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Removal of Furfural from Aqueous Solutions by Adsorption Using Organobentonite: Isotherm and Kinetic Studies

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ABSTRACT: Lubricant refineries are facing pollution problems associated with the occasional loss of furfural. This constitutes both an economic loss and an environmental hazard, especially for aquatic organisms. Some studies on the removal of furfural by adsorption onto hydrophobic polymeric resins (XAD-4 and XAD-7), activated carbon and the nanoporous material MCM-48 have been published, but none provides information on the adsorption of furfural onto clays.

In the present work, we have studied the efficiency of sodium bentonite modified with the cationic surfactant cethyltrimethylammonium bromide (CTAB) in the adsorption of furfural. The structures of both natural and modified bentonites have been examined using XRD and FT-IR analyses. Adsorption studies were performed in a batch system, with the effects of various experimental parameters such as the contact time, the organobentonite concentration, pH, the initial furfural concentration and the temperature being evaluated. Kinetic results showed that furfural could be removed by CTAB–bentonite after contact for 6 h, with the adsorption process being well described by the pseudo-second-order reaction model. Furfural sorption onto CTAB–bentonite was characterized by a linear isotherm, with the adsorption capacity towards furfural being reduced by increasing temperature. A comparison of furfural adsorption capacities revealed that the capacities decreased in the following order: CTAB–bentonite > XAD-4 > XAD-7.

1. INTRODUCTION

Various forms of human activities constitute a hazard to the natural environment through the introduction of harmful pollutants. The release of complex chemicals from petrochemical industries, oil refineries, oil-processing and chemical plants into the environment has been considered a major source of air and water pollution (Borghei and Hosseini 2008). Many of these materials are either not biodegradable or act as inhibitors for biological systems. They often have a toxic effect on life systems and require preventive action to reduce the pollution from the source.

The removal of inorganic and organic contaminants from wastewater has been extensively studied using biological and various physicochemical processes, including adsorption phenomena. Activated carbon is one of the most commonly used sorbents for the removal of hazardous pollutants from aqueous solutions, because it has a large surface area and a high adsorption capacity. However, it is non-selective in its action and requires expensive regeneration processes

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(Cadena 1989). As an alternative, materials which are available in abundance in Nature, recyclable, cheaper and presenting interesting adsorption properties, e.g. clays such as speolite, smectite, bentonite, alunite and perlite, are attracting increasing attention (Özcan *et al*. 2004).

Clay minerals and modified clays have been widely used as adsorbents for the removal of toxic metal ions and organic pollutants from aqueous solutions, due to their low cost, large specific surface areas, chemical and mechanical stabilities, layered structures and high cation-exchange capacities (Wang *et al*. 2009). Bentonite is a 2:1 clay mineral which is predominantly composed of montmorillonite clay. The surface of bentonite is hydrophilic in nature because inorganic cations, such as Na^+ and Ca^{2+}, are strongly hydrated in the presence of water. As a result, the adsorption efficiency of natural bentonite for organic molecules is very low. However, the adsorption properties of bentonite may be improved by modification of the clay mineral surface with a cationic surfactant. Replacement of inorganic exchangeable cations with cationic surfactants occurs according to an ion-exchange mechanism (Boyd *et al*. 1988b; Gitipour *et al*. 1997). This is favoured by van der Waals interactions between the organic surfactant cations and the reduced solvent shielding of ions in the inter-lamellar environment (Sheng *et al*. 1996; Boyd *et al*. 1988a,b), the nature of the exchanged mineral surfaces readily changing from hydrophilic to hydrophobic. As a consequence, the organo-clay complex is an excellent adsorbent for the removal of non-ionic organic compounds (NOCs) from water (Xu *et al*. 1997; Zhu *et al*. 2000; Sheng *et al*. 1998), such as polycyclic aromatic hydrocarbons (PAHs) (Chen and Zhu 2001) and phenolic compounds (Zhu *et al*. 2000).

The sorption mechanism of the organic contaminant by the organo-clay is dependent on the structure of the quaternary ammonium compound employed. Another important factor is the polarity of the adsorbent surface. Polar adsorbents (hydrophilic) have a higher affinity for polar substances, whereas non-polar adsorbents (hydrophobic) have a larger affinity for non-polar adsorbates (Freitas *et al*. 2007).

In the present work, the elimination of furfural, classified as a hazardous and particularly toxic pollutant for aquatic bodies (WHO 2000), has been investigated. Furfural is an aromatic aldehyde with a cyclic structure, obtained from biomass rich in pentosan (e.g. sugar cane bagasse, corncobs, etc.) (Chheda *et al*. 2007). Various methods have been tested for the removal of furfural, including photo-oxidation degradation (Borghei and Hosseini 2007), membrane separation (Sagehashi *et al*. 2007), and adsorption onto hydrophobic polymeric resins (XAD-4, XAD-7) (Weil *et al*. 2002), activated carbon (Singh *et al*. 2009) and the nanoporous material MCM-48 (Anbia and Mohammadi 2009). However, no data have been published to date on the separation of furfural from dilute aqueous solutions using organo-clays. Thus, a principal objective of the present study was to evaluate the capacity of surfactant-modified clay for removing furfural from water in the presence of an organic cation containing a long alkyl chain (e.g. cetyltrimethylammonium bromide). The optimal mass of the cationic surfactant on the clay mineral necessary for the removal of furfural has been examined. The influence of pH, contact time, initial furfural concentration and temperature for the adsorption onto modified bentonite has been investigated in an attempt to obtain an understanding of the adsorption mechanism through the use of kinetic and isotherm equations.

2. MATERIALS AND METHODS

2.1. Adsorbent and adsorbate

The clay mineral used in this study was obtained from the Hammam Boughrara deposit in western Algeria. Its chemical composition is listed in Table 1 and confirms that the bentonite sample

TABLE 1. Chemical Composition of Raw Bentonite

Constituents	Content (wt%)
SiO_2	60.45
Al_2O_3	24.39
Fe_2O_3	0.79
CaO	2.81
MgO	2.60
Na_2O	2.88
K_2O	0.87
LOI[a]	5.25
SiO_2/Al_2O_3	2.47

[a] Loss on ignition at 1000 ºC.

consisted essentially of montmorillonite. Its SiO_2/Al_2O_3 ratio of 2.47 indicates that it was a member of the phyllosilicate family (Mansria *et al.* 2009).

X-Ray diffraction (XRD) analysis of the bentonite powder demonstrated that montmorillonite was the major constituent, with various impurities such as kaolin (K), quartz (Q) calcite (Ca) and organic matter also being present. Several treatments were employed to eliminate the impurities from the bentonite sample. Thus, fractions with diameters < 2 μm obtained by sedimentation were subsequently saturated three times with 1 M NaCl for 24 h to replace all the interfoliary cations with Na^+ ions, thereby making the sample homo-ionic. After such saturation, the bentonite sample was washed with distilled water until a negative chloride test was obtained with 0.1 M $AgNO_3$. This purified sodium montmorillonite clay is referred to below as sodium bentonite. Its structural formula was $(Si_{7.37}Al_{0.63})^{IV}(Al_{2.82}Mg_{0.46}Fe_{0.32})^{VI}(Ca_{0.07}Na_{0.85}K_{0.1})O_{20}(OH)_2 \bullet nH_2O$.

The cation-exchange capacity (CEC) of sodium bentonite as determined by the Methylene Blue method (Khar and Madsen 1995) was 118 mequiv/100 g clay, while its internal surface area was 126 m^2/g (standard BET nitrogen adsorption procedure).

Furfural and cetyltrimethylammonium bromide, $C_{19}H_{42}NBr$ (CTAB), were obtained from Acros Organics, Geel, Belgium.

2.2. Preparation of organobentonite

Organically-modified montmorillonite was synthesized via the aqueous exchange of the dissolved quaternary ammonium compound (CTAB) onto the internal and external mineral surfaces of sodium bentonite (Smith *et al.* 1990). This cationic surfactant can be adsorbed onto negatively charged clay surfaces and is not influenced by the solution pH. Relative to Na^+ ions, CTAB is strongly preferred by the exchange sites on montmorillonite (Wolfe *et al.* 1986) and is not easily displaced by smaller cations such as H^+, Na^+ or Ca^{2+} (Yan *et al.* 2007). It is soluble in water and exists as individually dissolved molecules in solutions of concentration below the critical micellar concentration (CMC) or as micelles above the CMC which occurs at 9×10^{-4} M at 25 ºC.

The organobentonites used in this study were synthesized in our laboratory using the procedure described by Bartelt-Hunt *et al.* (2003). Thus, organobentonite samples were obtained by dispersing 1 g of sodium bentonite in 100 mℓ of CTAB solutions at different mixing ratios to yield different concentrations of amine, ranging from 25% to 200% of the CEC. It has been reported that the adsorption of CTAB onto montmorillonite usually requires 4–6 h to attain equilibrium. The mixtures were agitated for 24 h at room temperature, employing a magnetic stirrer to guarantee equilibrium. The modified clays were collected by centrifugation, any superficially held adsorbate removed by washing several times with distilled water until the wash water was free from bromide anions (as tested by $AgNO_3$) and then dried at 60 ºC. The organo-clay produced is referred to as CTAB–bentonite below.

2.3. Characterization of organobentonite

The material showing the optimal rate of furfural fixation was characterized by infrared (IR) spectroscopy and X-ray powder diffraction (XRD) to establish any differences between the modified products and the starting sodium bentonite material. XRD analysis was undertaken using a D5000 diffractometer employing Cu Kα radiation. Infrared (IR) absorption spectra were determined over the 4000–400 cm^{-1} wavenumber range employing a JASCO 4200 spectrophotometer.

2.4. Adsorption studies

All adsorption experiments of furfural onto the organobentonites were performed employing a batch procedure with furfural solutions at natural pH and at room temperature.

To examine the effect of the organobentonite concentration on the removal of furfural from aqueous solutions, 50 mg quantities of CTAB–bentonite modified at various CEC percentages (25–200%) were placed in 50 mℓ of furfural solution of 100 mg/ℓ concentration contained in a series of Erlenmeyer flasks, which were then agitated continuously over a period of 24 h. After subsequent centrifugation at 3000 rev/min for 45 min, the concentration of the supernatant was measured at a wavelength, λ_{max}, of 275 nm using a double-beam SAFAS spectrophotometer.

The sorption kinetics were also studied by placing 50 mg samples of CTAB–bentonite in each of a series of Erlenmeyer flasks to which was added 50 mℓ of a furfural solution with an initial concentration of 100 mg/ℓ. The samples were then agitated for different contact times at a constant speed at room temperature.

The same mode of operation was followed in the study of the influence of pH on the adsorption employing various pH values over the range 3–11, using 0.1 N HCl and 0.1 N NaOH solutions to adjust the pH values of the furfural solutions.

Equilibrium isotherms were measured by introducing a constant mass of organo-clay (25 mg) into a series of 25 mℓ stoppered flasks containing 25 mℓ of furfural solutions with initial concentrations in the range 50–7000 mg/ℓ. The corresponding adsorption isotherms were measured at various temperatures (14, 30 and 60 ºC). The amount adsorbed, q_e (mg/g), was calculated using the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i and C_e are the initial and equilibrium concentrations (mg/ℓ) of furfural, respectively, m is the mass of adsorbent employed (g) and V is the solution volume (ℓ).

3. RESULTS AND DISCUSSION

3.1. X-Ray diffraction characterization

The XRD patterns for sodium bentonite and 80% CTAB–bentonite are depicted in Figures 1(a) and (b), respectively. Comparison of the patterns shows a substantial decrease in the intense lines

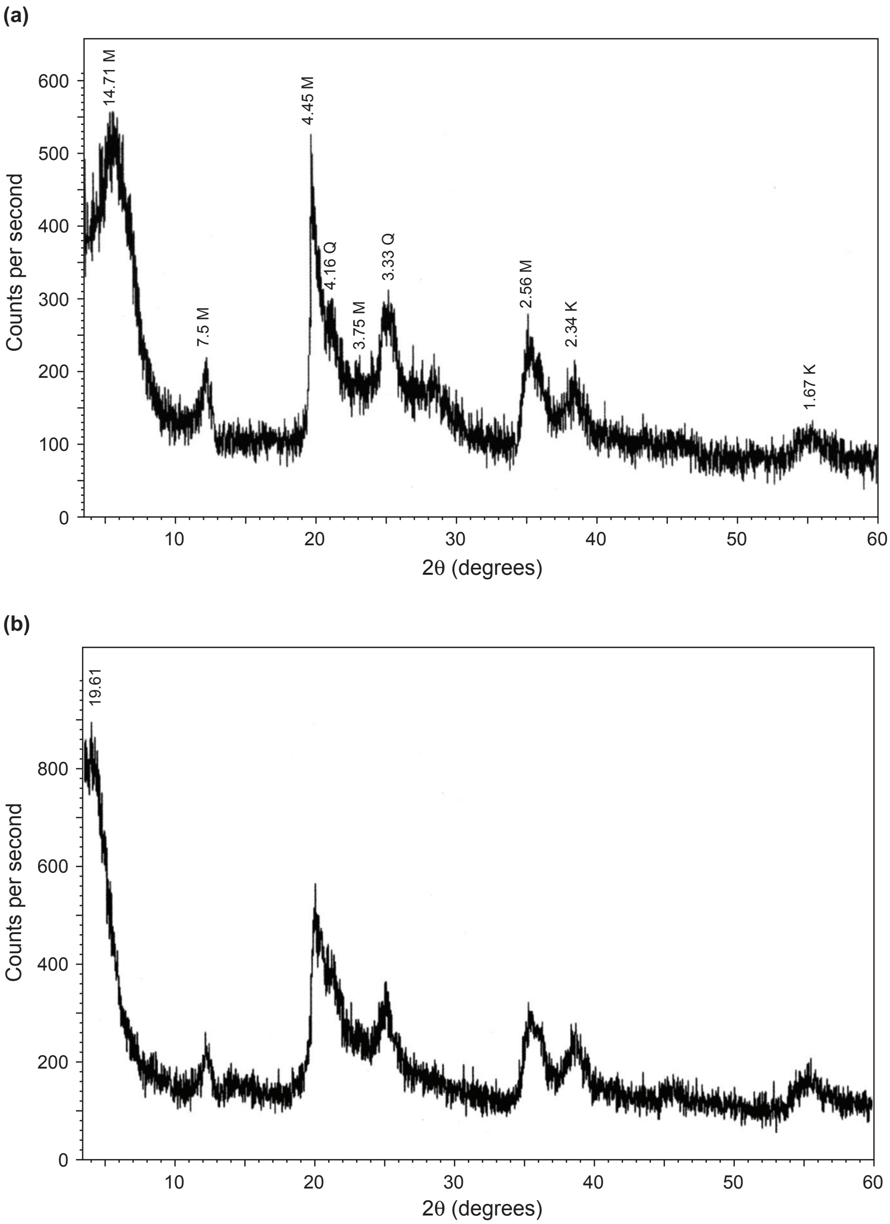

Figure 1. X-Ray diffractograms of (a) sodium bentonite and (b) 80% CTAB–bentonite. The letters associated with peaks in the trace depicted in part (a) correspond to the following: M, montmorillonite; Q, quartz; K, kaolinite.

for quartz in the spectrum for the organobentonite, since this component was partially removed after purification by sedimentation. Reflections relative to the [001] plane confirm the presence of montmorillonite with $d_{001} \sim 14.71$ Å, corresponding to a mineral containing two layers of water.

The interlayer distance d_{001} was 19.61 Å for the 80% CTAB–bentonite sample [Figure 1(b)], which is larger than that for the sodium bentonite sample. This indicates that introduction of the intercalated surfactant cation led to an increase in the interlayer spacing of bentonite. The orientation of the intercalated surfactant cations in the organobentonite interlayers may be determined from the dimensions of the surfactant cation (CTAB) and the interlayer spacing. The interlayer spacing is calculated by subtracting the thickness of the unit cell dimension (9.6 Å) from the measured basal spacing (d_{001}). For 80% CTAB–bentonite, this interlayer spacing (10 Å) was smaller than the length of the $CTAB^+$ cation but twice as large as the width of $CTAB^+$, thereby suggesting that the orientation of the $CTAB^+$ configuration in CTAB–bentonite might be a bimolecular layer arrangement (Zhu *et al*. 2008).

Zhu *et al*. (1998) observed that the interlayer spacing of CTAB–bentonite gradually increased as the amount of cethyltrimethylammonium cation employed in the synthesis of the organo-clays increased. However, above the CEC of the natural bentonite, the interlayer spacing (19.28 Å) did not increase further. Another study has shown that when all the exchange sites of bentonite are occupied by hexadecyltrimethylammonium cations ($HDTMA^+$), the inter-lamellar spacing was less than 20 Å (Lagaly 1982).

3.2. IR characterization of adsorption process

The FT-IR spectra of sodium bentonite, the modified bentonite (CTAB–bentonite) and the furfural-loaded CTAB–bentonite are depicted as traces a to c in Figures 2(a) and (b), respectively.

The spectrum of sodium bentonite (trace a) shows typical infrared bands for montmorillonite corresponding to the –OH stretching vibration of the silanol (Si–OH) groups at 3625.52 cm^{-1} and the HO–H vibration of water adsorbed onto the silica surface at 3457.74 cm^{-1}, respectively. The FT-IR spectrum of sodium bentonite also shows a band at 1641.05 cm^{-1} due to the –OH bending mode of adsorbed water. A broad band at 1031.37 cm^{-1} may be related to the stretch vibrations of the Si–O groups.

Normally, the C–H stretching bands of alkylammonium cations occur in the 3020–2800 cm^{-1} region (Kozak and Domka 2004). The spectrum of CTAB–bentonite (trace b) shows two sharp bands at 2921.63 cm^{-1} and 2852.2 cm^{-1} which may be ascribed to the asymmetric and symmetric stretching vibrations of the $–CH_3$ and $–CH_2$ groups, respectively, in the aliphatic carbon chain. In addition, a HCH bending vibration band also occurs at 1473.35 cm^{-1} in the IR spectrum of the organo-clay, indicating the formation of organic–inorganic hybrids (Bouberka *et al*. 2008). The existence of these peaks supports the modification of bentonite with CTAB. The band intensities decreased in the FT-IR spectrum of the furfural-loaded organobentonite (trace c) because the functional groups, especially those of CTAB, on the organobentonite surface were occupied by furfural molecules.

3.3. Effects of CTAB concentration on the adsorption rate of furfural

The adsorption of furfural onto bentonite modified with different percentage of the CEC is shown in Figure 3. It will be seen from the figure that, at values below the CEC of the clay, the amount of furfural adsorbed per unit weight of clay (x/m) increased as the amount of surfactant (CTAB) on the bentonite increased. According to the data depicted, the maximum removal of furfural

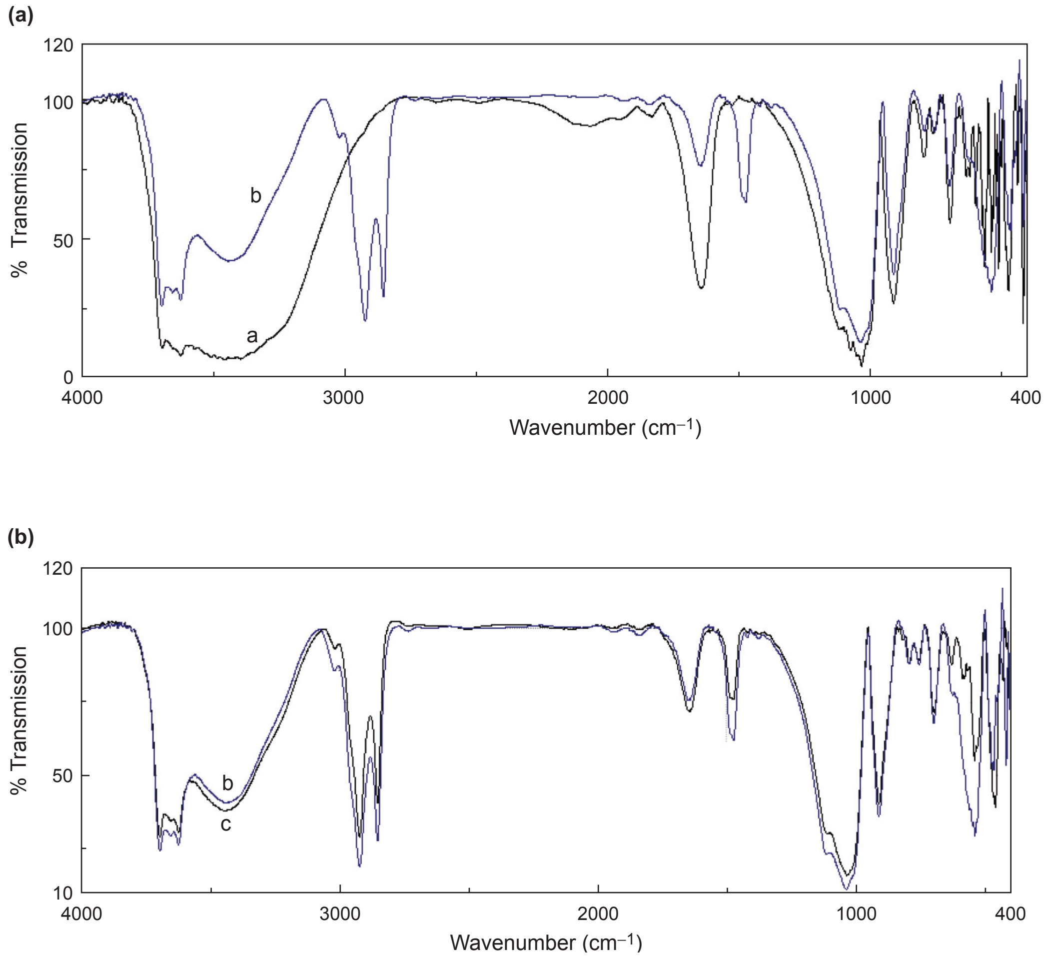

Figure 2. FT-IR spectra of sodium bentonite (trace a), CTAB–bentonite (trace b) and furfural-loaded CTAB–bentonite (trace c).

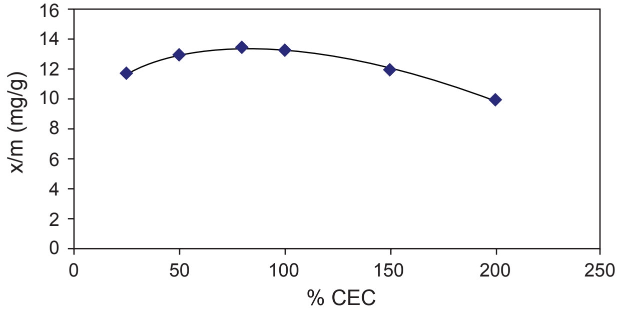

Figure 3. Effect of organobentonite dosage on the furfural uptake. Experimental conditions: initial conc. of furfural = 100 mg/ℓ, contact time = 24 h.

attained a virtually constant level when cation exchange was between 80% and 100% CEC. Beyond this level, the adsorption of the furfural decreased significantly.

The increase in adsorption percentage of furfural below the CEC value of the clay is probably due to the increased availability of active adsorption sites with increasing organobentonite concentration. This could possibly be due to an increase in the total organic carbon (TOC) and the interlayer spacing of organobentonite (Lee *et al*. 2002). However, this effect can also be interpreted as due to the co-adsorption of furfural into the adsorbed CTAB layer (Schieder *et al*. 1994).

The decrease in the equilibrium adsorption capacity of the organobentonite for furfural uptake can be attributed to two reasons. Firstly, the organobentonite particles aggregated with increasing adsorbent concentration. Hence, the total surface area of the adsorbent decreased and the diffusion path length of furfural increased. Secondly, an increase in the organobentonite concentration at constant concentration and volume of furfural led to desaturation of the adsorption sites (Senturk *et al*. 2009), leading to a decrease in the equilibrium adsorption capacity of the organobentonite. However, irrespective of the mechanism involved, these results imply that the ratio of CTAB to bentonite had a great influence on furfural removal.

3.4. Kinetic studies

The adsorption of furfural onto organobentonite (CTAB–bentonite) was studied as a function of the contact time in order to determine the time necessary to achieve equilibrium (Figure 4). As shown in the figure, the rate of adsorption of furfural was initially high, but then diminished as time progressed. This was probably due to the large number of vacant surface sites available for adsorption during the initial stages of the process. However, once these were occupied, the remaining vacant surface sites became increasingly difficult to be occupied by furfural as a result of repulsive forces. The time necessary to reach equilibrium was ca. 6 h.

The adsorption kinetics are very important in determining a mechanism for the adsorption process and to assess the performance of individual adsorbents. In the present work, different kinetic models including the pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to fit the experimental results.

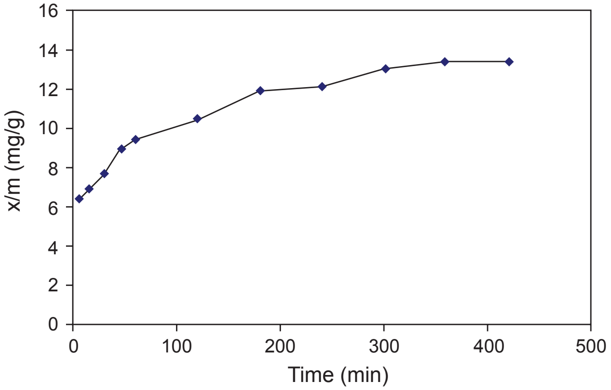

Figure 4. Effect of contact time on the adsorption of furfural onto CTAB–bentonite. Experimental conditions: initial conc. of furfural = 100 mg/ℓ.

The pseudo-first-order equation can be written as follows (Lagergren 1898):

$$\log q_e - q_t = \log q_e - k_1/2.303t \tag{2}$$

where q_e (mg/g) and q_t (mg/g) are the amounts of furfural adsorbed at equilibrium and at time t, respectively, while k_1 (min^{-1}) is the pseudo-first-order rate constant. If the plot of $\log(q_e - q_t)$ versus t is linear, this suggests the applicability of this kinetic model, with q_e and k_1 being determined from the intercept and slope of the plot, respectively.

The pseudo-second-order model may be written in the following form (Ho and McKay 1998):

$$t/q_t = \frac{1}{k_2 q_e} + \frac{1}{q_e t} \tag{3}$$

where k_2 [(g/(mg min)] is the rate constant for the pseudo-second-order model. In this case, if the plot of t/q_t versus t is linear, this indicates that the pseudo-second-order kinetic model is applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

Finally, the intra-particle diffusion equation may be expressed as (Weber and Morris 1963):

$$q_t = k_w t^{1/2} + c \tag{4}$$

where k_w [mg/(g $\mathrm{min}^{1/2}$)] is the rate constant for the intra-particle diffusion model. The values of k_w and c can be determined from the slope and intercept, respectively, of the linear plot of q_t versus $t^{1/2}$.

The values of the sorption rate constants k_1 and k_2, the predicted value of q_e and the respective correlation coefficients for the pseudo-first-order and pseudo-second-order models are listed in Table 2. The value of q_e determined from the pseudo-first-order model is not in good agreement with the experimental value. Hence, the adsorption of furfural onto organobentonite did not occur via a pseudo-first-order reaction. In contrast, the value of the correlation coefficient obtained for the pseudo-second-order model (0.995) is higher than that of the pseudo-first-order model (0.964), with the calculated and experimental values of q_e being close to each other. This indicates that the pseudo-second-order kinetic model provided a good correlation for the adsorption of furfural onto organobentonite. In the application of the intra-particle diffusion model, it was found that although the plots of q_t versus $t^{1/2}$ were linear they did not pass through the origin (see values of k_w, c and R^2 listed in Table 2). This finding indicates that the boundary layer effect, which is the basis of intra-particle diffusion, was not the only limiting-rate step. However, it is possible that other kinetic models operating simultaneously could control the rate of adsorption.

The results obtained from studies of the influence of pH on the adsorption of the furfural onto CTAB–bentonite indicated that this factor was of little importance in this case.

TABLE 2. Parameters of Various Models Applied to the Adsorption Kinetics of Furfural onto CTAB–Bentonite

Experimental	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		
q_e (mg/g)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 [(g/(mg min)]	q_e (mg/g)	R^2	k_w [mg/(g $\mathrm{min}^{1/2}$)]	c (mg/g)	R^2
13. 4	0.0085	7.18	0.964	0.047	13.92	0.995	0.4209	5.7591	0.973

3.5. Isothermal studies and the influence of temperature

Figure 5 presents the influence of temperature on the sorption isotherms of furfural from water onto CTAB–bentonite at 80% saturation of the CEC value of the organobentonite. It will be seen from the figure that this adsorption process produced a linear isotherm ($R^2 = 0.98$) which corresponds to the C-type isotherm in the Giles classification (Giles *et al.* 1960). This indicates that sorption occurred via the partition of furfural between the aqueous solution phase and the organobentonite phase formed by conglomeration of the alkyl chains of the CTAB cations. Similar results have been obtained previously for the adsorption of furfural by hydrophobic resins, where the corresponding plot was linear over the 0.1–1.0% concentration range of furfural (Weil *et al.* 2002).

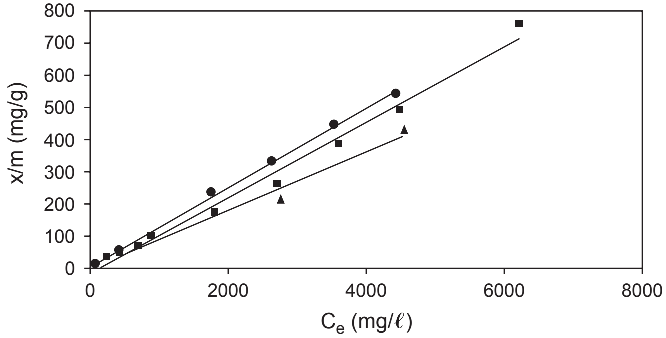

Figure 5. Effect of temperature on the adsorption isotherms for furfural onto CTAB–bentonite. Data points relate to the following temperatures: ■, 14 ºC; ●, 30 ºC ; ▲, 60 ºC.

The CTAB–bentonite isotherm data may be fitted by the linear isotherm model:

$$q_e = K_d C_e \tag{5}$$

where K_d is the sorption distribution coefficient which is equal to the slope of the sorption isotherm. In the present studies, K_d was equal to 0.116 ℓ/g.

The equilibrium adsorption isotherm is most important for understanding the mechanisms of adsorption systems. For the adsorption of organic contaminants onto organobentonites, two types of interactions occur between polar organic compounds and organobentonites, adsorption and partition, associated with the interfacial behaviour of organic compounds in the organobentonite/water system and related to the organic matter content and mineral surface, respectively, of the system. Surface adsorption may include ion-exchange, protonation, hydrogen bonding and coordination/ion–dipole reactions with clays.

Partition involves interactions between organic matter and NOCs. When a large organic molecule, such as hexadecyltrimethylammonium bromide (HDTMAB), interacts with bentonite, the partition process plays an important role. In this case, the adsorption of organic contaminants is conceptually similar to the dissolution of organic contaminants in a bulk-phase organic solvent. This mechanism arises from the change in surface properties from hydrophilic to hydrophobic because the long tails of the organic molecules form a hydrophobic phase in the organobentonite interlayer (Rawajfih and Nsour 2006).

Several researchers have also observed linear isotherms in the sorption of non-ionic organic compounds such as benzene and toluene onto HDTMAB clays (Boyd *et al.* 1988b; Zhu *et al.* 1998; Smith *et al.* 2003), indicating that the removal of organic compounds from solution via HDTMA–bentonites occurs typically through a partitioning process.

From the results depicted in Figure 5, it will be seen that a decrease occurred in the rate of furfural adsorption onto CTAB–bentonite at temperatures above 30 ºC. Increasing temperature has a negative influence on the adsorption capacities of adsorbents due to desorption of the adsorbate molecules at the adsorbent/solution interface. Similar effects of concentration and temperature have been observed by other authors (Freitas *et al.* 2007).

The uptake of furfural by CTAB–bentonite decreased with increasing temperature, which indicates that the adsorption process was probably exothermic. This may be attributed partly to the weakening of the attractive forces between furfural molecules and adsorbent sites (Özcan *et al.* 2005). The decrease in adsorption capacity of CTAB–bentonite at higher temperatures may also be attributed to the tendency of furfural molecules to escape from the solid phase into the bulk aqueous phase as the temperature of the system increases. This effect can be explained by assuming that, at higher temperatures, the total energy of the adsorbate molecules increases so that their tendency to desorb also increases; hence, the overall adsorption of the adsorbate species decreases. These findings suggest that low temperature would favour the adsorption of furfural, and indicates that the mechanism associated with the removal of furfural onto CTAB–bentonite is physical in nature. As a consequence, the adsorption equilibrium capacity is dependent on the temperature (Özcan *et al.* 2004).

This observation is in agreement with the results obtained for the hydrophobic polymers XAD-4 and XAD-7 (Weil *et al.* 2002). In this case, the authors reported that the best equilibrium conditions were also achieved at 30 ºC. These results may indicate that the predominant mechanism operating in the adsorption of furfural onto the three materials concerned (XAD-4, XAD-7 and CTAB–bentonite) was hydrophobic attraction.

3.6. Comparison of the furfural adsorption capacities of several adsorbents

The adsorption isotherms of furfural onto CTAB–bentonite and the polymeric adsorbents XAD-4 and XAD-7 are depicted in Figure 6. All these adsorption isotherms were determined for natural solution pH values at 30 ºC.

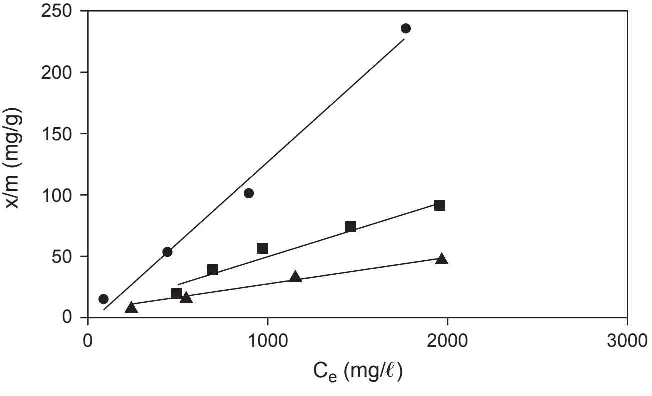

Figure 6. Comparison between the adsorption isotherms of furfural onto (●) CTAB–bentonite, (■) XAD-4 and (▲) XAD-7. Experimental conditions: natural pH values; $C_e \approx 2$ g/ℓ; temp. = 30 ºC.

As seen from Figure 6, CTAB–bentonite had the highest capacity for the adsorption of furfural relative to XAD-4 and XAD-7. Thus, at an equilibrium solution concentration of ca. 2 g/ℓ of furfural, CTAB–bentonite had an equilibrium adsorption capacity of ca. 235.6 mg furfural per g adsorbent compared to ca. 90 mg and 45 mg furfural per g dry XAD-4 and XAD-7 resin, respectively (Weil *et al*. 2002). This indicates that the furfural adsorption capacities decreased in the following order: CTAB–bentonite > XAD-4 > XAD-7.

Table 3 summarizes the best equilibrium loading for the adsorption of furfural on these different adsorbents, on activated carbon GAC (Lin *et al*. 2009) and on the nanoporous adsorbent MCM-48 (Anbia and Mohammadi 2009).

TABLE 3. Comparison of the Adsorption of Furfural onto Various Adsorbents

Adsorbent	Temp. (ºC)	Model	Capacity (mg/g)	References
GAC	–	Langmuir	374.4	Lin and Juang (2009)
MCM-48	–	Langmuir	196.1	Anbia and Mohammadi (2009)
XAD-4	30		90	Weil *et al*. (2002)
XAD-7	30		80	Weil *et al*. (2002)
CTAB–bentonite	30		536.3	Present study

It should be noted that the adsorption capacities of the adsorbents presented here vary significantly. They depend on the characteristics of the individual adsorbent, the extent of chemical modification and the solute concentrations employed.

5. CONCLUSIONS

The surface of natural bentonite was modified with the large organic cation cetyltrimethylammonium bromide (CTAB) in order to improve its capacity for the removal of furfural from aqueous solutions. FT-IR and XRD analyses confirmed the presence of the quaternary ammonium group in the interlayer space and suggested a bimolecular layer arrangement. The results of surface area and CEC estimations of the organobentonite showed that these values were smaller relative to that of sodium bentonite. Experimental results show that the adsorption of furfural increased as the amounts of CTAB incorporated into the adsorbent increased. This was attributed to an increase in the organic carbon content and in the interlayer spacing of the organobentonite. At adsorbent dosages greater than the CEC of bentonite, the amount of furfural removed diminished. The optimum contact time was ca. 6 h. The kinetic data for the adsorption process were well fitted by the pseudo-second-order and intra-particle diffusion models. However, intra-particle diffusion was not the sole rate-limiting step. The organophilic clay CTAB–bentonite provides a non-polar organic partitioning medium as a result of the conglomeration of flexible alkyl surfactant chains. It was found that the adsorption isotherm of furfural onto CTAB–bentonite was linear, with adsorption being favoured at lower temperatures. Surface modification of smectite clays by surfactants (CTAB–bentonite) offers a high adsorption capacity and an easy method for adsorbing large amounts of furfural. Thus, the immobilized interlayer surfactant species can be employed advantageously to concentrate and recover toxic species from petrochemical effluents.

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