

REMOVAL OF Hg(II) FROM AN AQUEOUS MEDIUM BY ADSORPTION ONTO NATURAL AND ALKYL-AMINE MODIFIED BRAZILIAN BENTONITE

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Abstract—Mercury ion removal from waste-waters has been the subject of extensive research. The aim of the present investigation was to report the incorporation of the *n*-alkylamine molecules onto a bentonite surface and the capacities of these new chelating moieties on this modified bentonite surface for mercury removal from water. Bentonite collected from the Amazon region, Brazil, was used in an intercalation process with polar *n*-alkylamine molecules of general formula $H_3C(CH_2)_n-NH_2$ ($n = 1$ to 4) in 1,2-dichloroethane. The natural and modified bentonite samples were characterized by elemental analysis, X-ray diffraction, helium pycnometry, mercury porosimetry, and ²⁹Si, ²⁷Al, and ¹³C nuclear magnetic resonance spectroscopy. Because of the increasing size of the molecules attached to the pendant chains, the metal-adsorption capability of the final chelating materials was measured in each case. The adsorption of Hg(II) on natural and modified bentonites was determined under different conditions. The effects of concentration of Hg(II), contact time, and pH were investigated; batch and dynamic adsorption experiments of Hg(II) were conducted on bentonite samples under various conditions. The ability of these materials to remove Hg(II) from aqueous solution was assessed by means of a series of adsorption isotherms at room temperature and pH 4.0. In order to evaluate the bentonite samples as adsorbents in a dynamic system, a glass column was filled with clay samples (1.0 g each) and fed with 1.8×10^{-4} mol dm⁻³ Hg(II) at pH 4.0. The energetic effects caused by adsorption of metal cations were determined by means of calorimetric titrations. Thermodynamics indicated the existence of favorable conditions for such Hg(II)–nitrogen interactions.

Key Words—Adsorption, Bentonite, Calorimetry, Dynamic Adsorption Procedures, Mercury.

INTRODUCTION

Pollution by divalent mercury is of great concern due to the potentially toxic effects of elevated levels of this pollutant in biological systems. Industrial activities, such as foundry, oil refinery, solid-waste incineration, and mining (Malm, 1996; Filho and Maddock, 1997), are largely responsible for mercury pollution. Several investigations (Barbosa, 1997; Limaverde and Campos, 1999) have reported that ecosystems in some rivers of the Amazon region are contaminated with mercury from illegal mining. Pressure from environmental authorities has forced the establishment of discharge limits which in turn require effective use of decontamination, separation, and purification methods (Nriagu *et al.*, 1992).

In recent decades new adsorbent materials, with large adsorption capacities, have been sought for use in environmental applications. The process of inserting organic neutral polar molecules into the nanospace of sheets of insoluble layered nanocompounds leads to well organized inorganic/organic structural layer materials (Diaz *et al.*, 2007). Advances in the field of organo-modified clay minerals are closely associated with development of new silylating agents such as *n*-

alkylamine molecules, to which pendant organic chains can create non-hydrolyzable silicon–carbon bonds. These bonds prevent leaching of the immobilized reagent to solution (Dey and Airoidi, 2008). Covalent bonding of chelated metal ions to a solid surface modifies the adsorption properties of the solid support and is one of the most important steps in developing selective hybrid material (Prado and Airoidi, 2001; Prado *et al.*, 2002; Carreno *et al.*, 2011). Investigations of the intercalation of a variety of amines, such as secondary, tertiary, cyclic, or aromatic amines into lamellar compounds have been reported (*e.g.* Ruiz and Airoidi, 2004). These amines are of interest because of the need to clarify the chemistry of layered metal silicates but also because the process leads to the preparation and characterization of a new intercalated phase. The option to use this new phase is related to the thermal stability and resistance to oxidation of the hybrid material (Kim and Yi, 1999; Lee *et al.*, 2001; Zolfigol *et al.*, 2002; Shawabkeh, 2006; Diaz *et al.*, 2007; Jänchen *et al.*, 2009).

The present study was undertaken to investigate the feasibility of using unmodified and modified bentonite clays as adsorbents in the extraction of toxic heavy metals present in waters from a variety of sources and industrial effluents. For this purpose, adsorption isotherms of Hg(II) from aqueous media at room temperature were established, bearing in mind the influence of

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different parameters such as solution pH, metal concentration, and contact time. The bentonite clay sample from the Amazon region was modified chemically with *n*-alkylamine molecules of the general formula $H_3C(CH_2)_n-NH_2$ ($n = 1$ to 4) in 1,2-dichloroethane.

MATERIALS AND METHODS

Raw material and reagents

The clay sample used in this investigation was obtained from the Uruará area, State of Amazonas, northern Brazil. From a natural sample of bentonite, the $<2 \mu m$ fraction was separated by sedimentation. A proportion of the raw bentonite was suspended in doubly deionized water (DDW) in a 500 cm^3 beaker for 14 h. It was further purified using the method of Moore and Reynolds (1993). This involves the stirring of the mixture in a 30% hydrogen peroxide solution until all effervescence had ceased. The supernatant was decanted and the bentonite clay washed thoroughly with DDW to remove traces of hydrogen peroxide before use. The suspended bentonite was centrifuged (4000 rpm, for 60 min) and oven dried at 343 K to obtain the bentonite sample, referred to hereafter as BEN (Jesenák and Hlavatý, 2000). The natural clay sample was activated in a stream of dry nitrogen by heating at $423 \pm 1 \text{ K}$ for 10 h and used immediately.

Only reagent-grade solvents and chemicals were used, including methanol, ethanol, toluene, and amines (all from Aldrich GmbH, Germany) of general formula $H_3C(CH_2)_n-NH_2$ ($n = 1-4$), *i.e.* ethyl-, propyl-, butyl-, and pentylamines (also from Aldrich). A stock standard solution, 5000.0 mg L^{-1} of Hg(II), was prepared from primary standard $HgCl_2$. Doubly distilled deionized water was used in the preparation of all solutions. Solutions of lesser Hg concentration were prepared by dilution of aliquots from the stock solution.

Organofunctionalization of bentonite

Different experiments were performed using bridged *n*-alkylamine as an intercalating agent to synthesize inorganic-organic hybrid layered materials. In the organofunctionalized bentonite structure, the organic reactive sites present in the initial organosilane could be incorporated into the interlayer space of layered phyllosilicates, covalently bonded to the surfaces of smectite-type inorganic layers. The intercalation process was carried out by suspending $\sim 50 \text{ mg}$ of the natural bentonite sample in 6.0 cm^3 of 1.50 mol dm^{-3} ethanol solution of each amine at room temperature. The final products were named BEN_{Ethyl} , BEN_{Propyl} , BEN_{Butyl} , and BEN_{Pentyl} and were filtered, washed with toluene and ethanol in sequence, and dried under vacuum at $230 \pm 1 \text{ K}$ for 15 h.

Characterization methods

The natural bentonite sample was analyzed by inductively coupled plasma optical emission spectro-

metry (ICP-OES) using a Perkin Elmer 3000 DV instrument. The oven-dried powdered sample weighing 230.0 mg was placed on weighed glass dishes and transferred quantitatively ($\sim 20 \text{ mg}$) to pre-cleaned nitric-acid digestion bottles. The sample was then digested with 7.0 cm^3 of concentrated nitric and hydrochloric acids (ratio of 1:3 by volume), with an identical volume of hydrofluoric acid (1.0 mol dm^{-3} at room temperature) over 5 days. The bentonite samples were cooled in an ice bath and 25.0 cm^3 of 0.10 mol dm^{-3} of boric acid was added with stirring, followed by DDW to bring the final volume to 100.0 cm^3 . A blank and a set of elemental standards [SiO_2 , $((NH_4)_2SiF_6/H_2O/1000 \text{ ppm})$, Al_2O_3 ($Al/HCl/100 \text{ ppm}$), CaO ($CaCO_3/HNO_3/60 \text{ ppm}$), MgO ($Mg/HNO_3/50 \text{ ppm}$), K_2O ($KCl/HNO_3/50 \text{ ppm}$), Na_2O ($NaCl/HNO_3/50 \text{ ppm}$), and Fe_2O_3 ($Fe/HNO_3/100 \text{ ppm}$)] had been run to calibrate the instrument.

Powder X-ray diffraction (XRD) patterns were recorded with a Philips PW 1050 diffractometer using $CuK\alpha$ (0.154 nm) radiation in the region between 2 and $53^\circ 2\theta$ at a speed of 2° per min and in steps of $0.050^\circ 2\theta$.

Nuclear magnetic resonance (NMR) spectra of the samples were obtained using a Bruker AC 300/P spectrometer at room temperature. For each run, $\sim 1 \text{ g}$ of solid sample was packed into a 7 mm zirconium oxide rotor. The measurements were obtained at frequencies of 59.63, 75.47, and 78.20 MHz, for Si, C, and Al, respectively, with a magic angle spinning of 4 kHz.

The elemental analysis (C, H, and N) was determined using a Perkin Elmer 2400 Series II micro-elemental analyzer, and at least two independent determinations were performed for organofunctionalized clay samples.

The cation exchange capacities (CEC) of natural and organofunctionalized bentonite samples were measured by the ammonium acetate method with a concentration of 2.0 mol dm^{-3} at pH 8.0 (Chamuah and Dey, 1982).

The Brunauer-Emmett-Teller (BET) surface area, pore diameter, and pore volume were obtained from nitrogen adsorption/desorption in a Micromeritics (Norcross, Georgia USA) ASAP 2000 BET surface analyzer system.

The density of the clay samples was measured using a Micromeritics Accupyc 1330 helium gas pycnometer. The analyses were performed at $298 \pm 1 \text{ K}$ and $1 \times 10^{-3} \text{ psig min}^{-1}$.

The sample porosity was measured using a Micromeritics 9400 porosimeter (33,000 psi). A $50.000 \mu m$ Hg evacuation pressure was utilized for the low-pressure phase, with 60 min evacuation time and 30 s equilibrium time for both the low- and high-pressure phases (45,000 psi).

Batch-adsorption study

The adsorption experiments were performed by a batch method, *i.e.* by suspending 20 mg of solid sample in 20.0 cm^3 of an aqueous solution of the respective cations at concentrations varying from 0.125 to

3.50 mmol dm⁻³, under orbital stirring for 24 h at 298±1 K (Guerra *et al.*, 2010). The solid was separated by centrifugation and supernatant solutions were carefully transferred to glass flasks to determine the concentrations of cations present. The final concentrations of the Hg ions were determined using a Perkin Elmer (San Jose, California, USA) Atomic Absorption (AA) Spectrometer model Analyst 200 operating with an air-acetylene flame and a Hg lamp ($\lambda = 253.60$ nm).

Adsorption isotherms were plotted as moles adsorbed (N_t) vs. solution concentration (C_S). The isotherms conformed to the Sips (1948) model, in which the Langmuir (1918) and Freundlich (1906) equations are combined (equation 1).

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

where C_S is the equilibrium concentration of the solute in the bulk solution (mol dm⁻³), K_S is the Sips isotherm constant, n is the Sips exponent ($0 \leq n \leq 1$), and N_S is the maximum number of moles adsorbed per gram of the adsorbent (mmol g⁻¹). The equilibrium data follow the Freundlich isotherm at lower initial solute concentrations but follow the Langmuir isotherm at high solute concentrations. The Langmuir model arises when $n = 1.0$ and the Freundlich when $K_S = 0$, with the number n often being <1 . The Sips model was derived by assuming an heterogeneous surface.

The effect of pH on adsorption for all clay samples was evaluated by varying this parameter from 1.0 to 8.0 by adding 0.10 mol dm⁻³ nitric acid or sodium hydroxide as required. The pH of the solutions was measured using a pH/Ion model 450 M Analyzer-BR (SP, Brazil).

The kinetic-process studies were identical to batch-adsorption experiments, but the aqueous samples were taken at pre-specified time intervals. The concentrations of Hg(II) in solution were measured in the same way as for equilibrium adsorption. The N_t (mmol g⁻¹) was calculated using the following equation:

$$N_t = \frac{N_i - N_e}{m} \quad (2)$$

where N_t (mmol dm⁻³) is the concentration of Hg(II) solution at a given amount of time (min). The kinetic parameters were calculated using the Lagergren pseudo second-order model (Lagergren, 1898).

Column-adsorption study

A glass column 15.0 cm long and with 0.50 cm internal diameter, containing a porous sintered glass disk at the bottom and a Teflon stopcock was packed with 1.00 g of bentonite in natural form and modified for each experiment, which occupied 5.0 cm³ of this column. The column was then filled from the top with 1.8×10^{-4} mol dm⁻³ of the Hg(II) at pH 4.0 and 3.0 cm³ min⁻¹ feeding

flow rate. The column effluent flow-rate was adjusted to 3.5 cm³ min⁻¹ using the stopcock and the solution depth, or hydraulic head, at the top was kept constant by feeding the column at the same flow rate as the effluent using a peristaltic pump (Milan Model 601, PR, Brazil). The column effluents were collected in 50.0 cm³ intervals using a fraction collector and Hg(II) was determined as above using a Flame Atomic Absorption Spectrometry (Analyst 200, Perkin-Elmer).

In order to evaluate natural and organofunctionalized bentonite clay samples as possible adsorbents for wastewater treatment of Hg(II)-containing effluents, breakthrough curves for Hg(II) using BEN_{Propyl}, BEN_{Propyl}, BEN_{Butyl}, BEN_{Ethyl}, and BEN as adsorbents were obtained; the values were determined by analyses of the BP1 (lower breakpoint) and BP2 (higher breakpoint), both of which were obtained after passing an effluent volume of 1.80×10^{-4} mol dm⁻³ of Hg(II) through the column of adsorbent.

Due to the continuous adsorption, the flow of Hg(II) solution creates a wave front as it flows through the bed composed of natural and organofunctionalized bentonite. The wave front is known as the 'mass transfer zone' (MTZ). In order to determine the MTZ, the amount of Hg(II) input into the column and the total amount removed were calculated; they correspond to the adsorption capacity until the breakthrough point (q_U), which is BP2, and the saturation point (q_T), respectively. Equations 3 and 4 were obtained through mass balance in the column using its saturation data based on its breakthrough curves, where the area below the curve ($1 - C/C_0$) up to the breakthrough point is proportional to q_U , and up to the point of exhaustion of the bed is proportional to q_T (Ernest *et al.*, 1997; Bertagnolli *et al.*, 2011).

$$q_U = \frac{C_0 V}{1000m} \int_0^{t_b} (1 - C|_{z=L}/C_0) dt \quad (3)$$

$$q_T = \frac{C_0 V}{1000m} \int_0^{t_{tot}} (1 - C|_{z=L}/C_0) dt \quad (4)$$

where q_U is the amount of adsorbent metal per unit of adsorbent mass up to the breakthrough point (mg g⁻¹), C is metal concentration in a solution in the column outlet (mg L⁻¹), C_0 is the initial metal concentration in the liquid state (mg L⁻¹), m (g) is the bentonite mass, t_b is time until breakthrough point (min), t_{tot} is time for total removal (min) and limit of concentration in a solution in the column outlet ($z=L$).

The MTZ can be calculated based on the q_U/q_T ratio according to equation 5 and has a maximum value which corresponds to the bed height (H_L).

$$MTZ = H_L \left(1 - \frac{q_U}{q_T} \right) \quad (5)$$

Thermodynamics

The thermal effects of the adsorption reaction were measured by calorimetric titrations using an isothermal calorimeter, Model LKB 2277, from Thermometric. In this titration, the Hg solution is added to a suspension of ~20 mg of the bentonite sample in 2.0 cm³ of water, under stirring at room temperature. For each calorimetric titration ~20 mg of original and organofunctionalized bentonite was suspended in a steel ampoule. The steel ampoule was connected to a rod that was fixed in the gold agitator, which was stirred vigorously at room temperature. After equilibrium was established, as demonstrated by the base line, the cation solution was added incrementally, in a previously programmed procedure of metal addition in the calorimetric vessel, at intervals of 2 h, using a microsyringe attached to the calorimetric vessel. For each increment, the thermal effect of titration at 298.15 K (Q_t) was recorded and, after each sequence of experimental titration procedures for all hybrid materials, constant thermal effects were obtained as expected for the end of such an operation. The same procedure was employed to monitor the thermal effect of cation dilution (Q_d) in the calorimetric solvent. No effect of water on the organofunctionalized surface was noted. By combining these two output thermal effects, the net (ΣQ_r) value was determined using the expression in equation 6 (Ruiz and Airoidi, 2004):

$$\Sigma Q_r = \Sigma(Q_t) - \Sigma(Q_d) \quad (6)$$

In the present study, the adsorption and thermodynamic data were fitted using the non-linear fitting method in the *Microcal Origin* 6.0 software. The thermodynamic values obtained were adjusted by the Levenberg-Marquardt criteria and interactions calculated by the Simplex methods to the modified Langmuir model (equation 7), adjusted to describe several types of systems consisting of porous materials (Dey and Airoidi, 2008):

$$\frac{\Sigma X}{\Sigma \Delta_r H} = \frac{\Sigma X}{\Delta_{\text{mon}} H} = \frac{1}{\Delta_{\text{mon}} H (K_L - 1)} \quad (7)$$

where ΣX is the sum of the mole fraction of each Hg(II) cation in solution, after adsorption, obtained for each experimental point of titrand addition. $\Delta_r H$ is the integral enthalpy of adsorption for each point of the calorimetric titration obtained by dividing the thermal effect resulting from adsorption by the number of moles of adsorbate measured, K_L is the proportionality constant which also includes the equilibrium constant. $\Delta_{\text{mon}} H$ is the thermal effect of formation of a monolayer on the surface. A plot of $\Sigma X / \Sigma \Delta_r H$ vs. ΣX gave the values of $\Delta_{\text{mon}} H$ and K_L , respectively, obtained from non-linear fitting of the calorimetric isotherms. The enthalpy of adsorption, $\Delta_{\text{mon}} H$, was calculated using equation 8 (Dey and Airoidi, 2008).

$$\Delta_{\text{mon}} H = \frac{\Delta_{\text{mon}} h}{N_S} \quad (8)$$

From K_S values, the Gibbs free energies ($\Delta_{\text{mon}} G$) were calculated using equation 9 and the entropy value can be calculated using equation 10.

$$\Delta_{\text{mon}} G = \Delta_{\text{mon}} G^0 + RT \ln K_S \quad (9)$$

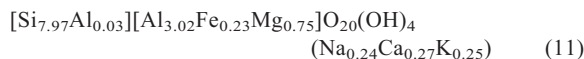
$$\Delta_{\text{mon}} G = \Delta_{\text{mon}} H - T \Delta_{\text{mon}} S \quad (10)$$

R is the universal gas constant.

RESULTS AND DISCUSSION

Characterization

The bulk geologic material used for investigation was a massive yellowish claystone consisting of 28.2% bentonite clay, 66.0% silt and 5.8% sand. Elemental analysis by ICP-OES of the original clay sample, BEN, gave results consistent with bentonite, with Si being the major component. The total mineralogical composition is 61.10, 18.40, 2.22, 2.18, 1.17, 0.84, and 0.72% of SiO₂, Al₂O₃, CaO, MgO, K₂O, Na₂O, and Fe₂O₃, respectively, and 13.37% of mass was lost in the ignition process, while the Mg, Ca, and K contents indicate variable amounts of cations which are suitable for the adsorption process. The composition of the original bentonite sample was calculated by chemical analysis, to give the unit-cell formula (equation 11):



The CEC of clay minerals is attributed to isomorphous substitution, broken bonds, and hydroxyl mobility in the clay structure (Jänchen *et al.*, 2009). The intercalation process increased substantially the total number of exchange sites in bentonite. The CEC value of 178.0 mmol/100 g of clay for the organofunctionalized bentonite (BEN_{pentyl}) is extremely large compared to natural bentonite at 88.7 mmol/100 g of clay. The significant increase in CEC obtained with the intercalation process can be attributed to unbalanced charges in the layer silicates and with altered coulombic forces (Table 1) (Xifang *et al.*, 2007; Kang *et al.*, 2009; Shu-li *et al.*, 2009).

The bulk density measurements obtained for natural and organofunctionalized bentonites revealed a significant decrease upon organic intercalation (Table 1), as expected, due to the lower density of *n*-alkylamine compared to silicate within the bentonite structure.

Density values obtained from pycnometry were used as the fluid (hexane) deployed in that technique can fill the empty spaces more easily and so may provide a more precise value for the solid matrix volume. This happens because of the aggregation state of gas and because of the small size of the molecules, resulting in greater permeability of the material. An increase in porosity

Table 1. Amounts of carbon (C), hydrogen (H), and nitrogen (N) found for bentonite intercalated with *n*-alkylamines, H₃C(CH₂)_{*n*}-NH₂ (*n* = 0–4); *d*₀₀₁ values; surface area (*S*_{BET}); real particle density (RD); C/N_T (degree of immobilization considering the elemental analysis data); C/N_T (degree of theoretical immobilization); porosity; and cation exchange capacity (CEC) of natural and modified bentonite and comparison of the properties of natural and modified bentonite with some other bentonite samples obtained from Chinese deposits.

Sample	C (mmol g ⁻¹)	H (mmol g ⁻¹)	N (mmol g ⁻¹)	C/N _C (calculated)	C/N _T (found)	<i>d</i> ₀₀₁ (nm)	<i>S</i> _{BET} (m ² g ⁻¹)	RD (g cm ⁻³)	Porosity (%)	CEC (mmol /100 g)	Reference
BEN _{Ethyl}	1.258	0.376	0.587	2.143	2	1.929	220.9	2.632	49.865	110.2	Current research
BEN _{Propyl}	2.547	0.408	0.753	3.382	3	2.265	354.8	2.685	57.056	134.8	Current research
BEN _{Butyl}	3.662	0.537	0.986	3.713	4	2.519	501.5	2.764	60.765	156.5	Current research
BEN _{Pentyl}	4.518	0.657	0.978	4.620	5	3.381	884.9	2.865	67.087	178.0	Current research
BEN	—	0.148	—	—	—	1.188	40.5	2.517	30.231	87.6	Current research
Bentonite(imp-B)	—	—	—	—	—	1.2267	31.5	—	—	88.7	Xifang <i>et al.</i> (2007)
Na-bentonite1	—	—	—	—	—	—	56.0	—	—	94.3	Shu-li <i>et al.</i> (2009)
Na-bentonite2	—	—	—	—	—	1.28	12.9	—	—	—	Kang <i>et al.</i> , (2009)

with intercalation of *n*-alkylamine in the structure of bentonite clay was verified, and was more pronounced in clays with smaller particle sizes.

The XRD patterns of natural and organofunctionalized bentonite (Figure 1a–e) exhibit 001 reflections corresponding, in the case of original bentonite, to a basal spacing of 1.188 nm, due to the presence of Na, Mg, and K cations and water molecules between the bentonite layers, the thickness of which is ~0.960 nm (Figure 1a), whereas, after the chemical modification process, the basal spacing increased to 3.381 nm because of the effective intercalation of the amine molecules in the interlayer space (Figure 1e). Given this information about the increased basal spacing, calculation of the volume occupied by the *n*-alkylamine in the layered structure of bentonite becomes possible and is based on the thickness of the bentonite layer (0.960 nm). That value is subtracted from the value of basal spacing of the organofunctionalized bentonite (3.381 nm) and so the space occupied by the bridged *n*-alkylamine was 2.521 nm, suggesting that the *n*-alkylamine molecules were intercalated successfully into the interlayer space of the natural bentonite structure. The great influence of the number of *n*-alkylamine ions on the surface and on the constitution and distribution of the ions was reported previously (Li *et al.*, 2007). The mass fraction of intercalated phyllosilicate can be estimated from the relative intensities of the XRD reflections originating from the ‘unchanged’ and the ‘expanded’ layers. In the intercalated sample, the degree of intercalation reaction was estimated to be ~91%, indicating that the *n*-alkylamine molecules were arranged in monolayers between the phyllosilicate layers.

Solid-state NMR spectroscopy can provide valuable information about the bonding of the pendant chains anchored on an inorganic backbone. For this purpose, Si and C nuclei were examined in order to better characterize the natural and organofunctionalized bentonite clays. The ²⁹Si NMR spectrum of the natural bentonite (Figure 2a) revealed resonances associated with two distinct structural Si environments, *Q*ⁿ = Si(OSi)_{*n*}(OH)_{4-*n*}, *n* = 3 and 4 (Albert and Bayer, 1991; Kosuge and Singh, 2001; Ruiz *et al.*, 2004), located at -93.0 and -108.0 ppm, respectively. The presence of Al in the bentonite structure observed in the elemental analysis was confirmed by the ²⁷Al NMR spectrum (Figure 2b), with a peak at 5.0 ppm (Al-O-OH). Because C was absent from the starting bentonite (Table 1), the observed peaks in the ¹³C NMR spectra of the organofunctionalized bentonite clay samples (Figure 2c–2f) were attributed to the attachment of *n*-alkylamine molecules to the lamellar structure. For example, the five peaks at 9.0, 19.0, 23.2, 27.1, and 37.2 ppm observed in the spectrum for BEN_{Pentyl} were attributed to the *n*-alkylamine C atoms numbered 1, 2, 3, 4, and 5, respectively (Hoorn *et al.*, 1997; Sales *et al.*, 2002).

In the newly formed organofunctionalized 2:1 phyllosilicate structures, the organic part was located within

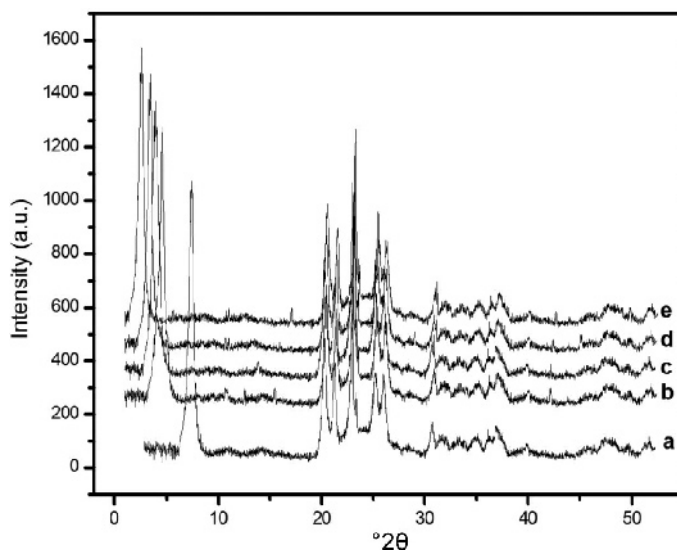


Figure 1. XRD patterns for unmodified and organofunctionalized bentonite samples: BEN (a), BEN_{Ethyl} (b), BEN_{Propyl} (c), BEN_{Butyl} (d), and BEN_{Pentyl} (e).

the interlayer space, as proven by the significant increases in d_{001} values for organofunctionalized bentonites (Figure 1b–e). The C, H, and N analyses (Table 1) revealed C/N ratios consistent with the organic molecules being intact in the dioctahedral 2:1 structure. The density of the intercalated $\text{H}_3\text{C}(\text{CH}_2)_4\text{-NH}_2$ in the bentonite was calculated to be $4.620 \text{ mmol g}^{-1}$ (BEN_{Pentyl}).

Effect of concentration on Hg(II) adsorption

The degree of immobilization on the surfaces of the organic molecules (Table 2), the maximum adsorption values (Table 3), the adsorption isotherms (Figure 3a), and the non-linear method applied for Sips equation were used to elucidate the maximum capacity of adsorption of the hybrid materials and the validity of the organofunctionalization process in clay minerals.

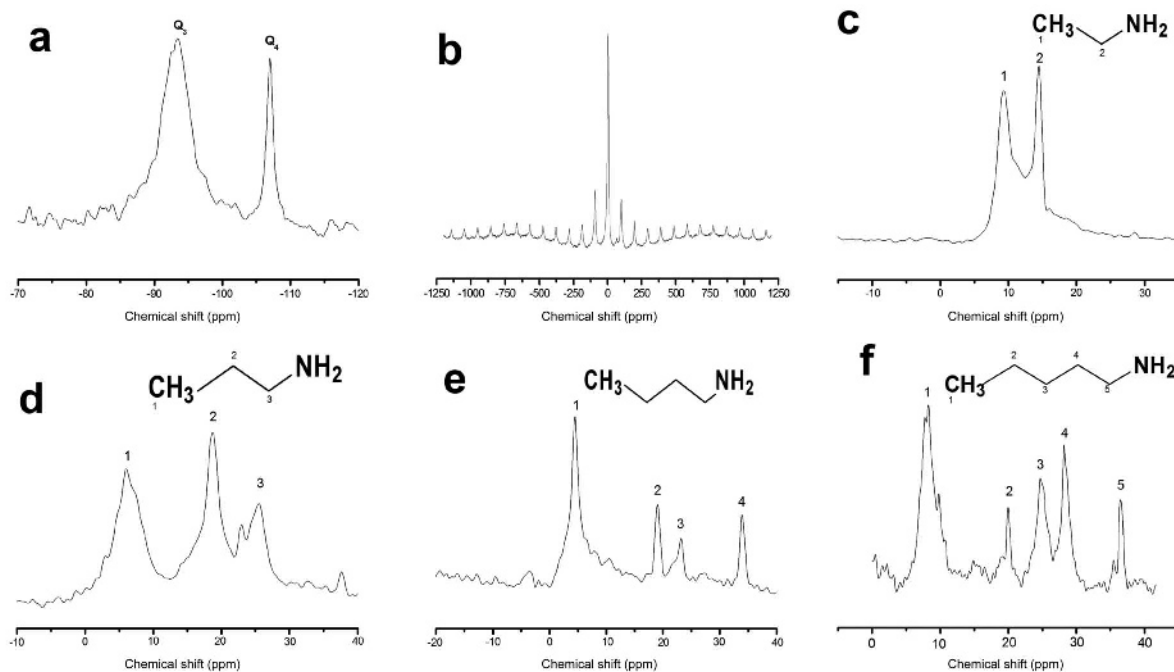


Figure 2. ^{29}Si MAS NMR spectrum of unmodified bentonite sample, BEN (a), ^{27}Al MAS NMR spectrum of unmodified bentonite sample, BEN (b), and ^{13}C MAS NMR spectra of organofunctionalized bentonite samples: BEN_{Ethyl} (c), BEN_{Propyl} (d), BEN_{Butyl} (e), and BEN_{Pentyl} (f).

Table 2. Comparison of the maximum adsorption capacity (N_f^{\max}) of Hg(II) on some natural and synthetic adsorbents from aqueous solution.

Adsorbent	Hg(II) (mg g ⁻¹)	Reference
Activated carbon from furfural	174.00	Yardim <i>et al.</i> (2003)
Macroalga <i>Cystoseira baccata</i>	329.00	Herrero <i>et al.</i> (2005)
Amazon soil	3.96	Miretzky <i>et al.</i> (2005)
SBA-15 functionalized with MTZ	220.65	Pérez-Quintanilla <i>et al.</i> (2006)
Camel bone charcoal	28.24	Hassan <i>et al.</i> (2008)
Dithiocarbamate-anchored polymer/organosmectite	157.30	Say <i>et al.</i> (2008)
Laterite (Guizhou province, China)	3.33	Xiaohong <i>et al.</i> (2008)
Amazon montmorillonite	246	Guerra <i>et al.</i> (2009)
Powdered activated carbon, PAC, derived from walnut shell	101.00	Zabihi <i>et al.</i> (2009)
Polyacrylamide aerogel	17.63	Ramadan <i>et al.</i> (2010)
Silica aerogel	11.60	Ramadan <i>et al.</i> (2010)
Polyacrylamide-silica aerogel	13.69	Ramadan <i>et al.</i> (2010)
BEN	60.03	Current research
BEN _{Ethyl}	97.20	Current research
BEN _{Propyl}	102.40	Current research
BEN _{Butyl}	107.59	Current research
BEN _{Pentyl}	109.14	Current research

The identity of the experimental isotherms was compared with the isotherm plotted using the Sips equation and the result was linear, thus indicating that the Sips model was mathematically correct. The experimental isotherms can saturate these basic reactive centers introduced into the natural bentonite structure. The same examples of different adsorbents focusing on the available mercury extraction data from aqueous solutions are listed for comparison with adsorbents used in this study (Table 2). Of the twelve different adsorbents investigated (Table 2), none had a greater adsorption capacity than the natural or modified materials for Hg(II) uptake, indicating that these bentonite samples in natural form and intercalated could be used in the removal of Hg(II) from aqueous solution. In addition, evaluation is complex because the efficiency depends on solution pH, temperature, adsorbent dose, initial Hg concentration, contact time, and other solution conditions. Therefore, comparison was made in terms of the most essential parameter, the maximum adsorption capacity (Stumm and Sulzberger, 1992; Leupin and Hug, 2005). The most important observation was that tested natural and organofunctionalized bentonite clays exhibit greater adsorption capacity than most of the powdered activated carbon (PAC) derived from walnut shell (Zabihi *et al.*, 2009) or dithiocarbamate-anchored polymer/organosmectite (Say *et al.*, 2008). According to the results, natural and modified Amazon bentonite clays may well be suitable for use in the treatment of contaminated drinking water where Hg(II) is at a low concentration, e.g. 2×10^{-4} mol dm⁻³.

The influence of the silylating agents [H₃C(CH₂)_{*n*}-NH₂ *n*=1-4] bonded covalently to the inorganic structure is clearly reflected in the increased adsorption capacity of the organofunctionalized bentonite samples due to

different basic centers (OH⁻ and NH₂) attached to the alkyl chains, as outlined by the saturation process, *i.e.* the metal filling the reactive centers on the surfaces of phyllosilicates (Salih *et al.*, 1998; Xiu-Wen *et al.*, 2007). The molecules of *n*-alkylamines anchored to the phyllosilicate basal layer surfaces containing basic nitrogen atoms on alkyl chains favor metal interaction, mainly with soft cations, due to the presence of the basic reactive centers, represented as good Lewis bases of amine centers (Inbaraj *et al.*, 2009). Based on the structural peculiarity, *i.e.* the presence of hydroxyl and amine groups on the natural or organofunctionalized bentonite clay surfaces, the adsorption can be related directly to the nitrogen atoms available; thus, metal ions can be anchored preferentially to these atoms. The ability of the organofunctionalized bentonite surfaces to adsorb cations from water is based on the free pair of electrons present on nitrogen atoms (Figure 3a).

The non-linear Sips model presents a significant advantage when used with experimental data, allowing the determination of the capacity of cations bonded to basic centers (N_f) and the evaluation of the constant related to the adsorption energy (K_S). The large CEC of the organofunctionalized bentonite sample was confirmed through the constant values of the adsorption process, K_S , N_S , and N_f , obtained using this model in the non-linear form, the results calculated by Sips equation gave the best approximation to the experimental data (Figure 3a).

Effect of contact time and kinetics of adsorption

Metal adsorption vs. contact time for a fixed amount of adsorbent (Figure 3b) revealed similar abrupt increases in the removal of Hg(II) for short times before reaching the adsorption equilibrium for the five systems studied. According to these data, equilibrium was

Table 3. Adsorption, thermodynamic, and kinetic data for Hg(II) adsorbed onto natural and modified bentonite samples (1.0 g dm⁻³ of clay, pH 4.0, time 40 min, and temperature of 298±1 K).

Sample	N_i^{max*} (mmol g ⁻¹)	N_i^{max**} (mmol g ⁻¹)	q_T (mg g ⁻¹)	q_U (mg g ⁻¹)	MTZ	N_c (mmol g ⁻¹)	N_{FEQ} (mmol g ⁻¹)	k_2 (mmol g ⁻¹ min ⁻¹)	$-\Delta_{mon}h$ (J g ⁻¹)	$-\Delta_{mon}H$ (kJ mol ⁻¹)	n	$K_S \times 10^{-3}$	$-\Delta_{mon}G$ (kJ mol ⁻¹)	$\Delta_{mon}S$ (J K ⁻¹ mol ⁻¹)
BEN	1.16±0.12	1.20±0.10	8.14	5.20	4.80	1.17±0.10	1.18±0.12	28.01±1	8.83±0.11	7.61±0.11	0.78	6.7±0.1	21.7±0.1	48±3
BEN _{Ethyl}	1.87±0.11	1.91±0.10	10.16	7.31	3.73	1.89±0.11	1.90±0.12	61.12±1	13.63±0.13	7.29 ±0.11	0.98	10.4±0.2	22.9±0.1	52±2
BEN _{Propyl}	1.97±0.12	1.98±0.13	11.11	8.23	3.44	1.99±0.12	2.00±0.12	70.11±1	14.28±0.12	7.25±0.12	0.98	11.3±0.2	23.1±0.1	53±3
BEN _{Butyl}	2.07±0.21	2.22±0.12	12.30	9.23	3.32	2.12±0.10	2.15±0.10	71.13±1	14.88±0.11	7.19±0.10	0.99	12.1±0.3	23.4±0.3	52±3
BEN _{Pentyl}	2.10±0.15	2.17±0.11	12.45	9.42	3.24	2.21±0.07	2.11±0.11	72.10±1	14.91±0.10	7.10±0.12	0.99	12.7±0.2	23.5±0.2	53±1

* Batch adsorption; ** Column adsorption

BP₁—lower breakpoint obtained after passing an effluent volume of 2.00×10^{-4} mol dm⁻³ of Hg²⁺ through the adsorbent column, the maximum amount of Hg²⁺ allowed is surpassed. BP₂—higher breakpoint obtained after passing an effluent volume of 2.00×10^{-4} mol dm⁻³ of Hg(II) through the adsorbent column after saturation of adsorption sites has occurred at pH 4.0 and 3.0 cm³ min⁻¹ feeding flow rate.

achieved at ~11, 15, 17, 20, and 26 min for BEN_{Pentyl}, BEN_{Butyl}, BEN_{Propyl}, BEN_{Ethyl}, and BEN, respectively. In comparison with other materials used for adsorption (Yardim *et al.*, 2003; Guerra *et al.*, 2009; Ramadan *et al.*, 2010), the equilibrium times obtained for bentonite/Hg(II) systems were short, suggesting an excellent affinity of the Hg(II) for these original and organofunctionalized phyllosilicates from aqueous solutions. In order to study the specific rate constant of Hg(II)-phyllosilicates systems, the Lagergren (1898) pseudo second-order rate equation (equation 12) was used, which generally works well with adsorption reactions controlled by chemical exchange.

$$N_t = \frac{(k_2 N_{FEQ}^2 t)}{(1 + N_{FEQ} k_2 t)} \quad (12)$$

where k_2 is the pseudo second-order rate constant (mmol g⁻¹min⁻¹), which is obtained from the non-linear method. Carrying out a set of experiments at room temperature and monitoring the amount adsorbed with time, the kinetics of the adsorption process can be established. The values of k_2 and N_{FEQ} for BEN, BEN_{Pentyl}, BEN_{Propyl}, BEN_{Butyl}, and BEN_{Ethyl} are presented (Table 3). The correlation coefficient of the pseudo second-order rate equation (R^2) for the non-linear regression is 0.998, suggesting that the kinetics of adsorption can be described very well by the pseudo second-order rate equation.

Effects of pH

A change in pH of the medium is one of the most important factors affecting the metal-recovery procedure, and is related to the formation of soluble metal complexes and subsequently to their stabilities in aqueous solutions. The surface charge of the adsorbent can be modified by changing the pH of the solution and the speciation of adsorbates in solution may change with pH. The Hg ions were examined within a pH range of 1.0–8.0. The influence of pH in the adsorption process of Hg(II) onto natural and organofunctionalized bentonite clays (Figure 3c) revealed maximum values of N_i^{max} at pH ≈ 4.0 for all systems. The adsorption of Hg on natural and organofunctionalized bentonite clay samples began at pH ≈ 1.0, then increased quickly with further increases in pH. Therefore, the efficiency of Hg with unmodified and organofunctionalized bentonites can be controlled by the initial pH of the solid/liquid reaction. The effects of initial pH on natural and organofunctionalized bentonite adsorption capacities was evaluated within the pH range from 1.0 to 4.0. The ability of BEN_{Pentyl}, BEN_{Butyl}, BEN_{Propyl}, and BEN_{Ethyl} surfaces to adsorb metallic cations from water is based on the lone pair of electrons present on nitrogen atoms, which are good Lewis base centers. The reason for a small adsorption capacity at high pH is the competition between the excess H⁺ ions in the medium and positively

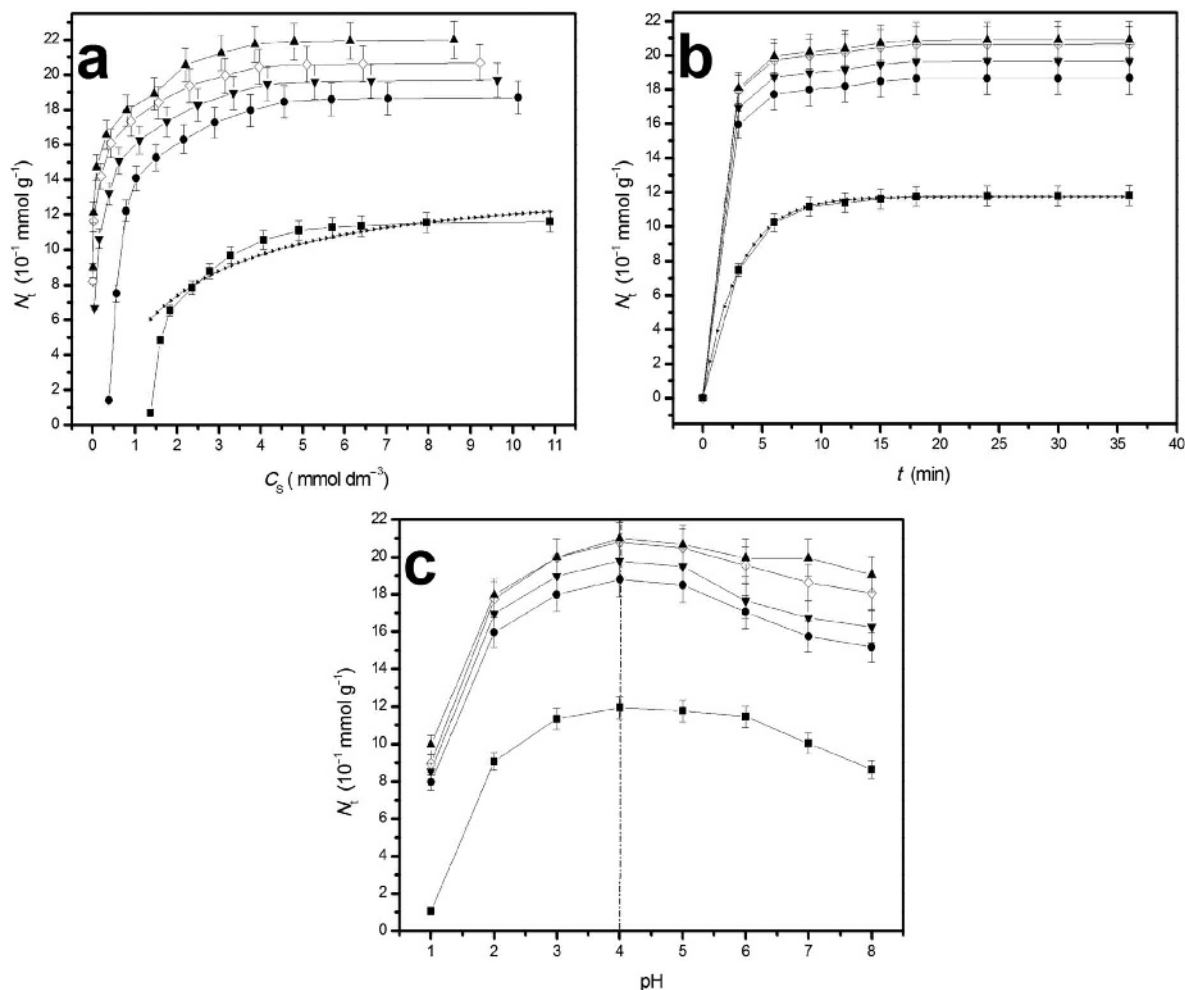


Figure 3. Effect of Hg(II) concentration, C_0 (a); contact time, t , (b); and pH (c) on Hg(II) adsorption onto unmodified and organofunctionalized bentonite clay samples from aqueous solution: BEN (■), BEN_{Ethyl} (●), BEN_{Propyl} (▼), BEN_{Butyl} (◇), and BEN_{Pentyl} (▲) (1.0 g dm^{-3} of clay and temperature controlled at $298 \pm 1 \text{ K}$). Isotherms calculated by the Levenberg-Marquardt method (▶).

charged cationic species present in solution. Also, greater acid concentrations suppress hydrolysis of the Hg ions (Brigatti *et al.*, 2005; Liu and Zhou, 2010).

Adsorption study in dynamic conditions

The layer structure of the intercalated bentonite is less stable than the natural bentonite as indicated by the formation of and fragmentation of clusters of particles during the adsorption experiment in column-flow conditions (N_f^{max} values, Figure 4). Smaller breakthrough points (BP₁) were determined when the Hg ion effluents from the column attained concentrations of $>0.010 \text{ mg dm}^{-3}$. The BP₁ value is related to the capacity of the adsorbents to retain the Hg(II) ion from aqueous media. The larger breakthrough points (BP₂) are related to the complete saturation of the bentonite samples with the Hg(II) ion.

Using an adsorption column packed with adsorbent reactive sites in which an inert carrier flows at a steady

rate (a dynamic system), the BP₁ value clearly indicated that the natural and organofunctionalized bentonite samples would be efficient adsorbents assisting in the decontamination of industrial effluents of toxic metal Hg(II). A single volume of the adsorbent is capable of removing completely at least 2.22 mmol g^{-1} of Hg(II) as observed for BEN_{Butyl}. The values for Hg(II) adsorption in a dynamic system were similar to values obtained in batch experiments (Table 3). Using a dynamic adsorption system, the maximum saturation of the natural and organofunctionalized bentonite samples by Hg(II) is very close to the values obtained in the batch-adsorption experiments for all systems.

Thermodynamics of adsorption

The applicability of organofunctionalized bentonites can be evaluated by determining physicochemical characteristics of the adsorbing system, including the number of molecules immobilized (Ruiz *et al.*, 2004).

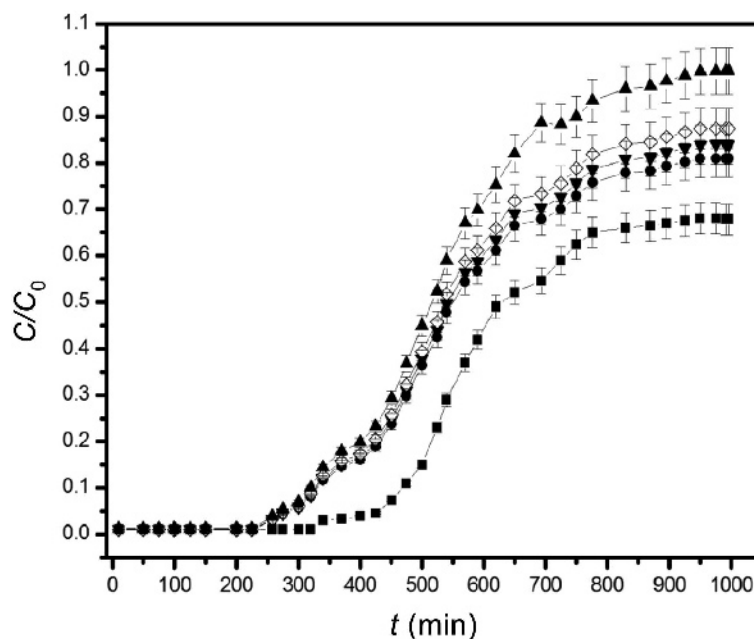


Figure 4. Breakthrough curves for 2.00×10^{-4} mol dm $^{-3}$ of Hg(II): BEN (■), BEN_{Ethyl} (●), BEN_{Propyl} (▼), BEN_{Butyl} (◇), and BEN_{Pentyl} (▲) (1.0 g dm $^{-3}$ of clay, pH 4.0, and temperature controlled at 298 ± 1 K).

Calorimetric titration of the organofunctionalized bentonites with a 0.050 mol dm $^{-3}$ solution of Hg(II) (Figure 5) revealed changes in the heat of adsorption of Hg(II) to the basic center on the modified surface of bentonite [Hg(II)-BEN_{Propyl}]. The spontaneous adsorption process was reflected in the thermodynamic data, enthalpy, entropy, and Gibbs free energy (Table 3). From a thermodynamic point of view, the exothermic and positive entropic adsorption values obtained showed a favorable set of results for the thermodynamics of mercury–nitrogen center interactions such as the thermodynamic values obtained with functionalized hybrid materials, BEN_{Pentyl} ($\Delta_{\text{mon}}H = 7.10 \pm 0.12$ kJ/mole, $\Delta_{\text{mon}}G = 23.5 \pm 0.2$ kJ/mole, and $\Delta_{\text{mon}}S = 53 \pm 1$ kJ/mole). The exothermic enthalpic adsorption values suggest a favorable neutralization between the acidic Hg atom and the hydroxyl groups on the natural bentonite structure and the basic nitrogen atom of the *n*-alkylmonoamine molecules on the lamellar structure of bentonite clay. The negative Gibbs free energy of adsorption demonstrates that a favorable reaction condition was established in the adsorption process. The positive entropic values are in accord with the displacement of water molecules, including those bonded to the mineral layers, which are reinforced by molecules that are hydrogen bonded to the active basic center, to favor the acid/base interaction at the liquid/solid interface (Lima and Airoidi, 2004).

The adsorption results and the thermodynamic data suggest that either the original or organofunctionalized bentonites investigated in this study could be used in the removal of toxic contaminant cations from water. The

potential for spontaneous reactivity of these systems, reflected in the negative Gibbs free energies and the positive entropic values, the success of *n*-alkylmonoamine molecules incorporated on grafted bentonite with high thermal stability, significant adsorption capacities, and favorable interaction data suggest that these surfaces can be applied to remove contaminant cations from aqueous medium.

SUMMARY

The development of economical and efficient new adsorbent materials for the removal of Hg(II) from groundwater is important in regions where human health is affected directly by elevated Hg(II) concentrations. Natural and modified bentonite clay samples were investigated as possible new adsorbents for the removal of Hg(II) from aqueous solutions. The bentonite intercalated with amines (*i.e.* with H₃C(CH₂)*n*-NH₂ (*n* = 1–4)) produced well defined lamellar hybrids classified as 2:1 type. The optimum pH for the adsorption of the Hg(II) ion ranged from 4.0 to 5.0 for all systems and the minimum contact time necessary for reaching equilibrium was ~11, 15, 17, 20, and 26 min for BEN_{Pentyl}, BEN_{Butyl}, BEN_{Propyl}, BEN_{Ethyl}, and BEN, respectively. Through calorimetric investigation, information about all systems was obtained, revealing exothermic enthalpy, negative Gibbs free energy, and positive entropy of adsorption. The thermodynamic data reflect the favorable cation/base center interaction at the solid/liquid interface. The results suggest the use of these materials for successful removal of heavy cations; aquatic

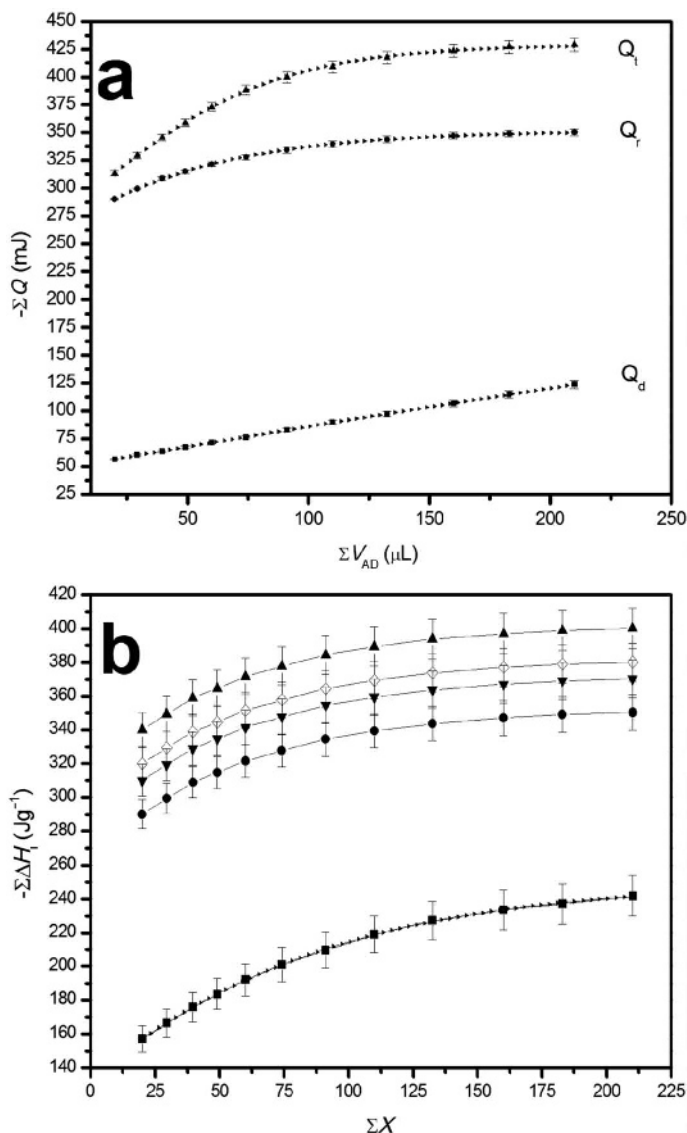


Figure 5. Thermal effect ($\Delta_{\text{mon}}H$, $\Delta_{\text{mon}}G$, and $\Delta_{\text{mon}}S$) of Hg(II) adsorption on organofunctionalized bentonite at 298 ± 1 K. The data points represent the thermal effect of Hg cation titration ΣQ_t (\blacktriangle), cation dilution ΣQ_d (\blacksquare), and the net thermal effect of interaction ΣQ_r (\bullet). ΣQ and V_{ad} values are the sum of the detected thermal effect and total injected volume of Hg(II) solution (a) and the net calorimetric data plotted in non-linear form by the Equation 7 for BEN (\blacksquare), BEN_{Ethyl} (\bullet), BEN_{Propyl} (\blacktriangledown), BEN_{Butyl} (\diamond), and BEN_{Pentyl} (\blacktriangle) (b).

ecosystems usually attain mercury levels of toxicological concern when affected directly by mercury-containing emissions from anthropogenic activities.

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