



Layered organoclay with talc-like structure as agent for thermodynamics of cations sorption at the solid/liquid interface

Syed Badshah, Claudio Airoidi*

Institute of Chemistry, University of Campinas, UNICAMP, P.O. Box 6154, 13084-971 Campinas, SP, Brazil

ARTICLE INFO

Article history:

Received 16 September 2010

Received in revised form 27 October 2010

Accepted 28 October 2010

Keywords:

Organoclay
1,2-Ethanedithiol
Cations removal
Thermodynamic
Phyllosilicate

ABSTRACT

A new silylating agent 2-mercaptoethyl-3-(triethoxysilyl)propylcarbamothioate was synthesized from the reaction of 1,2-ethanedithiol and 3-(triethoxysilyl)propylisocyanate. This precursor silylating agent and magnesium nitrate, using sol–gel conditions, yielded a layered organoclay with a talc-like magnesium phyllosilicate structure. Based on sulfur elemental analysis data, the maximum incorporation of organic moiety inside the clay-layer spaces gave 3.87 mmol g^{-1} , which talc-like structure was confirmed from a peak at 60° in the X-ray diffraction patterns. The basal distance of 1.65 nm was calculated from a peak at 5.31° . Infrared spectroscopy and nuclear magnetic resonance in the solid state for the carbon nucleus confirmed that the organic moiety is covalently bonded to the inorganic framework of the lamellar material. The success of hydrolysis and condensation reactions during the sol–gel process was confirmed by ^{29}Si NMR spectrum in the solid state by T^1 , T^2 and T^3 silicon species. The organic moiety of the hybrid material contains nitrogen, oxygen and sulfur basic centers available for divalent lead, copper and cadmium cation removal. Based on the Langmuir model, the maximum sorption capacities of the hybrid for these cations were 7.08, 4.01 and 1.86 mmol g^{-1} , respectively. The thermodynamic data (ΔH , ΔG and ΔS) for cation/basic center interactions at the solid/liquid interface were determined through calorimetric titration. The negative Gibbs energy, exothermic enthalpy and positive entropic values indicate spontaneous and favorable conditions to cation removal at the solid/liquid interface.

© 2010 Published by Elsevier B.V.

1. Introduction

Water pollution by toxic metals remains an important environmental issue having a major impact on public health and the economy. Industrial uses of metals and other domestic processes such as burning of fossil fuels, incineration of wastes, automobile exhausts, smelting processes, use of sewage sludge as landfill material and fertilizer have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments [1,2]. Among these metals traces of iron, copper, zinc and manganese are involved in several enzyme functionalities that participate in controlling various metabolic and signaling pathways, also being essential for maintaining health throughout life. An excess of these metals can create problems for both human health and the environment [3].

Water contamination with heavy metal ions such as mercury, cadmium and lead present dangers to both human life and the environment due to their acute toxicity, even when they are present in trace concentrations [4]. These metals do not degrade biologically

like organic pollutants and also disrupt body functions by accumulating in vital organs and glands in humans such as in the heart, brain, kidneys, bones, liver and thyroids [5].

Lead has no known physiologically relevant role in the body itself [6], but causes a vast number of harmful effects, interferes in bone and teeth metabolisms, for example, alters also the permeability of blood vessels and collagen synthesis [7]. Cadmium accumulates mostly in the liver and kidneys and interferes with calcium and vitamin D metabolism, and when associated with lead in the body it can cause structural and functional damage to the thyroid glands [8].

Various sorptive materials such as activated charcoal [9], zeolites [10], and clays [11] have been used to capture metal ions from aqueous solution. The main clay features for pollutant trapping from the environment include their high specific surface areas associated with their small particle size, low cost and their occurrence in most soil and sediment environments [12]. However, the inherent limitations of these materials as sorbents for heavy metals are their low loading capacity, relatively small metal ion binding constants, and low selectivity to diverse types of metal [13].

To avoid the above-mentioned limitations, the reactions of clay minerals with reagents containing metal chelating functions have recently been explored in an effort to enhance both the heavy metal

* Corresponding author. Tel.: +55 19 35213055.

E-mail address: airoidi@iqm.unicamp.br (C. Airoidi).

binding capacities of clays and their selectivity to specific types of metals [14,15]. For this, hybrid clay minerals based on talc-like magnesium phyllosilicate structures have recently been proposed as heavy metal sorbents. Synthesized nickel, copper or zinc phyllosilicates with nitrogen [16,17] and sulfur [18,19] basic centers attached to the pendant organic chains have the ability to extract heavy cations from aqueous solutions at the solid/liquid interface. Such layered or lamellar clay minerals can be synthesized by intercalation of various organic species into the interlamellar galleries of naturally occurring lamellar compounds or by post-synthesis treatment in the presence of an organoalkoxysilane [19,20]. On the other hand, inorganic–organic hybrid phyllosilicates have been synthesized through the sol–gel process using copolymerization of trialkoxysilanes in the presence of metallic ions with some advantages over the natural ones, as the resulting compounds have high degrees of purity and can be also chemically modified in subsequent stages [21,22].

The aim of the present investigation is focused on the synthesis of lamellar organoclay, a talc-like magnesium phyllosilicate structure. The lamellar hybrid is a member of a known family of 2:1 trioctahedral phyllosilicates formed by an octahedral sheet occupied by a hexacoordinated magnesium atoms sandwiched between two tetrahedral silicate layers [23], containing pendant organic moiety chains covalently bonded to the inorganic matrix, with attached available basic centers coordinate cations, which interactive process at the solid/liquid interface has been thermodynamically determined.

2. Materials and methods

2.1. Reagents

All chemicals, magnesium nitrate hexahydrate (Carlo Erba), methanol (Synth), sodium hydroxide (Merck), 3-(triethoxysilyl)propylisocyanate (Aldrich), 1,2-ethanedithiol (Aldrich), and nitrates of lead, copper and cadmium (Vetec) were reagent grade and used as received. The metallic solutions were prepared in doubly distilled water, purified with a Millipore Milli-Q to $18.2 \text{ M}\Omega \text{ cm}^{-1}$.

2.2. Synthesis of a new thiocarbamate organosilane

A new thiocarbamate organosilane was synthesized by a solvent free and catalyst free reaction of 3-(triethoxysilyl)propylisocyanate and 1,2-ethanedithiol. In a typical synthesis, 37.0 mmol (3.10 cm^3) of 1,2-ethanedithiol was added dropwise to 37.0 mmol (9.16 cm^3) of 3-(triethoxysilyl)propylisocyanate, under a nitrogen atmosphere, with continuous stirring for 30 min at 318 K. The reaction contents were then allowed to cool at room temperature, producing a new organosilane with thiocarbamate functional group.

2.3. Sol–gel synthesis of layered organoclay

The talc-like hybrid organoclay was obtained by mixing the newly synthesized silylating agent with a methanolic solution of magnesium nitrate, keeping the Si/Mg molar ratio equal to 1.33. For this reaction, 7.0 g (27.0 mmol) of magnesium nitrate hexahydrate was dissolved in 75 cm^3 of methanol in a polyethylene flask. The methanolic solution of the newly synthesized silylating agent was added dropwise at room temperature under vigorous magnetic stirring. The white suspension was precipitated by slow addition of 0.50 mol dm^{-3} sodium hydroxide, until the pH reached 11.5 [24]. The white precipitate was aged without stirring for 24 h at 323 K, filtered,

followed by twice washing the solid with 200 cm^3 of doubly distilled water and the solid was dried under vacuum for 24 h at 323 K.

2.4. Sorption and thermodynamics

The presence of nitrogen, oxygen and sulfur basic centers attached to the pendant organic chains of the synthesized clay have the potential to remove heavy metal ions from aqueous solution. The cation removal capacity of the hybrid clay was determined through the batchwise method. Thus, 20 mg of clay sample was suspended in 25.0 cm^3 of corresponding cationic solution, varying from 7.0×10^{-4} to $8.0 \times 10^{-3} \text{ mol dm}^{-3}$ in concentrations in a series of flasks, at $298 \pm 1 \text{ K}$. The time to reach equilibrium was previously established as 4 h for all experiments, then 6 h was chosen to ensure maximum sorption [25,26]. After reaching equilibrium, the solid was filtered and the amount of metal remaining was quantified in the supernatant using inductively coupled plasma optical emission spectroscopy (ICP OES). For each experimental point, the repeatability was checked by at least one duplicate run.

The thermal effect evolved from the interaction of cations/basic centers at the solid/liquid interface was determined by a calorimetric titration technique performed using a LKB 2277 microcalorimeter [27]. For the calorimetric titration, a known amount, near to 20 mg, of organoclay, suspended in 2.0 cm^3 of water inside the calorimetric vessel was vigorously stirred at $298.15 \pm 0.20 \text{ K}$. A microsyringe with a corresponding cation solution of known concentration (0.10 mol dm^{-3}) was coupled to the calorimetric vessel. The addition of cation solution to the calorimetric vessel was performed by injection of a series of fixed volumes of 10 mm^3 in a programmed procedure at intervals of 2 h, using an auxiliary pumping system. From this process, the decrease in thermal effects with successive increments of titrand was obtained as the reaction reached the plateau to define the isotherms. To complete the titration the titrand solution was diluted in water and also the organoclay was dispersed in the same solvent.

2.5. Characterizations

The amount of organic chains attached to the inorganic network inside the layered spaces of the hybrid clay was calculated on the basis of carbon, hydrogen, nitrogen and sulfur percentages, determined through elemental analysis on a Perkin-Elmer, model 2400 elemental analyzer.

The infrared spectra of the samples were measured on a MB-series model Bomem FTIR spectrophotometer, using pressed KBr pellets with a pressure of 5 ton cm^{-2} , with 32 scans in the $4000\text{--}400 \text{ cm}^{-1}$ range and resolution of 4 cm^{-1} .

^{29}Si NMR spectra in the solid state were performed on an INOVA 500 spectrometer at room temperature. The spectra were obtained with a pulse repetition time of 3 s and contact time of 1 min with 59.61 MHz frequencies. ^{13}C NMR spectra in solid state were performed on a Bruker AC 300/P spectrometer at room temperature. The measurements were taken at 75.47 MHz frequencies with a magic spinning of 4 kHz. The pulse repetition time was 3 s and the contact time was 3 ms. In order to increase the signal to noise ratio of the solid state spectra, the cross polarization and magic angle spinning (CP/MAS) technique was used for both nuclei.

The X-ray powder diffraction patterns (XRD) of the synthesized organoclay were collected on a Shimadzu model XD3A diffractometer (40 kV, 30 mA), in the range of $2\theta = 1.5\text{--}70.0^\circ$ using nickel-filtered $\text{Cu-K}\alpha$ radiation with a wavelength of 1.54 nm. From this data the interlayer spacing of the compound can be calculated.

The thermogravimetric curve was obtained with a TA instrument, coupled to a model 1090 B thermobalance, using a heating

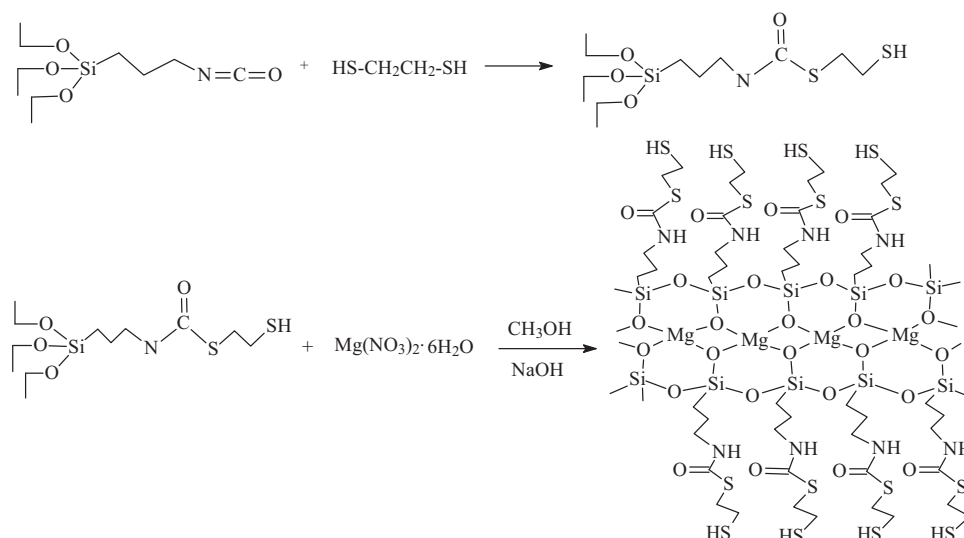


Fig. 1. Synthetic sol-gel procedure of newly synthesized silylating agent 2-mercaptoethyl 3-(triethoxysilyl)propylcarbamothioate from 3-(triethoxysilyl)propylisocyanate and 1,2-ethanedithiol to obtain the talc-like organoclay.

rate of 0.167 K s^{-1} under an argon flow $30 \text{ cm}^3 \text{ s}^{-1}$, from 298 to 1250 K.

The scanning electron microscopy (SEM) measurements were obtained with a JEOL JSM 6360-LV scanning electron microscope, operating at 20 kV. The samples were grounded and fixed onto a double-faced carbon tape adhered to a gold support and carbon-coated in a Bal-Tec MD20 instrument.

A Perkin-Elmer model 3000 DV inductively coupled plasma optical emission spectrometer was used to determine the amount of divalent lead, copper and cobalt cations remaining in solution after sorption processes.

The thermal effects at the solid-liquid interface were obtained with an isothermal calorimeter, Thermometric LKB 2277. The injections of titrand were performed using a syringe pump of 0.50 cm^3 connected to 18 k gold cannula.

3. Results and discussion

A schematic representation of the sol-gel process employed to synthesize the layered inorganic-organic hybrid clay in two

well-established steps is shown in Fig. 1. The newly synthesized silylating agent reacted with magnesium nitrate that results in rapid formation of lamellar inorganic-organic hybrid clay. From the structural point of view, an inorganic network having organic chains, originating from silylating agents attached to the inorganic layer forms the inorganic-organic hybrid clay. The net inorganic structure of this synthetic hybrid is similar to that found in natural talc, where the inorganic network is composed of tetrahedral-octahedral-tetrahedral layers. From this self-arrangement, the octahedral layers contain a magnesium atom coordinated to four oxygen atoms in the same plane and its octahedral coordination is completed by two other oxygen atoms located out of the horizontal plane. The tetrahedral layer is composed of silicon atoms located in the center of tetrahedron, in which two basal corners of the tetrahedron are occupied by oxygen atoms, the third position has carbon atom attached from the silylating agent and the apical oxygen is bonded to the magnesium atom [28].

The degree of the functionalization of organic moiety bonded to the inorganic tetrahedral layer of the hybrid material can be calculated on the basis of elemental analysis data. These values

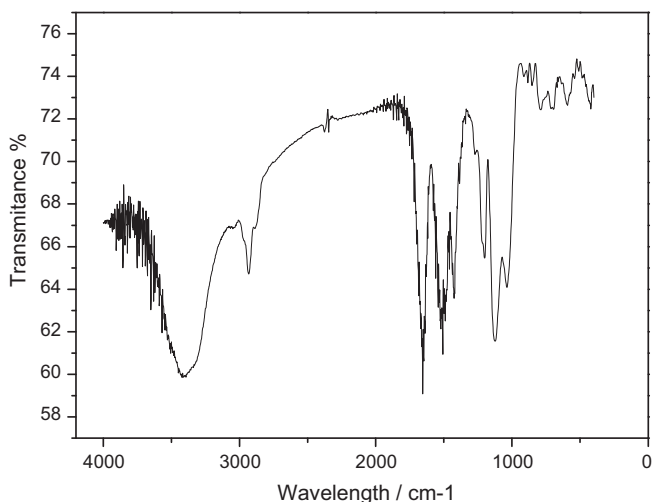


Fig. 2. The infrared spectrum of the hybrid clay.

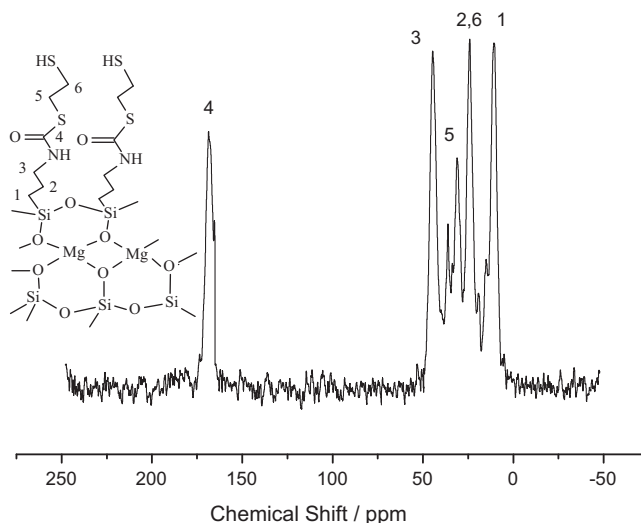


Fig. 3. ¹³C NMR spectrum in the solid state of the synthesized organoclay.

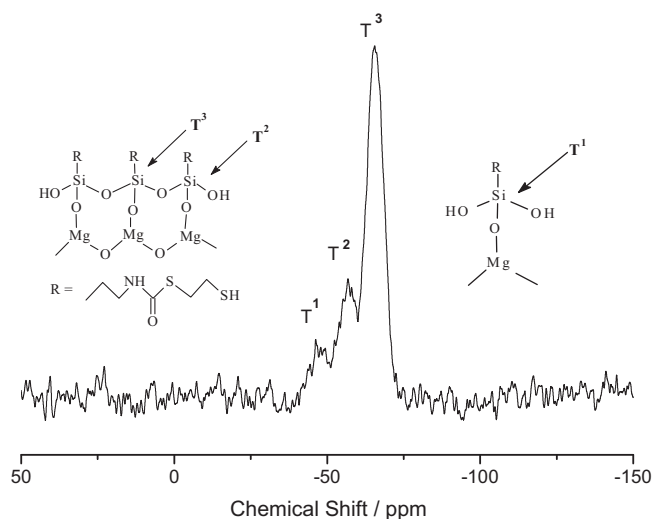


Fig. 4. ^{29}Si NMR spectrum in the solid state of the synthesized organoclay.

for the synthesized organoclay were found to be 13.62, 2.56, 2.69 and 12.40% for carbon, hydrogen, nitrogen and sulfur, respectively. The quantity of organic moiety attached to the lamellar spaces of the synthesized clay ($L_0 = 3.87 \text{ mmol g}^{-1}$) was calculated from the percentage of sulfur, whose value is not affected by the presence of possible humidity or due to possible unhydrolyzed ethoxide groups, using the following expression [29]:

$$L_0 = \frac{\%S \times 10}{\text{sulfur atom mass}} \quad (1)$$

3.1. Infrared spectroscopy

The characteristic absorptions originating from pendant organic chains inside the lamellar cavity and the inorganic framework were obtained in the FTIR spectrum, as shown in Fig. 2. The organic moiety covalently bonded to the interlayer space was confirmed by the appearance of vibration bands assigned to symmetrical and asymmetrical C–H stretching bands at $2920 (\nu_s\text{-CH}_2)$ and $2860 \text{ cm}^{-1} (\nu_a\text{-CH}_2)$, respectively. Other important characteristic bands corresponding to N–H stretching and bending vibrations were located at 3275 and 1420 cm^{-1} , respectively. The hybrid material showed an intense and sharp band at 1675 cm^{-1} that was assigned to $\nu(\text{C=O})$ stretching related to thiocarbamate, indicating that the organic group was covalently attached to the structural layered material. The Si–C stretching band was observed at 1200 cm^{-1} and the bands at 1026 and 1121 cm^{-1} were attributed to Si–O–Si stretching vibrations. The presence of these bands indicates the formation of a

tetrahedral layer in the organophyllosilicate. The vibration band at 544 cm^{-1} was attributed to the presence of the Mg–O bond of the organoclay octahedral layer [30].

3.2. Solid state NMR spectroscopy

Solid state ^{13}C NMR/MAS spectrum for the synthesized organoclay showed signals in good agreement with the proposed structure, containing the newly organosilane covalently bonded to the inorganic structure. All peaks are assigned as numbered in the formula inserted in the left hand side of Fig. 3 that shows well-formed signals at 11.2, 24.8, and 44.3 ppm, attributed to the C1, C2/C6 and C3 carbons of the organic moiety, respectively. Another peak at 32.1 ppm was assigned to C5 methylene carbon of the synthesized organoclay. An intense and sharp peak with a chemical shift value 167.6 ppm was assigned to carbonyl carbon C4 of the thiocarbamate moiety. This evidence strongly supports the presence of the organic chain bonded to the inorganic layered structure of the hybrid material.

^{29}Si NMR spectroscopy in the solid state provides valuable information related to different silicon species that constitute the structure formed, as well as the degree of condensation between the silicate sheets in the lamellar hybrid structure. The spectrum of the hybrid showed three distinct signals at -47 , -56 and -67 ppm that are attributed to the organic silicon species T^1 , T^2 and T^3 , respectively, as shown in Fig. 4. These T^n species are derived from the trifunctional alkoxy silane used for the synthesis of magnesium organosilicates, where $\text{T}^n = \text{RSi}(\text{OM})(\text{OSi})_{n-1}(\text{OH})$ species. The superscripts number on T^n are associated with the number of siloxane bonds ((Si–O)), while R represents the organic moiety bonded to the silicon atom through silicon–carbon bond and M is related to the octahedral coordinated magnesium ion. The peak assignments are supported by previous results for analogous systems, involving modified silica and phyllosilicates [17]. By comparing the intensities of the peaks, it is clear that T^3 peak is higher than those of the other species. Thus, the highest intensity suggested that this species caused this degree of condensation, with lower number of defects in the hybrid structure [23].

3.3. Scanning electron microscopy and X-ray powder diffraction

The scanning electron microscopy (SEM) images of the organoclay were taken in order to investigate the morphology of the sample material, as shown the photomicrographs in Fig. 5, that indicate well-formed particles with irregular shapes and sizes. The particle size was in random form which can be related to the poorly crystalline structure of the hybrid due to the presence of the organic chain inside the lamellar structure. A decrease in crystallinity for

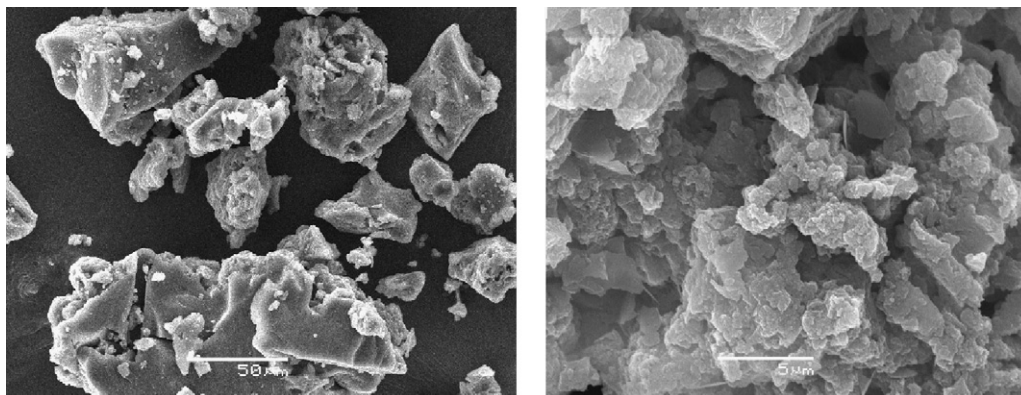


Fig. 5. Scanning electron microscope images of the synthesized organoclay material.

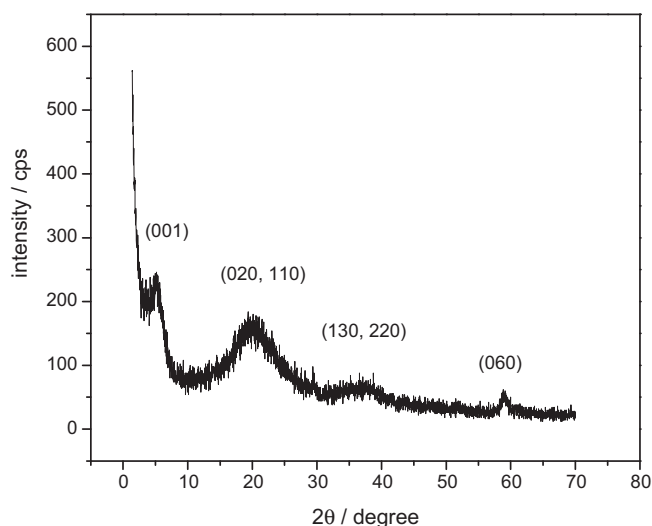


Fig. 6. X-ray diffraction patterns for the organoclay.

this kind of phyllosilicate with similar hybrid structure has also been reported [31].

The lamellar characteristics and the basal spacing of the hybrid were also calculated through X-ray diffraction pattern data. Four main diffractions were observed for 2θ values at 5.31, 20.0, 35.0 and 59.0°, as shown in Fig. 6. According to the general diffraction patterns for this type of hybrid, these peaks correspond to (001), (020, 110), (130, 220) and (060) reflections, respectively. Based on the 001 reflection, the calculated basal distance value demonstrated an increase to 1.65 nm, which differs from the inorganic parent talc, as characterized as nearer to 1.0 nm [32]. The increase in the basal distance can be explained by the presence of the organic chain covalently bonded to the inorganic layer inside the interlayer space, supported by considering the length of the 2-mercaptoethyl-propylcarbamothioate chain, as calculated as 1.60 nm with ACD/ChemSketch 9.04 software. A peak of low intensity at $2\theta = 59^\circ$ corresponds to the reflection in the 060 plane and is in agreement with trioctahedral layer formation, which is the characteristic peak of naturally occurring talc phyllosilicate [28]. The broadness of all these peaks compared to those of the parent talc materials express the poorer organization of the synthesized structural hybrid. This fact can be attributed to the immobilization of the organic chain inside the interlayer space, leading to a disordered inorganic framework or a turbostratic arrangement of stacked crystalline plates or both [33].

3.4. Thermogravimetry

The thermal degradation of the organoclay is shown in the thermogravimetric curve and the steps of decomposition are demonstrated through the derivative curve from room temperature to 1200 K, as shown in Fig. 7. The thermogravimetric curve presented a continuous mass loss, without defining steps, indicating a total value of 62.2% mass loss with a large residue, nearly 35%, due to the inorganic hybrid composition, as expected. However, the derivative curve gave five main steps with maximum inflections at 335, 378, 484, 640, 687 and 762 K, respectively. The first two peaks should be associated with the release of remaining solvent and adsorbed water molecules from inside the lamellar spaces of the clay followed by three other peaks due to the decompositions of the bonded organic moiety. The last step is related to hydroxyl group condensations, corresponding to water molecule displacement, after silanol group condensation, to form siloxane groups in the inorganic structure [34].

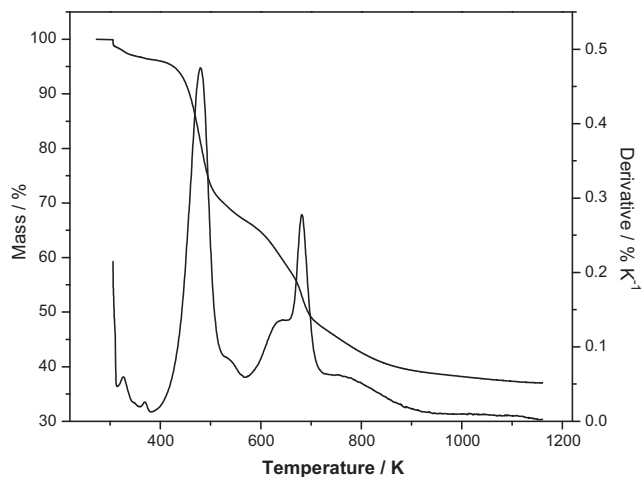


Fig. 7. Thermogravimetric and derivative curves for the hybrid clay.

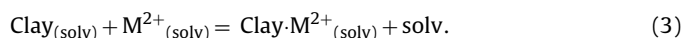
3.5. Sorption and calorimetric studies

The hybrid clay was employed to extract divalent lead, copper and cadmium cations from dilute aqueous solutions, in order to explore the Lewis basic properties of the sulfur, nitrogen and oxygen centers attached to the pendant organic chains. The sorption capacity (mmol g^{-1}) was calculated by the following expression:

$$Nf = \frac{ni - ns}{m} \quad (2)$$

where Nf is the number of moles sorbed by the hybrid material, ni and ns are the initial and supernatant number of moles after equilibrium and m is the mass of the hybrid material.

The sorption phenomenon is a competitive process between the solvent (solv) molecules bonded to the layers of the hybrid and the cationic solute (M^{2+}) dispersed in solution. The solvent molecules are gradually displaced by cations to reach equilibrium, as outlined schematically in the reaction:



When the sorption remains constant, a monolayer is supposed to form and the chemical interaction between the metallic ion and the organoclay can be followed by applying the Langmuir sorption isotherm, as shown in Fig. 8. The experimental data was adjusted to the following general modified Langmuir equation model:

$$\frac{Cs}{Nf} = \frac{Cs}{Ns} + \frac{1}{Nsb} \quad (4)$$

where Cs (mmoldm^{-3}) is the concentration of the cation in the supernatant solution at equilibrium, Nf is defined as before (mmol g^{-1}), Ns is the maximum amount of solute sorbed per gram of sorbent (mmol g^{-1}), which also depends upon the number of sorption sites, and b is a constant. All these sorption studies were based on the linearized form of the sorption isotherm derived from a Cs/Nf as a function of Cs plot, as represented in Fig. 9. Angular coefficient of the linearized data, gives the Ns value, which refers to the number of moles that is necessary to obtain cation monolayer formation on the hybrid surface, while the linear coefficient gives the value of constant b . Ns is a useful parameter for the thermodynamic approach that was developed by calorimetry [16].

The covalently attached organic pendant chains inside the layered spaces contain the basic centers that are available to form complexes with the chosen divalent cations and a summary of the results involving such sorptions is listed in Table 1. The maximum sorption capacity showed a sequence that is in good agreement with the experimental number of moles sorbed. Thus, lead cation

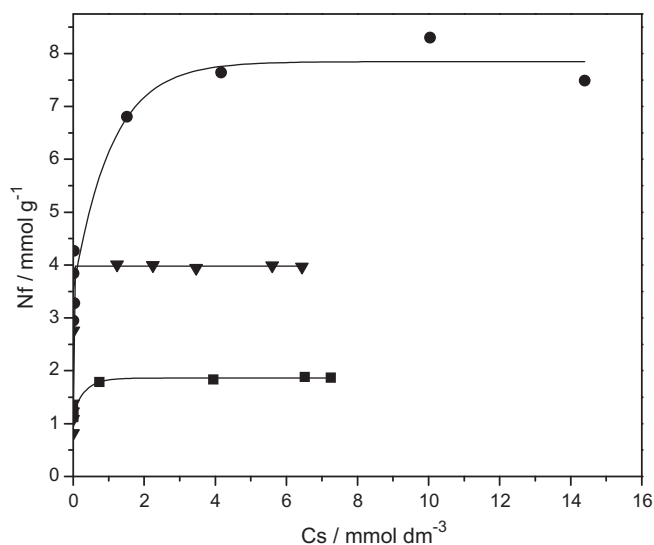


Fig. 8. Langmuir sorption isotherms of Pb^{2+} (●), Cu^{2+} (▼) and Cd^{2+} (■) on the organoclay at 298 ± 1 K.

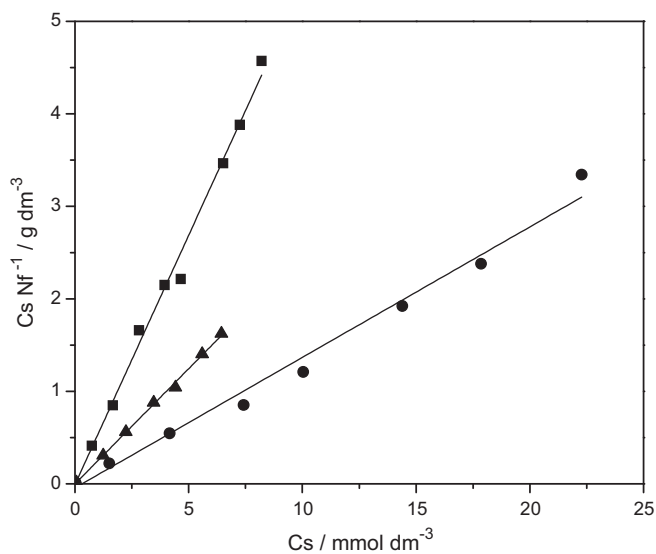


Fig. 9. Linearized Langmuir sorption isotherms of Pb^{2+} (●) Cu^{2+} (▲) and Cd^{2+} (■) on the organoclay at 298 ± 1 K.

gave a large sorption capacity of 7.08 mmol g^{-1} , followed by copper and cadmium with 4.01 and 1.86 mmol g^{-1} , respectively, which sequence of sorption is given by the order $\text{Pb} > \text{Cu} > \text{Cd}$.

The thermodynamics of cation–basic center interactions at the solid/liquid interface were performed by calorimetric titration of organoclay with the three divalent cations. The thermal effects obtained from such interactions were determined in separate calorimetric experiments. The values from the complete thermodynamic cycle for this series of interactions involve the organoclay suspended (sp) in aqueous (aq) solution that interacts with each

Table 1

Number of moles sorbed (N_f), maximum sorption capacity (N_s), constant (b) and correlation coefficient (r) for the interaction of divalent cations (M^{2+}) with the organoclay at 298 ± 1 K.

M^{2+}	N_f (mmol g^{-1})	N_s (mmol g^{-1})	b	r
Cu	3.97	4.01	316.35	0.9988
Pb	7.74	7.08	3.25	0.9948
Cd	1.85	1.86	73.13	0.9978

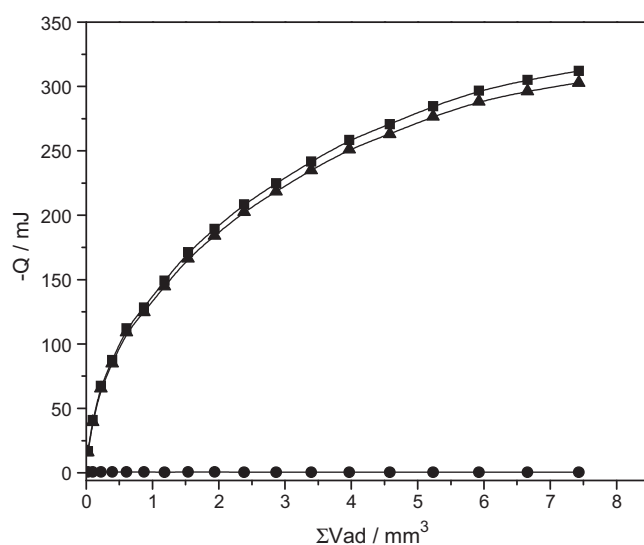
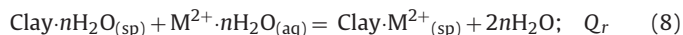
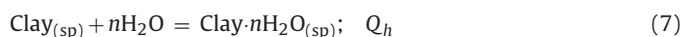
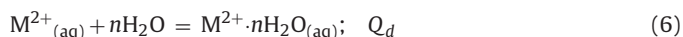
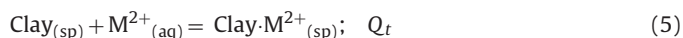


Fig. 10. Calorimetric titration of 19.20 mg of organoclay sample suspended in 2.0 cm^3 of water with 0.10 mol dm^{-3} cadmium nitrate solution at 298.15 ± 0.20 K. The set of data refer to the sum of the thermal effects of direct titration Q_t (■), dilution Q_d (●) and the resultant effect Q_r (▲) versus the total injected volume of titrant solution ΣV_{ad} .

divalent cation (M^{2+}), which is represented by the sequence of reactions:



During each calorimetric titration the experiment was carried out in duplicate run and the thermal effect of titration (Q_t), dilution (Q_d) and hydration (Q_h) for each point was also determined and the resulting net thermal effect (Q_r) of sorption was obtained from the following expression:

$$Q_r = Q_t - Q_h - Q_d \quad (9)$$

As the experimental thermal effect of hydration of the as-synthesized clay was null, to give $Q_h = 0$, the preceding equation is reduced to

$$Q_r = Q_t - Q_d \quad (10)$$

An example of calorimetric titration curves for cadmium cations is shown in Fig. 10. The resulting net thermal effect values for cation/basic center interaction were adjusted to a modified Langmuir equation, given by Eq. (11).

$$\frac{\Sigma X}{\Sigma \Delta_r H} = \frac{1}{(K-1)\Delta_{mono}H} + \frac{\Sigma X}{\Delta_{mono}H} \quad (11)$$

where ΣX is the sum of the mole fractions of the cation solution after sorption and X is the mole fraction obtained for each point of titrant addition. $\Delta_r H$ is the integral enthalpy of sorption for each point of the calorimetric titration, obtained by dividing the net thermal effect resulting from sorption by the number of moles of sorbate, K is the proportionality constant that also includes the equilibrium constant. $\Delta_{mono}H$ is the thermal effect of formation of a monolayer on the surface. An example of a plot of $\Sigma X/\Delta_r H$ versus ΣX for cadmium cation is shown in Fig. 11 and gives $\Delta_{mono}H$ values and K , obtained from the angular and linear coefficients of the

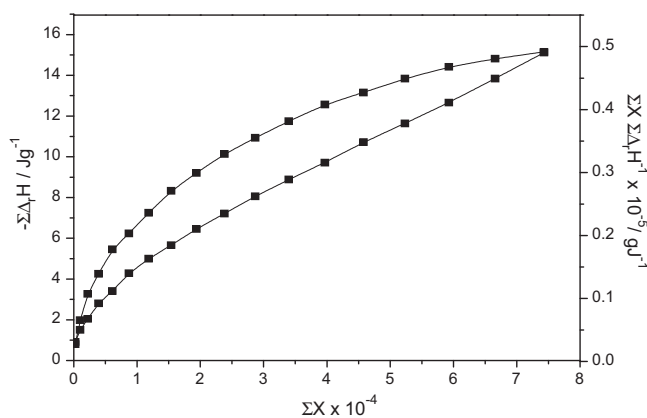


Fig. 11. Langmuir sorption isotherm and its linearized form obtained from integral enthalpy of sorption $\Sigma\Delta_r H$ versus molar fraction ΣX obtained from the calorimetric titration of 19.20 mg of organoclay suspended in 2.0 cm³ of water with 0.10 mol dm⁻³ cadmium solution.

linearization of the calorimetric isotherm. The enthalpy of sorption ΔH was calculated using the expression:

$$\Delta H = \frac{\Delta_{mono}H}{N_s} \quad (12)$$

From K values, the Gibbs energy is obtained from expression (13) and the entropy by Eq. (14).

$$\Delta G = -RT \ln K \quad (13)$$

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

The set of thermodynamic data obtained for this system is listed in Table 2. The exothermic molar enthalpic values in the sequence -8.50 ± 0.01 , -4.01 ± 0.02 and -2.90 ± 0.01 kJ mol⁻¹ for cadmium, copper and lead, respectively, follow the same order as the hydrated volumes for these cations, which are 173.2, 147.8 and 143.4 cm³ mol⁻¹, respectively [35].

From the equilibrium constant based on expression (12), the calculated Gibbs energy gave negative values for all cases, which clearly shows that the processes of cation–basic center interactions at the solid/liquid interface were spontaneous in nature. For this process there is a favorable contribution from the exothermic enthalpic values. On the other hand, the entropic values are also favorable with positive values, which are related to the displacement of the solvent molecules initially bonded to the cation coordination sphere or to the displacement of water molecules which were hydrogen bonded to the nitrogen, sulfur and oxygen basic centers of the pendant organic moiety inside the lamellar spaces. Consequently, the sorbed water molecules displaced to the reaction medium contribute to the disorder of the system, causing an increase in entropy. Similar behavior has also been observed for interactive effects involving similar heterogeneous systems [36]. The series of the thermodynamic values obtained represented by exothermic enthalpy, negative Gibbs energy and positive entropy showed that the cation–basic center interaction at the solid/liquid interface is a favorable process for all three determinations.

Table 2

Thermodynamic data for the sorption of divalent cations (M²⁺) on the organoclay at the solid/liquid interface at 298.15 ± 0.20 K.

M ²⁺	$-\Delta_{mono}H$ (Jg ⁻¹)	$-\Delta H$ (kJ mol ⁻¹)	ln K	$-\Delta G$ (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Cu	16.12	4.01 ± 0.02	8.58	21.2 ± 0.3	57 ± 2
Pb	20.57	2.90 ± 0.01	8.82	21.9 ± 0.1	63 ± 1
Cd	15.78	8.50 ± 0.01	8.96	22.2 ± 0.3	46 ± 2

4. Conclusions

A self-assembled lamellar organoclay with talc-like structure has been synthesized through hydrolysis and condensation reactions of a newly synthesized silylating agent and magnesium salt under ambient conditions. The organic chains inside the layers of the clay contain multiple chelating sites that were used for divalent lead, copper and cadmium removal from aqueous solutions. Based on the Langmuir model at ambient conditions, the hybrid showed higher lead cation sorption in comparison to copper and cadmium cations. Thermodynamic studies of divalent cation sorption based on calorimetric titration showed that the cation–basic center interactions at the solid/liquid interface were spontaneous and favorable, as reflected by negative Gibbs energies, negative enthalpies and positive entropies. The presence of soft and hard basic centers attached to pendant organic chains makes to this hybrid material a candidate material for a number of applications in metal coordination chemistry. This research can be extended to use such hybrid phyllosilicate for other toxic metals and as well as for possible dye removal from industrial effluents.

Acknowledgements

The authors are indebted to FAPESP for financial support and to TWAS/CNPq and CNPq for fellowships to S.B. and C.A.

References

- [1] I.L. Agadic, M.K. Mitchell, B.R. Payne, Highly effective adsorption of heavy metal ions by a thiol functionalized magnesium phyllosilicate clay, *Environ. Sci. Technol.* 35 (2001) 984–990.
- [2] D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Heavy metal adsorbents prepared from the modification of cellulose: a review, *Bioresour. Technol.* 99 (2008) 6709–6724.
- [3] S.J.S. Flora, M. Mittal, A. Mehta, Heavy metal induced oxidative stress & its possible reversal by chelation therapy, *Indian J. Med. Res.* 128 (2008) 501–523.
- [4] I.E. Agbozu, I.K.E. Ekweozor, K. Opuene, Survey of heavy metals in the catfish *Synodontis clarias*, *Int. J. Environ. Sci. Technol.* 4 (2007) 93–97.
- [5] S.A. Ray, M.K. Ray, Bioremediation of heavy metal toxicity with special reference to chromium, *Al Ameen J. Med. Sci.* 2 (2009) 57–63.
- [6] L.D. White, D.A.C. Slechta, M.E. Gilbert, E.T. Castiglioni, N.H. Zawia, M. Virgolini, A.R. George, S.M. Lasley, Y.C. Qian, M.R. Basha, New and evolving concepts in the neurotoxicology of lead, *Toxicol. Appl. Pharmacol.* 225 (2007) 1–27.
- [7] H. Needleman, Lead poisoning, *Annu. Rev. Med.* 55 (2004) 209–222.
- [8] A.S. Yousif, A.A. Ahmed, Effects of cadmium (Cd) and lead (Pb) on the structure and function of thyroid gland, *Afr. J. Environ. Sci. Technol.* 3 (2009) 078–085.
- [9] C. Namasivayam, D. Sangeetha, R. Gunasekaran, Removal of anions, heavy metals, organics and dyes from water by adsorption onto a new activated carbon from *Jatropha husk*, an agro-industrial solid waste, *Process Saf. Environ. Prot.* 85 (2007) 181–184.
- [10] E. Erdem, N. Karapinar, R. Donate, The removal of heavy metal cations by natural zeolites, *J. Colloid Interface Sci.* 280 (2004) 309–314.
- [11] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, *Miner. Eng.* 19 (2006) 463–470.
- [12] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1999) 2469–2479.
- [13] L. Mercier, C. Detellier, Preparation, characterization and applications as heavy metals sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite, *Environ. Sci. Technol.* 29 (1995) 1318–1323.
- [14] G. Sheng, S.A. Boyd, A dual function organoclay sorbent for lead and chlorobenzene, *Soil Sci. Soc. Am. J.* 63 (1999) 73–78.
- [15] L. Mercier, T.J. Pinnavaia, A functionalized porous clay heterostructure for heavy metal ion (Hg²⁺) trapping, *Microporous Mesoporous Mater.* 20 (1998) 101–106.
- [16] M.G. Fonseca, C.R. Silva, J.A.S. Barone, C. Airoidi, Layered hybrid nickel phyllosilicates and reactivity of the gallery space, *J. Mater. Chem.* 10 (2000) 789–795.
- [17] R.K. Dey, A.S. Oliveira, T. Patnaik, V.K. Singh, D. Tiwary, C. Airoidi, Grafting of organosilane derived from 3-glycidoxypropyltrimethoxysilane thiourea onto magnesium phyllosilicate by sol–gel process and investigation of metal adsorption properties, *J. Solid State Chem.* 182 (2009) 2010–2017.
- [18] M.G. Fonseca, C. Airoidi, Mercaptopropyl magnesium phyllosilicate—thermodynamic data on the interaction with divalent cations in aqueous solution, *Thermochim. Acta* 359 (2000) 1–9.
- [19] M.G. Fonseca, C. Airoidi, New layered inorganic–organic nanocomposites containing n-propylmercapto copper phyllosilicates, *J. Mater. Chem.* 10 (2000) 1457–1463.

- [20] T. Mizutani, Y. Fukushima, A. Okada, O. Kamigaito, Synthesis of nickel and magnesium phyllosilicates with 1:1 and 2:1 layer structures, *Bull. Chem. Soc. Jpn.* 63 (1990) 2094–2298.
- [21] K.A. Carrado, L. Xu, R. Csencsits, J.V. Muntean, Use of organo- and alkoxy-silanes in the synthesis of grafted and pristine clays, *Chem. Mater.* 13 (2001) 3766–3773.
- [22] J.A.A. Sales, G.C. Petrucelli, F.J.E. Oliveira, C. Airoidi, Some features associated with organosilane groups grafted by the sol–gel process onto synthetic talc-like phyllosilicate, *J. Colloid Interface Sci.* 297 (2006) 95–103.
- [23] A.S.O. Moscofian, C. Airoidi, Synthesized layered inorganic–organic magnesium organosilicate containing a disulfide moiety as a promising sorbent for cations removal, *J. Hazard. Mater.* 160 (2008) 63–69.
- [24] L. Ukrainczyk, R.A. Bellman, A.B. Anderson, Template synthesis and characterization of layered Al- and Mg-silsesquioxanes, *J. Phys. Chem. B* 107 (1997) 531–539.
- [25] M.A. Melo Jr., C. Airoidi, Energetic features of copper and lead sorption by innovative aminoalcohol-functionalized cobalt phyllosilicates, *Dalton Trans.* 39 (2010) 10217–10227.
- [26] F.J.V.E. Oliveira, E.C.S. da Filho, M.A. Melo Jr., C. Airoidi, Modified coupling agents based on thiourea, immobilized onto silica. Thermodynamics of copper adsorption, *Surf. Sci.* 603 (2009) 2200–2206.
- [27] C.B.A. Lima, C. Airoidi, Crystalline calcium phenylphosphonate–thermodynamic data on *n*-alkylmonoamine intercalations, *Thermochim. Acta* 400 (2003) 51–59.
- [28] S.L. Burkett, A. Press, S. Mann, Layered inorganic–organic nanocomposites based on 2:1 trioctahedral phyllosilicates, *Chem. Mater.* 9 (1997) 1071–1073.
- [29] D.P. Quintanilla, I. Del Hierro, M. Fajardo, I. Serra, 2-Mercaptothiazoline modified mesoporous silica for mercury removal from aqueous media, *J. Hazard. Mater.* 134 (2006) 245–256.
- [30] C.R. Silva, M.G. Fonseca, J.S. Barone, C. Airoidi, Layered inorganic–organic talc-like nanocomposites, *Chem. Mater.* 14 (2002) 3829–3836.
- [31] M.G. Fonseca, C.R. Silva, C. Airoidi, Aminated phyllosilicates synthesized via a sol–gel process, *Langmuir* 15 (1999) 5048–5055.
- [32] M. Jaber, J.M. Brandle, L. Delmotte, R.L. Dred, New range of Al–Mg organoclays with tailored hydrophobicity: incorporation of fluoride as a local probe to study the octahedral character, *Microporous Mesoporous Mater.* 65 (2003) 155–163.
- [33] M. Jaber, J.M. Brandle, L. Delmotte, R.L. Dred, Formation of organoclays by a one step synthesis, *Solid State Sci.* 7 (2005) 610–615.
- [34] M.A. Melo Jr., F.J.V.E. Oliveira, C. Airoidi, Novel talc-like nickel phyllosilicates functionalized with ethanolamine and diethanolamine, *Appl. Clay Sci.* 42 (2008) 130–136.
- [35] Y. Marcus, *Ion Solvation*, John Wiley, New York, 1985.
- [36] T.R. Macedo, G.C. Petrucelli, C. Airoidi, Sorption and thermodynamics of cation–basic center interactions of inorganic–organic hybrids synthesized from RUB-18, *Thermochim. Acta* 502 (2010) 30–34.