

Adsorption of phenol onto surfactants modified bentonite

M. C. Díaz-Nava · M. T. Olguín · M. Solache-Ríos

Received: 28 February 2011 / Accepted: 1 November 2011 / Published online: 24 November 2011
© Springer Science+Business Media B.V. 2011

Abstract Bentonite was modified with hexadecyltrimethylammonium bromide or benzylhexadecyldimethyl ammonium chloride. Phenol adsorption kinetic and isotherms experiments were performed; in both cases, phenol was determined in the aqueous solutions by UV–Vis spectroscopy. The results showed that the adsorption of phenol depends on the kind of surfactant, and pH of the solutions. The adsorption was higher for the clay modified with benzylcetyldimethylammonium chloride than hexadecyltrimethylammonium bromide.

Keywords Phenol · Surfactant · Clay · Bentonite · Adsorption

Introduction

Various toxic chemicals have been released into the environment as industrial wastes, causing serious water and soil pollution problems. Removal of organic contaminants from waste water has been extensively studied by using various physicochemical and biological techniques [1–3].

Water pollution by phenol and phenolic compounds is of great public concern. Among the several currently known physical chemical and biological methods which are in use

for wastewater treatment, adsorption still continues to be one of the most widely used processes [4–6].

Bentonites can adsorb cationic, anionic and neutral species [7–9]. The adsorption capacities due to the cationic and anionic exchange and the binding energy varied widely. Bentonite typically has low organic carbon content; then, neutral solute adsorption by partition into the bentonite organic matter is relatively weak in aqueous media [3, 10].

The clays have the capacity to expand and they can adsorb big molecules such as surfactants and phenol in the inter layers. The properties of modified bentonite may be altered significantly produced by the exchange of organic cations (typically having a quaternary ammonium and aliphatic structure) with inorganic ions (e.g., H^+ , Na^+ , Ca^{2+}) [11]. The organobentonites are organophilic, when the organic functional groups of quaternary ammonium cations are not strongly hydrated by water, as a result, organobentonites are powerful adsorbents for nonionic organics compounds [12]. Organobentonite could effectively remove organic pollutants from water, and it has been suggested that it may be use in wastewater treatments [3].

Alternative adsorbents have been considered for the sorption of phenol compounds. Examination of phenol adsorption onto the raw, HDTMA- and 2MNaOH-modified clinoptilolite showed that the HDTMA-modified zeolite is characterized by the best ability for phenol sorption from aqueous solution. Sorption efficiency of the 2MNaOH-treated clinoptilolite was about a half as high by magnitude as the HDTMA-modified zeolite. The best efficiency of phenol removal (>90%) was observed from solutions of low phenol concentrations (<5 mg/L) onto the HDTMA-modified zeolite. It was suggested that the film diffusion is the rate determining step of phenol sorption by the raw and the 2MNaOH-modified clinoptilolite, while the particle diffusion for the HDTMA-modified clinoptilolite [13].

M. C. Díaz-Nava
División de Estudios del Posgrado e Investigación,
Av. Tecnológico s/n, Ex Rancho La Virgen,
Instituto Tecnológico de Toluca, 52140 Metepec,
MEX, Mexico

M. T. Olguín (✉) · M. Solache-Ríos
Departamento de Química, Instituto Nacional de Investigaciones
Nucleares, A. P.18-1027, Col. Escandón, Delegación
Miguel Hidalgo, 11801 Mexico, DF, Mexico
e-mail: teresa.olguin@inin.gob.mx

Capacity of the natural zeolite (phillipsite) for sorption of phenol has been also investigated [14].

An organophilic pillared clays-based adsorbent was prepared by incorporating hexadecyltrimethylammonium (HDTMA) during the synthesis of conventional aluminum pillared clays. The presence of the HDTMA surfactant enhanced the adsorption ability of the clays toward the removal of three toxic phenol compounds from aqueous systems. The results showed the adsorption affinity decreased in the following sequence: 3,5 dichlorophenol > 3-monochlorophenol > phenol [15].

The potential use of acid-activated montmorillonite as adsorbent for the removal of 2,4,5-trichlorophenol from aqueous solution was reported. The increase in adsorbent mass, pH and temperature resulted in a lower 2,4,5-trichlorophenol loading per unit weight of the acid-activated montmorillonite, but an increase of adsorption was observed when initial concentration of 2,4,5-trichlorophenol increases. It was found that the pseudo-second-order kinetic model was best to predict the experimental results. The result obtained indicated that the adsorption was physisorption [16].

Organoclays has been prepared using montmorillonite and tetradecyltrimethylammonium bromide (TDTMA) the adsorbed p-nitrophenol intercalates the organoclay and displaces the surfactant molecules or rearranges the structure of surfactant molecules within the organoclay interlayer. In addition, the different sorption mechanisms involving adsorption and/or partition may affect the sorption of p-nitrophenol onto organoclays [17].

Polydiallyldimethylammonium (PDADMA) and cationic surfactant cetyltrimethylammonium (CTMA) were applied simultaneously to modify montmorillonite, and their sorption characteristics for phenol were investigated. It was found that both CTMA and PDADMA were intercalated into the interlayer spaces of the montmorillonite. organomontmorillonite showed much better sorption capacity towards phenol than the corresponding montmorillonite. The possible reason for the enhanced sorption capacity is that the intercalation of PDADMA caused a change in the arrangement of the CTMA micelles, which might then lead to the increased affinity towards phenol. It was suggested that intercalation of cationic polymers could be a possible method for increasing the sorption capacity of the traditional surfactant synthesized organo montmorillonites [18].

Although there are some papers on phenol adsorption on surfactant modified bentonites [19–21], the characteristics of each natural material is different because the elemental compositions and the cation exchange capacities, play an important role on the modification and therefore on the adsorption properties of this materials. No reports were found about phenol adsorption by hexadecyltrimethylammonium and benzylhexadecyldimethylammonium modified bentonite

under the same experimental conditions, such as the amount of these surfactants adsorbed, after exhaustive washes, the contact time between the phenolic species and the organobentonites, the surfactant modified bentonites which define the kinetic of the processes and the initial concentration of the phenolic species in the solutions at different pH values to found the maximum capacities of the surfactant modified bentonites for the different chemical phenolic species. Therefore the aim of this research was to evaluate the adsorption properties of surfactants modified bentonite to remove phenol from aqueous solutions considering the characteristics and the amount of the surfactant on the surface of the modified clay and the chemical species of phenol found at different pH values in the system.

Materials and method

Materials

Bentonite (clay mineral), named in this work as B, was obtained from “Químicos Reactivos y Minerales S. A. de C. V.” The solid was sieved and the grain size of 200 mesh was chosen. Hexadecyltrimethylammonium bromide (HDTMA-Br) or benzylhexadecyldimethylammonium chloride (BCDMA-Cl) were purchased from Aldrich and specified to be ≥ 99 and 97% purity, respectively.

Bentonite characterization

Elemental composition

Si, Al, Ca, Mg and Fe were determined in the bentonite by induced coupled plasma atomic emission spectroscopy (ICP). The equipment used was a spectrometer Thermo Jarrell Ash, Model Iris/AP Duo. 200 mg of each sample were treated with a hydrofluoric, hydrochloric and perchloric acids mixture solution (1:1:1). The treatment was done using a microwave oven Mars 5, model CEM. Potassium and sodium were determined by atomic absorption spectroscopy.

Specific areas

The BET specific areas were determined by standard multi-point techniques of nitrogen adsorption, using a Micromeritics Gemini 2360 instrument. The samples were heated at 353 K for 24 h before specific areas were measured.

X-ray diffraction

X-ray diffraction patterns of the bentonite samples were obtained with a Siemens D500 diffractometer coupled to a

copper anode X-ray tube. Conventional diffractograms were used to identify the clay mineral and to verify crystalline structure.

Cation exchange capacity

The cation exchange capacities (CEC) of the bentonite before any treatment were determined adapting the method reported by Ming et al. [22] as follows: bentonite samples were left in contact with 1 M sodium acetate buffered solution at pH 5 for 18 h to eliminate the carbonate coating on the material. Then, the samples were left for 18 h with 20 mL of 1 M potassium chloride solution at pH 7, the phases were separated, the procedure was performed twice. The solids were washed until no presence of chloride ions was indicated in the washing solution using a AgNO_3 test. Then, the samples were left for 6 h with a 0.2 M of cesium chloride solution, the phases were separated, and the clays were again treated with the cesium chloride solution for 10 min, the procedure was done twice. Potassium was determined in the remaining aqueous phase by atomic absorption spectroscopy.

Preparation of surfactant modified bentonites

Surfactant modified bentonite (SMB)

The bentonite was mixed with 840 mmol/L of HDTMABr or BCDMACl. The concentration of the surfactants solutions were prepared considering the CEC of the bentonite previously determined. The mixtures were shaken for 48 h at 303 K. Then, the clay samples were separated from the solution and they were washed 55 times with distilled water to eliminate the excess of surfactant. The samples were identified as SMB-H and SMB-B, respectively.

The surfactants retained by the clay samples were determined as follows: the solids were dried at 298 K for 12 h, then they were milled and the surfactant loading was assessed by total carbon analysis (a CE-Instrument EA-1110 CHNS-O analyzer). The difference in carbon content between the unmodified samples and the modified samples was considered to be entirely due to the surfactant in the clay.

Adsorption experiments

Adsorption kinetic

Kinetic removal of phenol by B and SMB samples were performed as follows: 100 mg of each adsorbent and 10 mL aliquots of a 10 mg/L phenol solution at pH 6 and 11 were placed in centrifuge tubes and shaken for different times (15, 20 and 30 min, 1, 3, 5, 8, 12, 18, 24, 48 and 72 h) at 298 K, later the samples were centrifuged and decanted. The phenol

concentrations in the solutions were determined. The pH of each solution was measured before and after treatments.

Adsorption isotherms

100 mg of B and SMB samples were mixed with 10 mL of phenol solutions (from 5 to 100 mg L⁻¹) at 298 K and constant stirring at pH 6 and 11 for 48 h. The mixtures were centrifuged and decanted; all experiments were performed in duplicate. Finally, phenol concentration was determined.

Phenol determination in the aqueous solutions

The concentrations of phenol in the aqueous solutions were determined by using an UV–Vis spectrophotometer analyzer Perkin Elmer Lambda 10 at 268 or 286 nm depending on the phenol chemical species present in the solutions at different pH values, phenol is the predominant species at pH 6 and phenolate at pH 11.

Calibration curves using solutions of phenol and phenol/HDTMABr or phenol/BCDMACl in the concentration range for phenol between 5 and 50 mg/L and 5 mg/L of HDTMABr or BCDMACl solutions were used for the quantification of phenol after the adsorption processes (kinetic and isotherms).

Results and discussion

Bentonite characterization

Elemental composition

The elemental composition of bentonite (B) was Si 27.07 ± 1.3 Wt%, Al 6.91 ± 0.02 and Mg 1.55 ± 0.05 , these are the principal constituents of the primary structure of the clay and Na (1.68 ± 0.03 Wt%), K (0.62 ± 0.01 Wt%) and Ca (1.03 ± 0.06 Wt%) could participate in the ion exchange processes. Fe (1.26 ± 0.01 Wt%) was also found in the bentonite mineral.

Specific area

The specific area for the clay was 59.97 m²/g. It has been reported specific areas from 80 to 300 m²/g [23] for clays of the smectites group however, values lower than 80 m²/g have been reported for montmorillonite, for example a value of 29.57 m²/g [24] was reported for a montmorillonite from Turkey.

X-ray diffraction

The components found by X-Ray diffraction for the clay were montmorillonite (Join Committee of Powder

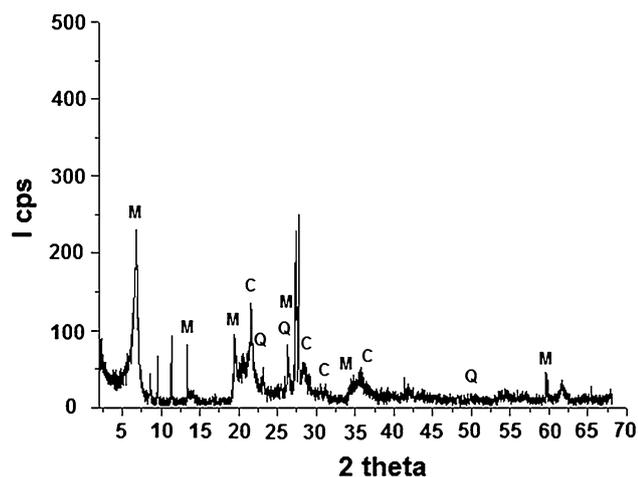


Fig. 1 X-ray diffraction pattern of bentonite, B (*M* montmorillonite, *C* cristobalite, *Q* quartz)

Table 1 Concentrations of the surfactants in the SMB

SMB	C _i H · B (mmol/L)	% Total carbon	L _M (meq _[H, B] ⁺ /100 g)	CEC%
SMB-H	840	20.46 ± 0.019	68	104
SMB-B	840	16.16 ± 0.018	75	116

65 meq/100 g correspond to 100% of the CEC for bentonite

C_i initial concentration of surfactant, *H* HDTMA, *B* BCDMA

Diffraction Standards (JCPDS) 13-0135), cristobalite (JCPDS 39-1425) and quartz (JCPDS 33-1161) (Fig. 1).

Cation exchange capacity

The cation exchange capacity (CEC) for the untreated bentonite was 78 meq/100 g. The CEC is similar to the values reported for bentonites from 80 to 120 meq/100 g [23].

Characteristics of the SMB

Table 1 shows that the bentonite retains 68 meq/100 g of the surfactant HDTMA-Br and 75 meq/100 g of the surfactant BCDMA-Cl. The quantities of the surfactants adsorbed are equivalent to 104 and 116% of the cation exchange capacity of the clay. The quantities of surfactants retained by the bentonite (Table 1) are higher than a value reported for a bentonite (48 meq/100 g) from Iraq [21] and for the Montmorillonite K30 (Fluka Co.) 33.2 meq/100 g [12].

Sabah and Celik [25] studied the adsorption mechanism of quaternary salts of ammonium on clay mineral (sepiolite), they reported that the adsorption process takes place in two steps. The first one is mainly the ion exchange of the cations of the surfactant and the magnesium ions of the

octahedral sheets of the clay. The second step is characterized by interaction combinations of aliphatic chains through van der Waals forces and ion exchange process. However, some aliphatic chains of the surfactant may be retained in the interlayer spaces of the clays. It is difficult to determine the quantity of surfactant retained strictly by ion exchange process [26] or hydrophobic interactions in the sites between the layers.

Zhang et al. [27] proposed that the stability of HDTMA⁺ in montmorillonite depends on the ionic exchange, size of the aliphatic chains of the surfactant and the van de Waals interactions between the surface of the clay and the aliphatic chains of the surfactant. In this case, the quantities of surfactants retained in the SMB after the samples were washed several times were HDTMA⁺ = 104% and BCDMA⁺ = 116% of the CEC.

Gates et al. [28] determined the orientation of trimethylphenylammonium (TMPA) in the interlayer of smectites using plane-polarized infrared spectroscopy. It was observed that the orientation of trimethylphenylammonium in the interlayers of smectites is such that the phenyl-N bond is parallel to the 001 surface. The orientation dependence of TMPA with density and location of layer charge indicated that mineral structure factors are important in controlling solution-phase reactions at mineral surface.

Organic cations are strongly retained by the clay surface until the concentration of the cation on the clay approaches the cation exchange capacity [10]. This fact was confirmed in this work, the surfactant modified bentonites were washed with distilled water 55 times and it was found that the HDTMA⁺ was retained in 104% of the effective cation exchange capacity of the clay. The higher adsorption of BCDMA⁺ (116%) could be related to the interaction of the phenyl groups with the surface of the clay material.

Removal of phenol

Adsorption kinetics

Figure 2 shows that at pH of 6, the SMB-H removes about 0.93 ± 0.09 mg of phenol per gram, SMB-B removes 1.0 ± 0.14 mg of phenol per gram and the untreated bentonite does not remove any phenol at all. The results indicate that the adsorption of phenol by the SMB with BCDMA⁺ is slightly lower than using the surfactant modified clay with HDTMA⁺, this behavior can be attributed to the phenyl group in the last surfactant; in both cases a mono layer of surfactant is formed, which favored the orientation of the phenyl groups of BCDMA⁺ in parallel form to the layers of the clay and therefore the formation of a bigger hydrophobic surface [28]. It is important to note that the phenol adsorption equilibrium was reached in 1 h of contact time for both materials, SMB-H and SMB-B.

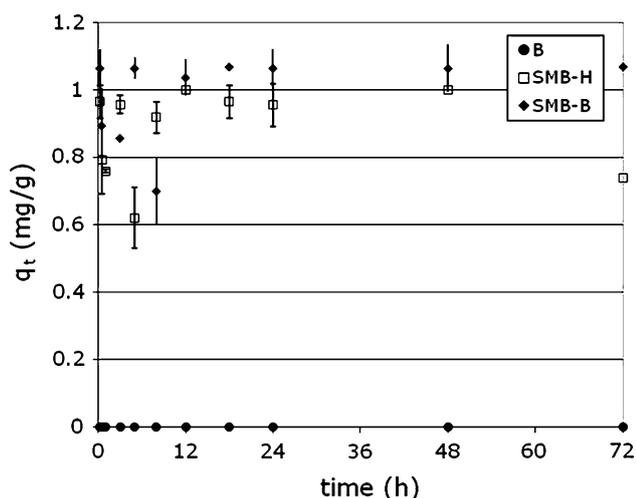


Fig. 2 Adsorption of phenol (q_t) from aqueous solutions at pH 6 by B, SMB-H and SMB-B samples as a function of time

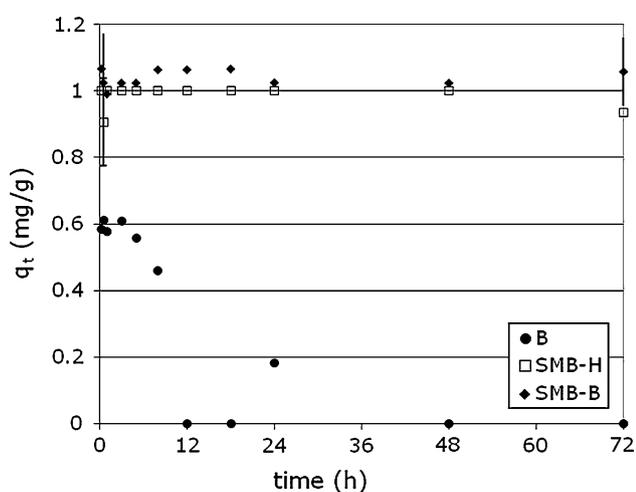


Fig. 3 Adsorption of phenol (q_t) from aqueous solutions at pH 11 by B, SMB-H and SMB-B samples as a function of time

At pH 11, the adsorption of phenol was 0.98 ± 0.02 mg/g for SMB-H and 1.04 ± 0.02 for SMB-B samples (Fig. 3). In these conditions the untreated clay mineral adsorbed 0.6 mg/g in the first 3 h and then a desorption process of phenol was observed.

The clays have the property that they can expand their layer structure and they may allow big molecules such as surfactants and phenols, therefore surfactant modified clays may remove higher quantities of phenol than surfactant modified zeolites. In this work, phenol was removed in a 100% in most of the adsorption kinetics systems. In general the adsorption of phenol by the SMB can take place in two ways: adsorption and partition [29]. However, it is not possible to determine the quantities of phenol adsorbed by the different mechanisms. The quantity of phenol removed and the mechanism involved depend on the molecular structure of the surfactant, the quantity of surfactant in the

clay, the solute species and the cation exchange capacities of the surfactant modified clay samples [11].

Different results have been reported for the removal of phenol from aqueous solutions using surfactant modified clays. Mortland et al. [30] found that modified montmorillonite with 900 meq of HDTMA⁺/kg does not remove any phenol from aqueous solutions. On the other hand Zhang et al. [27] found that the surfactant modified clay removes phenol.

Dentel et al. [31] reported that with the modified clay with dimethyldiethylammonium in about 88% of its CEC, the removal of phenol is higher at low pH values, in this conditions phenol is found as neutral molecule and it can be retained on the modified clay by the partition mechanism. However the lowest removal of phenol was found in pH values between 7.4 and 5.

Stapleton et al. [32] studied the effect of chemical species on the adsorption of organic compounds. They found that the adsorption of pentachlorophenol on a modified monmorillonite with HDTMA⁺ decreases as the deprotonated species increases in the solution when the pH increased. The same authors have proposed that the mechanism involved in the adsorption of pentachlorophenol on the modified clay is partition, and the phenolate is adsorbed as a counterion.

Yapar and Yilmaz [24] reported the removal of phenol from aqueous solutions by a natural montmorillonite, they found a 10% removal using an initial concentration of 2,000 mg/L. Under these conditions, they suggested that it is possible the adsorption of phenol on a negatively charged surface through the polarization of π electrons and phenolate on the edges of montmorillonite through the ion exchange. In the case of phenolate, the adsorbed amount would not be comparable to the adsorption of the phenol molecule since the anion exchange sites of montmorillonite are very limited and the amount of phenolate is very low. Since phenol molecules interact strongly with water through the hydrogen bonding promoted by the dipole moments of the molecules, the water and phenol, adsorbed amounts depend on the relative magnitudes of water-phenol and phenol-surface interactions.

In this work, phenol could be removed up to 0.6 mg/g with unmodified clay at pH 11 (Fig. 3); in these conditions the main species in solution is the ion phenolate, therefore the adsorption mechanism could be physadsorption.

The experimental data were adjusted to the models of Lagergren [33], Ho [34] and Elovich [35] using the program Statistica[®] 6.0, but they could not be adjusted to the last model. The kinetic parameters obtained are shown in Table 2.

In general, the experimental results, using the surfactant modified bentonites with HDTMA-Br or BCDMA-Cl, could be well adjusted to the models of Lagergren and Ho,

Table 2 Parameters obtained from kinetic models applied to the phenol adsorption by SMB samples

pH value	SMB	Kinetic model	q_e (mg phenol/g SMB)	Parameters	r^2	
6	SMB-H	Lagergren	0.857	$k_L = 2.41$	0.9733	
		Ho	0.857	$k = 6.34$ $h = 4.66$	0.9895	
	SMB-B	Lagergren	0.95	$k_L = 2.89$	0.9815	
		Ho	0.955	$k = 7.81$ $h = 7.12$	0.9899	
	11	SMB-H	Lagergren	0.857	$k_L = 4.77$	0.9999
			Ho	0.85	$k = 30.97$ $h = 22.38$	0.9988
SMB-B		Lagergren	0.955	$k_L = 2.83$	0.9792	
		Ho	1	$k = 5.81$ $h = 5.81$	0.988	

k_L 1/h, K g/mgh, h mgh/g

the r^2 values are between 0.9733 and 0.9999. The values of q_e (adsorption of phenol at equilibrium) are similar at pH values of 6 and 11. The removal of phenol was fast in all cases.

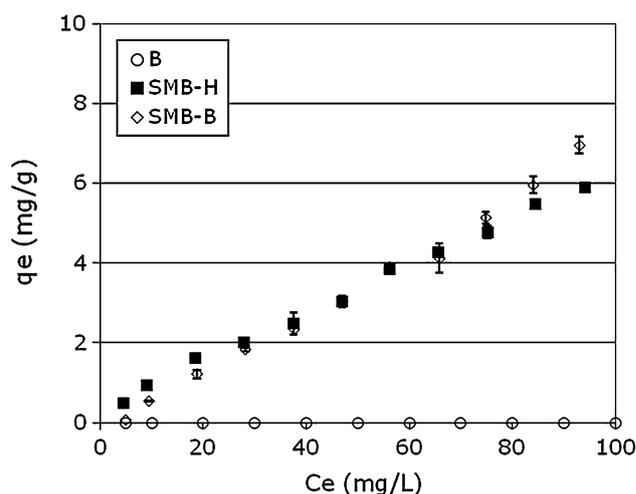
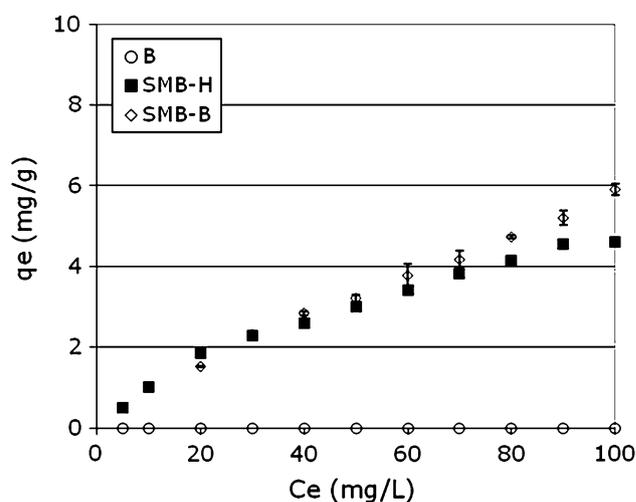
Considering that the surfactant modified bentonite has a homogeneous surface since the surfactant can be located in different sites of the surface and in the interlayer, the model most adequate to describe the kinetic adsorption process is the model of pseudo-second order [36]. However it is no clear the type of interactions between phenol and SMB samples.

According with the pseudo-second order kinetic model the k (pseudo second order rate constant) and h (initial rate constant) parameters vary with respect to the initial pH of the phenolic solutions and the surfactant used to modify the hydrophilic character of the bentonite. At pH 6 the k and h parameters are 1.2 and 1.5 times higher for SMB-B than SMB-H, respectively. At pH 11 the behavior is notably different because in this case the k and h parameters are 5.3 and 3.8 times higher for SMB-H than SMB-B, respectively. This fact confirms the importance of the pH on the phenol adsorption by SMB. On the other hand the k and h parameters are 4.8 times higher at pH 11 than at pH 6 for SMB-H, and the same parameters are 1.3 times higher at pH 6 than pH 11 for SMB-B.

Adsorption isotherms

Figure 4 shows the isotherms for phenol adsorption by B, SMB-H and SMB-B at pH around 6. In these conditions it was found that phenol uptake was higher for SMB-B (7.0 mg/g) than for SMB-H (6 mg/g).

Figure 5 shows the adsorption of phenol at pH 11 for B, SMB-H and SMB-B. It was found that phenol uptake was higher for SMB-B (6.0 mg/g) than for SMB-H (4.5 mg/g).

**Fig. 4** Adsorption isotherms of phenol from aqueous solutions by B, SMB-H and SMB-B at pH 6**Fig. 5** Adsorption isotherm of phenol from aqueous solutions by B, SMB-H and SMB-B at pH 11

As it is observed the experimental data follow a linear isotherm which is characteristic for adsorption of organic solutes by the partition mechanism described elsewhere [37]. The slope corresponds to the partition coefficient which are $K_d = 0.059$ and 0.074 L/g and $r^2 = 0.996$ and 0.991 for SMB-H and SMB-B, respectively.

In general, the experimental results of the phenol adsorption using the SMB-H and SMB-B, could be adjusted to the models of Langmuir and Freundlich, the r^2 values are between 0.6468 and 0.9901, respectively. According with the Langmuir model the q_m (amount of phenol adsorbed per unit weigh of adsorbent in forming a complete monolayer on the surface) parameter for both SMB-H and SMB-B are approximately twice higher at pH 6 than pH 11. It is also important to note that the q_m is higher for SMB-B at the same pH value than SMB-H.

Table 3 Parameters from isotherm models applied to the phenol adsorption by SMB

pH value	SMB	Isotherm model	Parameter	r^2	
6	SMB-H	Langmuir	$K_a = 1.3442$ $q_m = 13.966$	0.7346	
		Freundlich	$K_F = 0.59$ $n = 45.26$ $1/n = 0.0220$	0.9941	
	SMB-B	Langmuir	$K_a = 1.6751$ $q_m = 28.571$	0.6468	
		Freundlich	$K_F = 0.59$ $n = 45.28$ $1/n = 0.0220$	0.9901	
	11	SMB-H	Langmuir	$K_a = 0.9012$ $q_m = 7.622$	0.9704
			Freundlich	$K_F = 0.51$ $n = 13.2$ $1/n = 0.0757$	0.9492
SMB-B		Langmuir	$K_a = 1.3039$ $q_m = 13.055$	0.8606	
		Freundlich	$K_F = 0.53$ $n = 90$ $1/n = 0.0111$	0.9401	

K_a (L/mg), q_m (mg/g), K_F (mg/g)(L/mg)^{1/n}

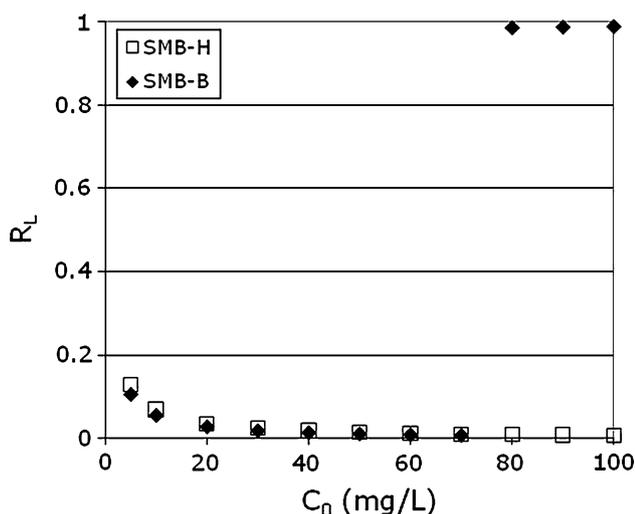


Fig. 6 Separation factors for both SMB-H and SMB-B at pH 6

The best adjustments of the isotherms experimental data were obtained with the model of Freundlich at pH 6 and 11 (Table 3).

In the Freundlich equation, $1/n$ is related to the adsorption intensity. This parameter is similar for the modified clays with HDTMA⁺ and BCDMA⁺ at pH 6. The adsorption intensities are different at pH 11, $1/n$ was higher for the modified clay with HDTMA⁺ than for the modified

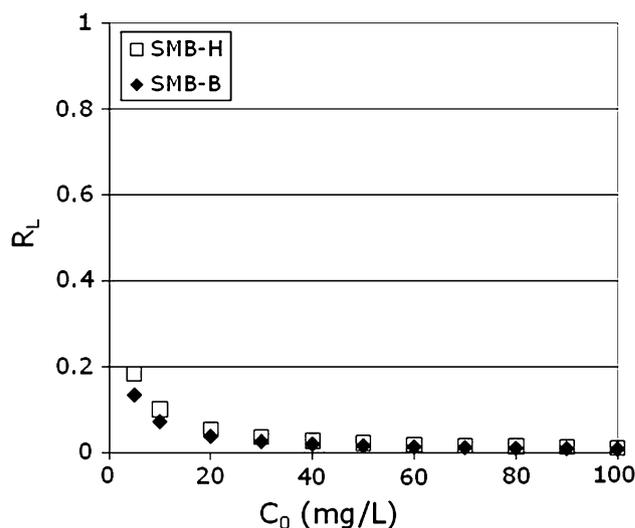


Fig. 7 Separation factors for both SMB-H and SMB-B at pH 11

clay with BCDMA⁺. This means that the phenolate present in the aqueous solution at pH 11, affects the adsorption intensity with the modified zeolite which contains a surfactant with a benzyl group.

Considering the parameters obtained from the Langmuir's isotherm model, the separation factors were calculated as follows [38]:

$$R_L = 1 / (1 + K_a C_0)$$

where K_a is the Langmuir constant (L/mg), C_0 is the initial concentration of phenol (mg/L).

According to Dermibaz et al. [39], if $R_L > 1$ then the adsorption is not favorable; if $R_L = 1$ the adsorption is linear; if $0 < R_L < 1$ the adsorption is favorable; and if $R_L = 0$ it is irreversible.

In general, the R_L values shown in Figs. 6 and 7 indicate that the removal of phenol increases as the concentrations of solutions increases and the adsorption is favorable.

Adsorption efficiencies

A series of dual-cation organobentonites has been synthesized by replacing the metal ions in bentonite with both long-chain alkyl quaternary ammonium cations, such as dodecyltrimethylammonium, benzyldimethyltetradecylammonium, cetyltrimethylammonium or hexadecyltrimethylammonium, octadecyltrimethylammonium, and short-chain alkyl quaternary ammonium cations, such as tetramethylammonium and it was found that the adsorption properties of phenol are affected by treatment conditions, such as pH, amount and type of organozeolite, shaking time, interlayer spacing, organic carbon contents in the organobentonites and the solubility of the phenolic compounds [11, 24]. Similar results were found in the present work.

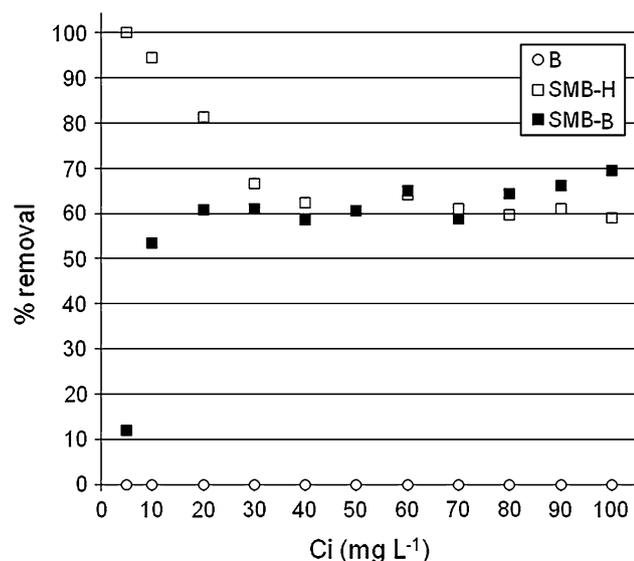


Fig. 8 Adsorption efficiencies of B, SMB-B and SMB-C to remove phenol from aqueous solutions at pH 6

Percentages of phenol removed from aqueous solution considering the initial phenol concentration are given in Figs. 8 and 9 at pH values of 6 and 11. The bentonite does not remove any phenol from the aqueous solutions at pH values of 6 and 11. At pH 6 and at low concentrations (below 30 mg/L) the most efficient material for the removal of phenol is SMB-H and for higher concentrations both materials SMB-H and SMB-B show the same efficiency. At pH 11 both materials show the same behavior and the removal efficiencies decrease as the concentration increases until 70 mg/L. The efficiencies of both materials to remove phenol from aqueous solutions at pH 11 were between 50 and 60%.

Conclusions

Montmorillonite is the main component of the bentonite tuff and the uptake of the surfactant by this material depends on both the cation exchange capacity and the chemical nature of the surfactant.

The kinetic experimental data were best adjusted to the pseudo-second order model and the type of surfactant to modify the clay as well as the pH of the phenol solution influence on the k parameter.

Although the isotherms show a linear behavior which is characteristic for adsorption of organic solutes by the partition mechanism, they could be best adjusted to the model of Freundlich. These results indicate that the adsorption mechanism involved is chemisorption on a heterogeneous material. The maximum capacity of the surfactant modified clays by phenol is obtained at pH 6

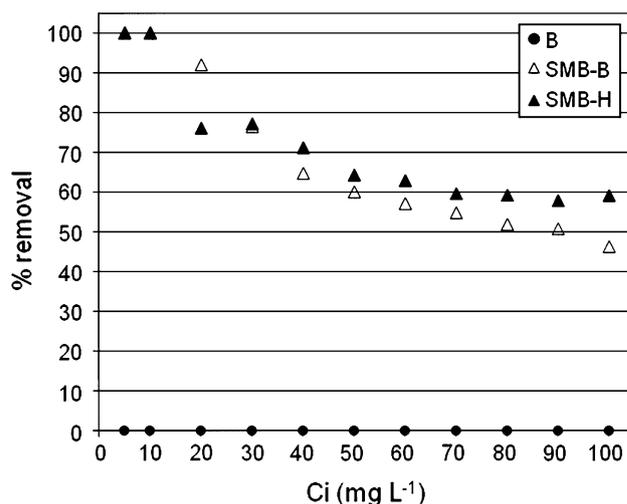


Fig. 9 Adsorption efficiencies of B, SMB-H and SMB-B to remove phenol from aqueous solutions at pH 11

and when the clay is modified with bencylhexadecyldimethylammonium chloride.

The adsorption and the mechanism involved in the removal of phenol by the surfactant modified bentonite depend on the molecular structure of the surfactant, the quantity of surfactant in the clay, the phenol chemical species in solution at different pH and initial concentration of the solute.

Acknowledgments The authors acknowledge financial support provided by CONACYT (Project 131174-Q) and they are also grateful to technician from Chemistry Department.

References

- Ahmaruzzaman, M., Sharm, D.K.: Adsorption of phenols from wastewater. *J. Colloid Interface Sci.* **287**, 14–24 (2005)
- HuH, J.K., Song, D.I., Jeon, Y.W.: Sorption of phenol and alkylphenols from aqueous solution onto organically modified montmorillonite and applications of dual-mode sorption model. *Sep. Sci. Technol.* **35**, 243–259 (2000)
- Mohd, R., Othman, S., Rokiah, H., Anees, A.: Adsorption of methylene blue on low-cost adsorbents: a review. *J. Hazard. Mater.* **177**, 70–80 (2010)
- Amit, B.: Removal of bromophenols from water using industrial wastes as low cost adsorbents. *J. Hazard. Mater. B* **139**, 93–102 (2007)
- Cortés-Martínez, R., Solache-Ríos, M., Martínez-Miranda, V., Alfaro-Cuevas, V.R.: Sorption behavior of 4-chlorophenol from aqueous solutions by a surfactant-modified Mexican zeolitic rock in batch and fixed bed systems. *Water Air Soil Pollut.* **183**, 85–94 (2007)
- Gupta, K.V., Srivastava, K.S., Tyagi, R.: Design parameters for treatment of phenolic wastes by carbon columns (obtained from fertilizer waste material). *Water Res.* **34**, 1543–1550 (2000)
- Eren, E.: Removal of lead ions by Unye (Turkey) bentonite in iron and magnesium oxide-coated forms. *J. Hazard. Mater.* **165**, 63–70 (2009)

8. Hu, B., Luo, H.: Adsorption of hexavalent chromium onto montmorillonite modified with hydroxylaluminum and cetyltrimethylammonium bromide. *Appl. Surf. Sci.* **257**, 769–775 (2010)
9. Richards, S., Bouazza, A.: Phenol adsorption in organo-modified basaltic clay and bentonite. *Appl. Clay Sci.* **37**, 133–142 (2007)
10. Smith, J.A., Jaffé, P.R., Chiou, C.T.: Effect on ten quaternary ammonium cations on tetrachloromethane sorption to clay from water. *Environ. Sci. Technol.* **24**, 1167–1172 (1990)
11. Lizhong, Z., Xiaogang, R., Shaobin, Y.: Use of cetyltrimethylammonium bromide-bentonite to remove organic contaminants of varying polar character from water. *Environ. Sci. Technol.* **32**, 3374–3378 (1998)
12. Juang, R.S., Lin, S.H., Tsao, K.H.: Sorption of phenols from water in column systems using surfactant-modified montmorillonite. *J. Colloid Interface Sci.* **269**, 46–52 (2004)
13. Sprynsky, M., Ligora, T., Lebedynets, M., Buszewski, B.: Kinetic and equilibrium studies of phenol adsorption by natural and modified forms of the clinoptilolite. *J. Hazard. Mater.* **169**, 847–854 (2009)
14. Garcia, J.E., Gonzalez, M.M., Notario, J.S.: Phenol adsorption on natural phillipsite. *React. Polym.* **21**, 171–176 (1993)
15. Wibulswas, R., White, D.A., Rautiuan, R.: Adsorption of phenolic compounds from water by surfactant-modified pillared clays. *Process Saf. Environ. Prot.* **77**, 88–92 (1999)
16. Zaghouane-Boudiaf, H., Boutahala, M.: Kinetic analysis of 2,4,5-trichlorophenol adsorption onto acid-activated montmorillonite from aqueous solution. *Int. J. Miner. Process.* **100**, 72–78 (2011)
17. Park, Y., Ayoko, G.A., Frost, R.L.: Characterisation of organoclays and adsorption of p-nitrophenol: environmental application. *J. Colloid Interface Sci.* **360**, 440–456 (2011)
18. Zhu, J., Wang, T., Zhu, R., Ge, F., Wei, J., Yuan, P., He, H.: Novel polymer/surfactant modified montmorillonite hybrids and the implications for the treatment of hydrophobic organic compounds in wastewaters. *Appl. Clay Sci.* **51**, 317–322 (2011)
19. Juang, R.S., Lin, S.H., Tsao, K.H.: Mechanism of sorption of phenols from aqueous solutions onto surfactant-modified montmorillonite. *J. Colloid Interface Sci.* **254**, 234–241 (2002)
20. Senturka, H.B., Ozdesa, D., Gundogdu, A., Durana, C., Soyulakb, M.: Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: equilibrium, kinetic and thermodynamic study. *J. Hazard. Mater.* **172**, 353–362 (2009)
21. Alkaram, U.F., Mukhlis, A.A., Al-Dujaili, A.H.: The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite. *J. Hazard. Mater.* **169**, 324–332 (2009)
22. Ming, D., Allen, E., Galindo, C., Henninger, D.: Methods for determining cation exchange capacities and composition of native cations for clinoptilolite. In: *Memories of the 3rd International Conference on the Occurrence, Properties and Utilization of Natural Zeolites*. Cuba, 31–35 (1995)
23. Sun-Kou, M.R., Volzone, C., Sapag, K.: Las arcillas y sus diferentes aplicaciones en adsorción. In: Rodríguez, F. (ed.) *Adsorbentes en la solución de algunos problemas ambientales*, Red Temática V F: Red Iberoamericana de adsorbentes para la protección ambiental. Madrid, España (2004)
24. Yapar, S., Yilmaz, M.: Removal of phenol by using montmorillonite, clinoptilolite and hydrotalcite. *Adsorption* **10**, 287–298 (2004)
25. Sabah, E., Çelik, M.S.: Adsorption mechanism of quaternary amines by sepiolite. *Sep. Sci. Technol.* **37**, 3081–3097 (2002)
26. Li, Z.: Oxyanion sorption and surface anion exchange by surfactant-modified clay minerals. *J. Environ. Qual.* **28**, 1457–1463 (1999)
27. Zhang, Z.Z., Sparks, D.L., Scrivner, N.C.: Sorption and desorption of quaternary amine cations on clays. *Environ. Sci. Technol.* **27**, 1625–1631 (1993)
28. Gates, W.P., Teppen, B.J., Bertsch, P.M., Aiken, S.C.: Sorption of aromatics in the interlayer space of organo-clays. *Schriftenr. Angew. Geowiss.* **1**, 41–48 (1997)
29. Zhu, L., Chen, B., Shen, X.: Sorption of phenol, *p*-nitrophenol and aniline to dual-cation organobentonites from water. *Environ. Sci. Technol.* **34**, 468–475 (2000)
30. Li, Z., Burt, T., Bowman, R.S.: Sorption of ionizable organic solutes by surfactant-modified zeolite. *Sci. Technol.* **34**, 3756–3760 (2000)
31. Dentel, S.K., Bottero, J.Y., Khatib, K., Demougeot, H., Duguet, J.P., Anselme, C.: Sorption of tannic acid, phenol and 2,4,5-trichlorophenol on organoclays. *Water Res.* **29**, 1273–1280 (1995)
32. Stapleton, M.G., Sparks, D.L., Dentel, S.K.: Sorption of pentachlorophenol to HDTMA-clay as a function of ionic strength and pH. *Environ. Sci. Technol.* **28**, 2330–2335 (1994)
33. Lagergren, S.: Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenka Vetenskapsakademiens Handlingar* **24**, 1–39 (1898)
34. Ho, Y.S.: Pseudo-isotherms using a second order kinetic expression constant. *Adsorption* **10**, 151–158 (2004)
35. Chien, S.H., Clayton, W.R.: Application of Elovich equation to the kinetics of phosphate release and sorption on soils. *Soil Sci. Am. J.* **44**, 265–268 (1980)
36. Ho, Y.S., McKay, G.: Pseudo-second order model for sorption processes. *Process Biochem.* **34**, 451–465 (1999)
37. Haggerty, G.M., Bowman, R.S.: Sorption of chromate and other inorganic anions by organo-zeolite. *Environ. Sci. Technol.* **28**, 452–458 (1994)
38. Ho, S., Huang, C.T., Huang, H.W.: Equilibrium sorption isotherms for metal ions on tree fern. *Process Biochem.* **37**, 1421–1430 (2002)
39. Demirbaz, O., Alkan, M., Dogan, M.: The removal of victoria blue from aqueous solutions by adsorption on a low-cost material. *Adsorption* **8**, 341–349 (2002)