly held atoms within layers contrasts with those weakly bonded in the perpendicular direction. A variety of designs from these crystalline-layered compounds emerge for several self-organized solids, in which the layers carry a net electrical charge compensated by counter ions inside the gallery region. These charge-balancing ions inside the interlayer space are generally accessible to water molecules, which cause a structure swelling in the perpendicular to the layer direction [1, 2].

A great number of these solids have been useful as host to favor organic molecule insertions into the nanolayer spaces, with the purpose to synthesize inorganic–organic supramolecular systems, to enable applications in many fields, such as catalysis and toxic substance removal from the environment [3, 4].

The series of layered polysilicates kenyaite, makatite, kanemite, ilerite and magadiite define a class of compounds formed by tetrahedral units with distinct layer thickness

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[5, 6]. These self-arranged structures are normally equilibrated by hydrated alkali cations, having layers that can graft silylating agents directly onto the inorganic network or enable intercalation of a series of polar organic molecules, as demonstrated mainly for magadiite [1–3].

This set of as-synthesized polysilicates with negatively charged multiple tetrahedra silicate sheets possesses the general formula $Na_2O{\cdot}14SiO_2{\cdot}nH_2O$, with ion-exchange capacity, normally obtained by replacing the original sodium ions by protons, other cations or large quaternary ammonium ions [2, 5–8]. When the surface is acidified, an increase in silanol groups occurs that presents utility directly related to the covalent grafting of silylating agents formation in the interlayer space. The pendant chains can be used to provide the function of organophilicity inside the interlayer cavity. By choosing the bulkiness and the amount of the modifying organic groups, the resulting properties are derived from the selective and specific guest species [7]. For this purpose, the success of this design consists in exploring new synthesized agents of the general formula $X_3Si–Y$, where Y is the organofunctional moiety and X is normally a hydrolysable group such as chloride or alkoxide, which favors covalent bond formation on the inorganic surface [9]. The normal organofunctionalization procedure involves the direct interaction of any silylating agent with free hydroxyl groups available on the inorganic surface, to yield chemically modified surfaces with new properties, which differ considerably from the precursor.

The profitability of these chemically modified polymeric materials depends not only on the availability of the pendant molecules, but also on to the characteristics of the basic centers. One of the most useful properties associated with these chains is to explore the potential activity of the attached basic centers within the organic moieties for cation removal from aqueous and nonaqueous solutions [6, 8].

Taking into account the interest in exploring immobilization onto interlayer materials with silylating agents that can expose basic sulfur atoms attached to the pendant chains, the present investigation deals with the synthesis of organofunctionalized layered magadiite. The well-characterized pendant silylating moieties that covalently bonded inside the cavities on the sequence of lamella were successfully used to obtain the thermal effects of lead and cadmium cation removal from aqueous solutions at the solid/liquid interface were determined, in order to obtain the thermodynamic data for this system.

Experimental

Chemicals

The chemical reagents silica gel (Aldrich) with average pore size of 10 nm, sodium hydroxide (Merck), 3-mercaptopropyltrimethoxysilane (Aldrich), toluene (Synth) and acetone of analytical grade were used in the synthetic procedure or as solvent during template removal. Lead and cadmium nitrates (Vetec) and deionized water were used in all sorption and calorimetric experiments.

Characterization

Infrared spectra for the samples as KBr pellets were obtained by accumulating 32 scans on a Bomem Spectrophotometer, MB-series, in the 4000–400 cm^{-1} range, with 4 cm^{-1} of resolution, by applying Fourier transformation. The samples organic content was determined by the quantities of nitrogen, hydrogen and carbon in a Perkin-Elmer model PE 2400 elemental analyzer. Nuclear magnetic resonance spectra for silicon and carbon nucleus were recorded with a Bruker AC 300/P spectrometer at room temperature. For each spectrum, about 1 g of solid sample was compacted into a 7-mm zirconium oxide rotor. The measurements were taken at frequencies of 75.47 and 100.62 MHz for silicon and carbon nuclei, with a magic angle spinning of 4 kHz. In order to increase the signal-to-noise ratio of the solid-state spectra, the CP/MAS technique was used, with pulse repetitions of 3 s and contact time of 5 ms for the silicon and carbon nuclei. X-ray diffraction patterns were obtained on a Shimadzu XRD-3000 diffractometer (35 kv, 25 mA), in the $2\theta = 1.4–70°$ range, applying a nickel-filtered CuKα radiation with a wavelength of 0.154 nm. Thermogravimetric curves were obtained using a Shimadzu TG 50 apparatus, under argon atmosphere at a flow rate of 1.67 $cm^3\ s^{-1}$, with a heating rate of 0.167 K s^{-1}. The amount of lead and cadmium sorbed was determined by the difference between its initial concentration in the aqueous solution and that found in the supernatant, by using a Perkin-Elmer 3000 DV ICP-OES apparatus. For each experimental point, the reproducibility was checked by at least one duplicate run. Calorimetric measurements were taken in an isothermal Thermometric LKB 2277 calorimeter.

Synthesis and immobilization

Sodium magadiite was synthesized using hydrothermal conditions as previously described [2, 10]. Briefly, a suspension containing 8.0 g of silica gel in 54 cm^3 of water with 2.4 g of sodium hydroxide was heated at 423 K for 72 h in a sealed Teflon-lined vessel. The white product was then washed with deionized water until neutral pH, centrifuged and dried at 320 K for 24 h, to yield a solid named Na-Mag. For the grafting process, 1.0 g of sample was organofunctionalized with 5.0 cm^3 of 3-mercaptopropyltrimethoxysilane (MPTS) using toluene as solvent, carrying out this reaction in a flask for 96 h at 333 K, to obtain a new organofunctionalized material, named Mag-MPTS.

Sorption experiments

All sorption experiments were performed in duplicate, using a batch process in which nearly 20 mg of Mag-MPTS was suspended into a series of polyethylene flasks containing 25.0 cm^3 of divalent lead or cadmium nitrate solutions with concentrations ranging from 7.0×10^{-4} to 7.0×10^{-3} mol dm^{-3}. The suspensions were shaken for 24 h in an orbital bath at 298 ± 1 K. The supernatant solutions were separated from the solid by decantation, and aliquots were taken to determine the amounts of cation remaining through ICP-OES. The amount of the cation sorbed during the experimental assays (mmol dm^{-3}) was calculated by Eq. (1), where N_f is the number of moles sorbed, n_i and n_s are the number of moles in the initial and supernatant solutions after establishing the equilibrium, and m is the mass of the sorbent used in each individual determination [6, 10].

$$N_f = (n_i - n_s)/m \quad (1)$$

The experimental data related to the number of moles in supernatant in each point of titration, C_s, and the N_f obtained were fitted to a modified Langmuir equation (Eq. 2) in order to determine the maximum adsorption capacity, N_s, the constant b being related to the chemical equilibrium at the solid/liquid interface [11].

$$\frac{C_s}{N_f} = \frac{1}{N_s b} + \frac{C_s}{N_s} \quad (2)$$

The thermal effects obtained from the sorption interactions were followed by calorimetric titrations [6, 12, 13]. From each procedure, three independent operations were required to complete the thermodynamic cycles: (1) the thermal effect due to Mag-MPTS/cation interaction (Q_t), (2) hydration of the solid (Q_s) and (3) cation solution dilution (Q_d). For Q_t determination, the metallic solution is added to a suspension of about 20 mg of the Mag-MPTS sample in 2.0 cm^3 of water, under stirring at 298.15 ± 0.20 K. Increments of 10.0×10^{-6} dm^3 of cation solution were added to the chemically modified lamellar compound to obtain the thermal effect of interaction (Q_t). As the thermal effect of hydration of the suspended inorganic solid sample in water gave null value [6], the net thermal effect (Q_r) is given by Eq. (3):

$$\sum Q_r = \sum Q_t - \sum Q_d \quad (3)$$

The enthalpy associated with cation/Mag-MPTS interaction can be determined by adjusting the sorption data to a modified Langmuir equation to calculate the integral enthalpy involved in the formation of a monolayer per unit sorbent mass $\Delta_{mon}H$ [6, 14, 15], given by Eq. 4:

$$\frac{\sum X}{\sum \Delta H} = \frac{1}{(K-1)\Delta_{mon}H} + \frac{X}{\Delta_{mon}H}, \quad (4)$$

where ΣX is the sum of the molar fraction of the cation (Pb^{2+} or Cd^{2+}) in solution at equilibrium, $\Delta_{mon}H$ is the resulting enthalpy from the interactive process (J g^{-1}), which is obtained by dividing the thermal effect obtained from Q_t by the mass of the Mag-MPTS, and K is a proportionality constant including the equilibrium constant. The $X/\Delta H$ versus X plot provides the angular and linear coefficients, which enable determination of the thermal effect involving the monolayer $\Delta_{mon}H$ and K values, respectively. The molar enthalpy (ΔH) of the process can be calculated by Eq. (5)

$$\Delta H = \frac{\Delta_{mon}H}{N_S} \quad (5)$$

From K values, the free Gibbs energies were calculated by Eq. (6)

$$\Delta G = -RT\ln K \quad (6)$$

and the entropy value can be calculated through Eq. (7)

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Results and discussion

The infrared spectrum of Na-Mag presented a broad band centered at 3450 cm^{-1} that corresponds to OH stretching, due to the presence of water hydrogen bonded molecules, as shown in Fig. 1. The absorptions found in the 1000–1250 cm^{-1} interval are related to SiO_4 units of the main skeleton structure, and in particular, the strong band centered at 1103 cm^{-1} is attributed to Si–O stretching bond. The intratetrahedra symmetrical stretching band referred to the Si–O–Si bond is observed at 791 cm^{-1}, the tetrahedra deformation O–T–O at 485 cm^{-1} and a ring vibration at 576 cm^{-1} [2, 4, 16]. After the mercaptopropyl immobilization, nearly the same set of bands for the inorganic backbone was presented. The most significant change is the appearance of the C–H stretching bands at 2852, 2925 and 2956 cm^{-1}. Also the appearance on band at 1233 cm^{-1} assigned to the Si–C stretching is observed, which is a first good indication regarding to prove the organic moiety immobilization at the silicic structure [4]. On the other hand, it was not observed the presence of the S–H stretching band [17] that could be detected centered at 2550 cm^{-1}. This absence was already reported for similar materials with a relative small amount of mercapto group which are more intense in the Raman spectra [18, 19]. These results give some indicatives for the organofunctionalization achievement; however, ^{29}Si NMR is a valuable tool to provide unequivocal results to prove the silicon–carbon bonding formed, as it will be further described.

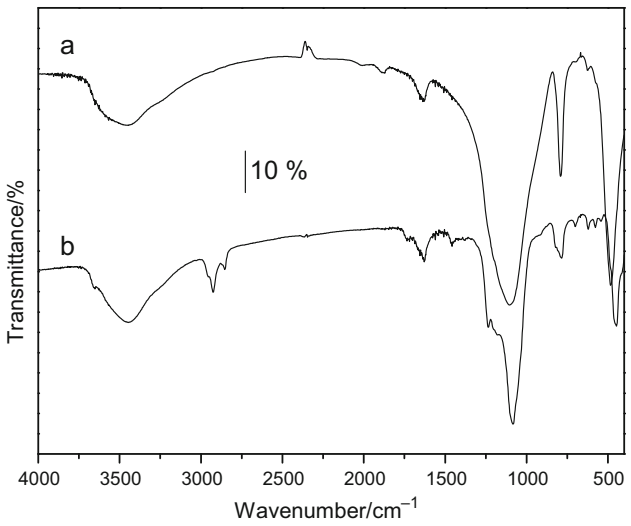


Fig. 1 Infrared spectra of layered Na-Mag (**a**) and the organofunctionalized Mag-MPTS (**b**), separated by 40 % transmittance for clarity

X-ray diffraction patterns of Na-Mag and Mag-MPTS are shown in Fig. 2. Sodium magadiite showed a d_{001} peak, corresponding to a Na-Mag basal distance at 2θ 5.8° of 1.52 nm, in agreement with previous results [2, 7]. The other peaks are related to the crystalline planes of the inorganic lamellar structure and were indexed as d_{002}, d_{003} and d_{202} at 2θ 11.5, 17.2 and 25.9°, respectively. Other plane assignments are shown in Fig. 1. For Mag-MPTS, a considerable modification of patterns was observed. The first peak, located at 2θ 5.4°, corresponds to the basal distance of 1.61 nm, while a lower intensity and broader signal are centered at 2θ 7.7°, corresponding to a 1.15 nm distance. There is also a halo at 2θ 20.8° and the plane reflections 021, 202 and 203 located at 2θ 24.4°, 25.9° and 2θ 280.4°, respectively. These results indicate that the insertion of the silane occurred partially inside the interlamellar magadiite space and in the external surface, whereas some particles were exfoliated, than two 001 reflections were observed. The basal interlayer distance depends on the length of the intercalated silane, its position and the presence or absence of hydration water. Despite the crystallinity decreasing for the synthesized Mag-MPTS, its lamellar structure was preserved.

Solid-state NMR spectroscopy is an important auxiliary tool to elucidate the structure of silylating agents attached to layered inorganic silicates [14]. Evidence of alkylsilyl groups bonded in the interlayer surface of the polysilicate magadiite is demonstrated through ^{13}C-MAS/NMR in Fig. 3. The pendant molecule covalently bonded on the Mag-MPTS structure, represented by C1, C2 and C3 carbon atoms indicated the insertion of the spacer group inside the structure, to give the chemical shift at 12, 23 and 28 ppm, respectively. Due to its higher mobility, C3 presents higher intensity; however, the proportion is similar for all carbon chemical shifts in agreement with the silane employed.

The crystalline Na-Mag compound presented the ^{29}Si NMR spectrum, as shown in Fig. 4. The peaks are assigned to Q^3 and Q^4 units at −98.5 and −110 ppm, respectively, values that are in agreement with the proposed layered structure [15]. Q^3 species corresponds to the silicon atom bonded to three other oxygen atoms that are also bonded to silicon atoms of the inorganic network and one oxygen atom bonded to hydrogen to form a silanol group, which is a hydrophilic group on the magadiite surface [7]. On the other hand, Q^4 signal indicates a silicon atom bonded to

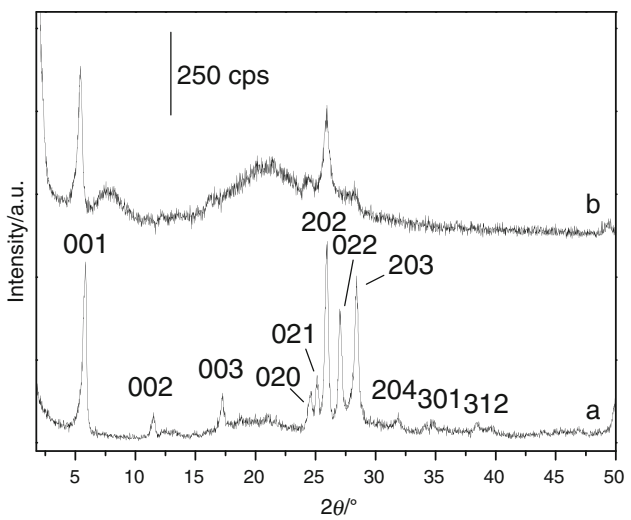


Fig. 2 X-ray diffraction patterns for layered Na-Mag (*a*) and the chemically modified Mag-MPTS (*b*) compounds

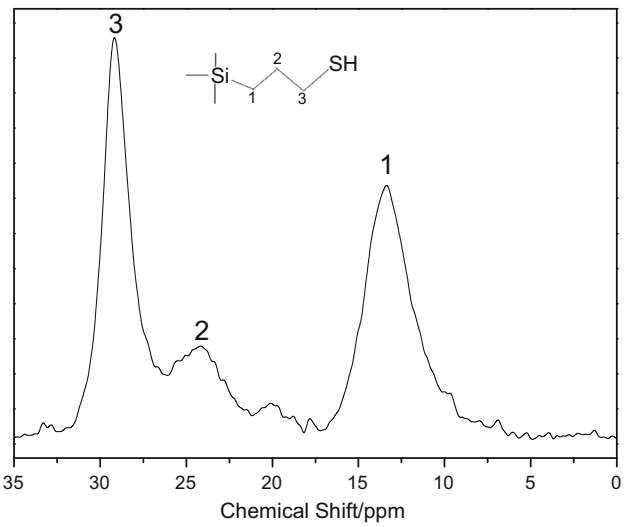


Fig. 3 ^{13}C NMR spectrum in the solid state for the chemically modified magadiite Mag-MPTS

four oxygen atoms in the inorganic structure. As the precursor magadiite is covalently bonded to the silylating agent, the silicon–oxygen carbon bonded formed on inorganic network gave signals that correspond to *T* species, as attributed to T^3 and T^2 at −64 and −55 ppm, respectively [7, 8, 20]. Based on the presence of these signals, the values indicate that the magadiite surface was successfully anchored with the silane molecule, as previously suggested by the X-ray diffraction results.

The thermogravimetric curve for the precursor lamellar compound Na-Mag and the organofunctionalized Mag-MPTS and corresponding derivative curves are shown in Fig. 5. Based on the decomposition curves, a decrease in mass is observed without clear defining plateaus; however, from the derivative curve, it is possible to detect different decomposition events. Na-Mag eliminated different water molecule contents [2, 6], which have been explained hence: (a) an initial step from room temperature to 371 K corresponding to water physically sorbed on inorganic surface, (b) a second stage between 371 and 450 K due to water of crystallization and (c) in the last step from 450 to 619 K corresponding to condensation residual silanol groups, as shown in Fig. 6a. These results indicate a higher hydration level of thirteen water molecules for each two sodium ions, if compared with the most reported nine water molecules for the same amount of sodium ions [2, 6]. Likewise, for Mag-MPTS the derivative curve presented stages of mass losses starting up to 410 K, referring to the water elimination, as expected in smaller amount than observed for Na-Mag due to its hydrophobicity. Between 410 and

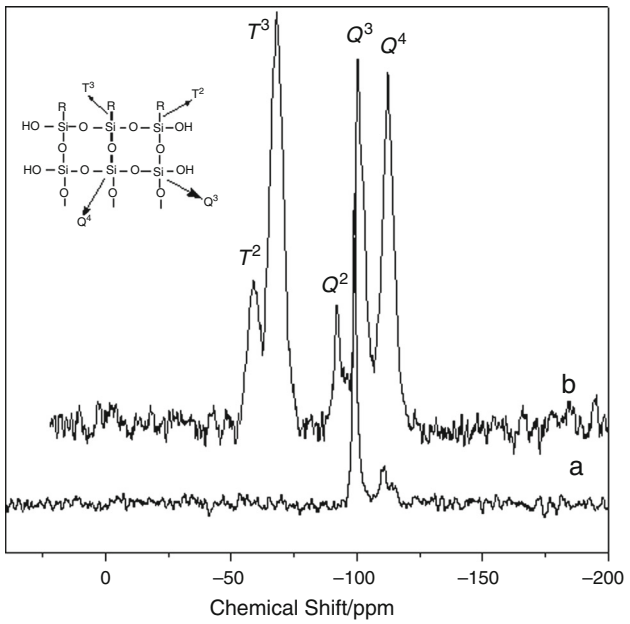


Fig. 4 ^{29}Si NMR spectra in the solid state for Na-Mag (*a*) and anchored Mag-MPTS (*b*)

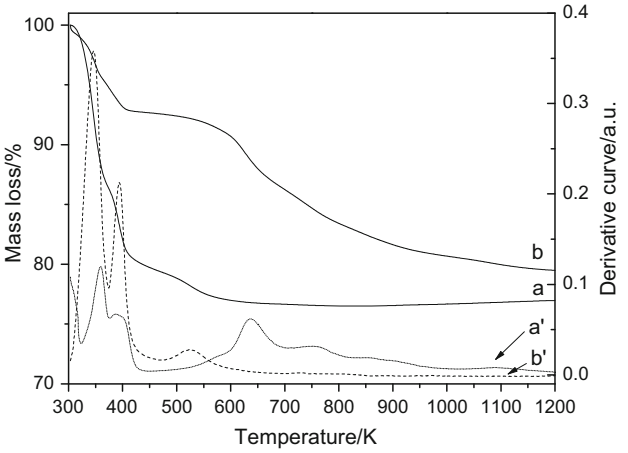


Fig. 5 Thermogravimetric curves for layered Na-mag (*a*) and immobilized Mag-MPTS (*b*), and thermogravimetric derivative curves for Na-mag (*a*′) and anchored Mag-MPTS (*b*′)

600 K, the mass loss is referring the remaining water. At higher temperatures the mass loss is due to the organic silylating moiety and the condensation of silanol, as shown in Fig. 5. Finally, the precursor magadiite leaves inorganic residue at temperature above 600 K and the chemically modified compound presents a different behavior up to 1000 K, suggesting that the some inorganic carbon must remain at that temperature; however, it is correct to say that at least 85 % sodium sites were occupied with a MPTS group considering only TG results. Elemental CHN analysis, which provides higher accuracy for the organic amount determination than TG, indicated that all sodium sites were replaced by MPTS groups at Mag-MPTS sample, which shows that not all organic groups were carbonized during the TG experiment. Carbon amounts of

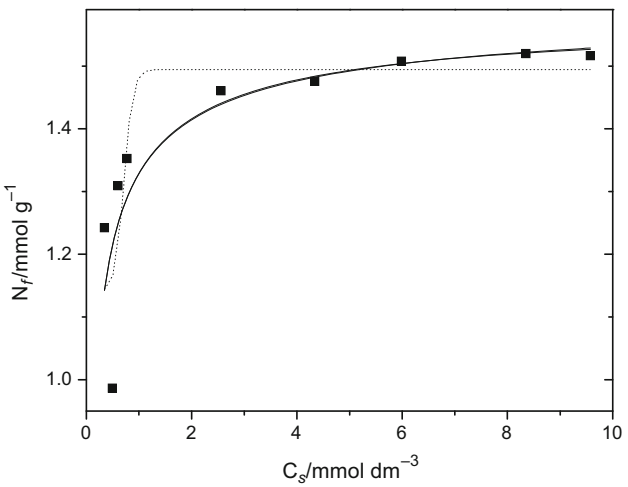


Fig. 6 Pb^{2+} adsorption isotherm for Mag-MPTS at 298 ± 1 K raw data (*filled square*), Langmuir (*dashed line*) and Freundlich (*continuous line*) curves

16.4 and 0.18 % were found for Mag-MPTS and Na-Mag samples, respectively. Despite the surface functionalization, distribution and some unreacted MPTS cannot be determined by TG or elemental CHN analysis. On the other hand, the absence of ^{0}T and ^{1}T signals at ^{29}Si NMR indicates the absence of oligomers or free MPTS at the sample.

The number of moles of cations N_f sorbed on Mag-MPTS is an important parameter to express affinity for cation/basic center interactions that gave the values of 1.54 ± 0.01 and 2.72 ± 0.08 mmol g^{-1} for lead and cadmium removed from aqueous solution, respectively. In spite of distinct maximum sorption capacity for both cations, however, similar behavior for these isotherms was obtained, as represented for lead in Fig. 7. Compared with the Na-Magadiite adsorption capacity of 0.048 and 0.89 mmol g^{-1} for lead and cadmium, respectively [21, 22], the improvement on the adsorption capacity with immobilized mercapto groups was relevant.

These data were fitted to the modified Langmuir, Eq. (2), as given by C_s/N_f as a function of C_s, which enable calculation of the linear and angular coefficients from the straight line, to obtain N_s and b values. Also Freundlich equation [6, 13] was applied resulting in a better fit, as shown in Fig. 6. Based on these results, the importance of the organofunctionalized magadiite to extract cations from an aqueous solution is clearly confirmed. Scheme 1 illustrates the possible divalent metal complexation on the sulfur atom attached to the pendant chain anchored on the magadiite surface.

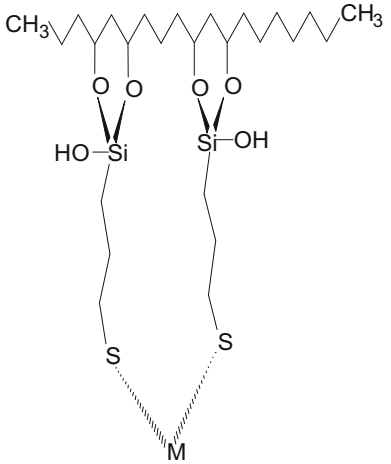
The sorption process was calorimetrically followed in aqueous solution, with intent to obtain thermodynamical data from the reactions. As mentioned before, the calorimetric technique is used as a direct method to determine the variation of enthalpy in the process [6, 23]. The net resulting thermal effects obtained from lead and cadmium nitrate interactions with chemically modified magadiite were determined in separate calorimetric experiments by subtracting the dilution effect in water from the total thermal effect. The effects of the complete thermodynamic cycle for this series of interactions involving a suspension (sp) of organofunctionalized magadiite (Mag-MPTS) in aqueous (aq) solution with these cations (M^{2+}) are represented by Eqs. (8–11), as follows:

$$\text{Mag-MPTS}_{(sp)} + M^{2+}_{(aq)} = \text{Mag-MPTS} \cdot M^{2+}_{(sp)},\ Q_t \quad (8)$$

$$\text{Mag-MPTS}_{(sp)} + n\text{H}_2\text{O} = \text{Mag-MPTS} \cdot n\text{H}_2\text{O}_{(sp)},\ Q_h \quad (9)$$

$$M^{2+}_{(aq)} + n\text{H}_2\text{O} = M^{2+} \cdot n\text{H}_2\text{O}_{(aq)},\ Q_d \quad (10)$$

$$\text{Mag-MPTS} \cdot n\text{H}_2\text{O}_{(sp)} + M^{2+} \cdot n\text{H}_2\text{O}_{(aq)} = \text{Mag-MPTS} \cdot M^{2+}_{(sp)} + 2n\text{H}_2\text{O},\ Q_r \quad (11)$$



Scheme 1 Proposed complexation model of divalent metal (M) in the organofunctionalized layered structure of Na-Mag derivatized with the silylating agent

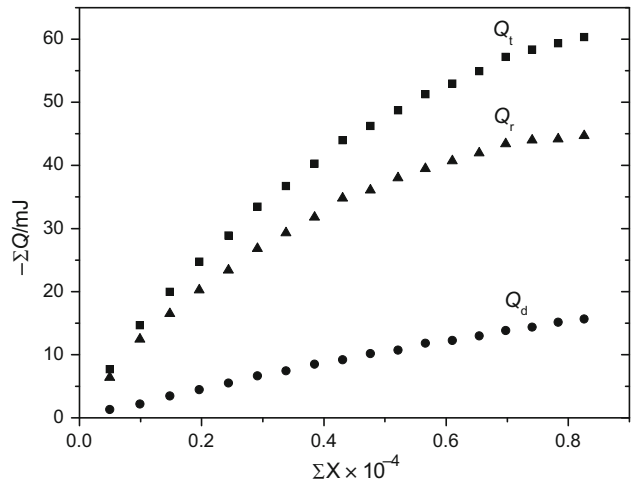


Fig. 7 Resulting thermal effects of the sorption isotherms of 0.10 mol dm^{-3} of Cd^{2+} on 20 mg of Mag-MPTS surface at 298.15 ± 0.20 K

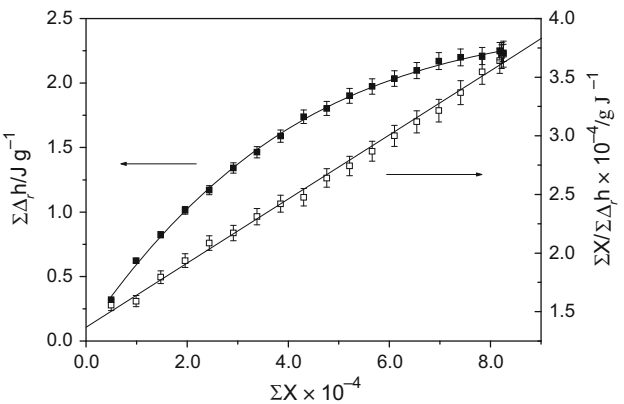


Fig. 8 Isotherm and linearization from calorimetric titration of Cd^{2+} (*filled square*) on the Mag-MPTS surface at 298.15 ± 0.20 K

Table 1 Thermodynamic data from the interaction of Mag-MPTS with divalent lead and cadmium (M) cations in aqueous solution, enthalpy of monolayer formation ($\Delta_{mon}H$), maximum amount of solute (N_s), equilibrium constant (K), enthalpy (ΔH), Gibbs energy (ΔG) and entropy (ΔS) at 298.15 ± 0.20 K

M	$-\Delta_{mon}H$/J g^{-1}	N_s/mmol g^{-1}	$-\Delta H$/kJ mol^{-1}	K	$-\Delta G$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Pb^{2+}	20.79 ± 0.04	1.54 ± 0.01	13.48 ± 0.05	10.8	26.8 ± 0.1	44 ± 1
Cd^{2+}	2.25 ± 0.07	2.72 ± 0.08	0.83 ± 0.03	9.9	24.5 ± 0.1	79 ± 1

The net thermal effect obtained from the calorimetric titration ($\sum Q_r = \sum Q_t - \sum Q_d$), as given by Eq. (11), is represented by the isotherms in Fig. 7. The net thermal effect linearized for cadmium is shown in Fig. 8. By applying Eq. (4) and the linearized data for these sorptions, the enthalpy involved in the formation of a monolayer, $\Delta_{mono}H$, can be obtained for all processes. This enables calculation of the molar enthalpy [6, 17] from Eq. (5). The Gibbs energy was determined from Eq. (6) for cation–basic center interactions on the Mag-MPTS surface, and the entropy was calculated with Eq. (7), the values being listed in Table 1. The enthalpic data are exothermic for both cation interactions with higher values for lead. The negative Gibbs energy for both kinds of interactions indicates that a spontaneous process of cation complexation occurred. The positive entropic values associated with this process suggests that while the interactions are in progress, the solvated water initially linked to cations and also those molecules hydrogen bonded to the basic center were displaced to the medium as the sorption took place, which increased the disorder in the system. Thus, the set of thermodynamic data determined is in agreement with a favorable complex formation [24, 25], being more pronounced for the softer lead cation.

Conclusions

The synthesis of sodium magadiite and its organofunctionalization was achieved successfully, with Na-Mag being more crystalline; however, the chemically modified self-organized compound was confirmed through ^{29}Si NMR, with appearance of T groups and also supported by thermogravimetry, as indicated through the loss of the organic silane moiety. The chemically modified lamellar compound sorbed lead and cadmium ions with maximum sorption values of 1.54 and 2.72 mmol g^{-1}, respectively. The metal/basic center interaction was quantitatively determined through calorimetric titrations. The thermodynamic data at the solid/liquid interface demonstrated the properties associated with the affinity of sulfur/cation bonding. The spontaneity of such interactions is given by the negative Gibbs energy, exothermic enthalpy and positive entropy data, which characterize favorable interactive process.

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