



Structural characterisation of Arquad[®] 2HT-75 organobentonites: Surface charge characteristics and environmental application

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ARTICLE INFO

Article history:

Received 29 December 2010

Received in revised form 3 August 2011

Accepted 7 August 2011

Available online 12 August 2011

Keywords:

Bentonite

Arquad[®] 2HT-75

Organoclay

Surface charge

Adsorption

ABSTRACT

Organoclays are increasingly being used to remediate both contaminated soils and waste water. The present study was attempted to elucidate the structural evolution of bentonite based organoclays prepared from a commercially available, low-cost alkyl ammonium surfactant Arquad[®] 2HT-75. XRD, FTIR, SEM and zeta potential measurement were used to characterise the organoclays. In particular, the relationship between surface charge characteristics of the organoclays and their ability to remediate organic contaminants such as phenol and *p*-nitrophenol was investigated. The investigation revealed that the arrangement and conformation of surfactant molecules in the bentonite became more regular, ordered and solid-like as of Arquad[®] 2HT-75 loading increased. This also led to the formation of a positive zeta potential on the surface of organobentonites prepared with 3.57:1 and 4.75:1 surfactant–clay (w/w) ratio. The zeta potential values decreased with increasing pH of the suspension. The adsorption data of phenol and *p*-nitrophenol were best fitted to Freundlich isotherm model. The adsorption was controlled by multiple mechanisms of partitioning, physico-sorption and chemisorption. The outcomes of this study are useful for the synthesis of low cost organobentonite adsorbents for the remediation of ionisable organic contaminants such as phenol and *p*-nitrophenol from waste water.

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1. Introduction

Organoclay is often prepared by modifying natural clay mineral with quaternary ammonium surfactant. During this preparation, the hydrated cations (Na⁺, K⁺, Ca²⁺, Mg²⁺), which neutralise the excess negative charge evolving due to isomorphous substitution in the silicon tetrahedra and/or aluminium octahedra, are replaced by the quaternary ammonium cations in the clay interlayer. The quantity of surfactant molecules in excess to the cation exchange capacity (CEC) of clay mineral can incorporate into the clay structure by aggregation of organic molecules through mechanisms such as van der Waals interaction and hydrophobic bonding [1,2]. As a result, the natural clay minerals that are intrinsically hydrophilic in nature become hydrophobic. These modified clay products are extensively used in nanocomposites synthesis and adsorbent development.

Organoclays are prepared from a range of clay minerals and alkylammonium surfactants. Arquad[®] 2HT-75 is one of the surfactants which is commercially available and inexpensive, but

not been much studied for organoclay preparation. Chemically Arquad[®] 2HT-75 is di(hydrogenated tallow) dimethylammonium chloride (~75%) with 2-propanol (~14%) and water (~11%) impurity. Tallow is a hard fat consists chiefly of glyceryl esters of oleic, palmitic, and stearic acids (16–18 carbon chains) and extracted from fatty deposits of animals, especially from suet (fatty tissues around the kidneys of cattle and sheep). This surfactant does not have an accurate molecular weight because of the impurities and homologs present in it. Recently we demonstrated that Arquad[®] 2HT-75 is much less toxic to soil inhabiting microorganisms than other most widely used surfactants namely, hexadecyl trimethylammonium bromide (HDTMA) and octadecyl trimethylammonium bromide (ODTMA) [3]. The sorption behaviour of Arquad[®] 2HT-75 in soils also differs from that of HDTMA and ODTMA [3]. Being comparatively less toxic to soil microorganisms, Arquad[®] 2HT-75 derived organoclays might be more suitable for contaminant degrading microbes to thrive on them and thus successful development of bio-reactive organoclays [2]. Bio-reactive organoclay can serve dual functions of contaminant immobilisation and subsequent biodegradation or biotransformation by the microorganisms growing on the adsorbents [2].

Organoclays are proven technology for remediation of both organic and inorganic contaminants by adsorption [2,3]. Bentonite based Arquad[®] 2HT-75 organoclay was successfully used

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for adsorptive removal of hexavalent chromium from aqueous system under environmental conditions [4]. However, for the elucidation of mechanisms of interaction between organoclay adsorbent and the target contaminants in the environment, it is very much necessary to study the structural evolution of the modified clay adsorbents. The complete knowledge about the structural behaviour of the organoclays will also help to decide subsequent other use of the materials such as nanocomposites or catalysts synthesis. In this paper we report the preparation of organobentonites using various loading rates of Arquad® 2HT-75 and structural characteristics evolution of the clay products. We also present the surface charge behaviour of these modified clay minerals and their application for the adsorption of phenol and *p*-nitrophenol in the environment. These contaminants are frequently released into the environment from pesticides, dyes and pigments, polymer engineering, olive processing, petrochemicals and pharmaceutical industries and hence need remediation consideration.

2. Experimental

2.1. Materials and preparation

A locally available bentonite (QB) was used in this study. It was passed through a 300 μm sieve before use. The cation exchange capacity of the bentonite ($66.7 \text{ cmol}(\text{p}^+) \text{ kg}^{-1}$) was determined by the ammonia electrode method [5]. The dominant inorganic cation in the bentonite was Ca^{2+} . Arquad® 2HT-75 was purchased from Sigma–Aldrich, Australia. The loadings of surfactant for modification were adjusted as 0.60:1, 1.2:1, 1.79:1, 2.38:1, 3.57:1 and 4.75:1 surfactant–clay (w/w) ratio for QB-Aq1, QB-Aq2, QB-Aq3, QB-Aq4, QB-Aq5 and QB-Aq6, respectively. The organoclays were prepared in a cation exchange reaction at mildly elevated temperature (80°C) as reported earlier [4,6,7]. The required quantity of surfactant was dissolved in 500 mL deionised water on a magnetic stirrer heated to 80°C . Then 30 g clay ($\leq 300 \mu\text{m}$ size fraction) was added to it and the mixture was stirred continuously for 5 h. The reaction temperature was maintained at 80°C . Care was taken while stirring so that excess spume did not form during the reaction. Later, the organoclay was separated from the mixture by centrifugation and was washed several times with deionised water until a negative result for the presence of chloride was obtained with AgNO_3 . The organoclays were then dried at 60°C for 24 h in a hot air oven and crushed into powders in agate mortars. They were stored under moisture free conditions for further use.

2.2. Material characterisation

X-ray diffractograms of powdered QB and the organoclays were obtained using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) on a Lab X, XRD-6000, Shimadzu diffractometer (Shimadzu Corporation, Japan) operating at 40 kV and 30 mA between 1.5 and 65° (2θ) at a step size of 0.016° . The basal spacing (d) was calculated from the 2θ value using Bragg's equation. Infrared (IR) spectra were obtained using a Magna-IR™ spectrometer 750 (Nicolet Instrument Corp., USA) equipped with liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector and DRIFT (Diffuse Reflectance Infra-red Fourier Transform) accessories. Spectra over the 4000 – 400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm s^{-1} . The band component was analysed using PeakFit v4.12 software package (Hearne Scientific Software). Also, morphology of the organoclays was examined by a Philips XL30 FEG scanning electron microscope (SEM). The finely ground clay products were dried at room temperature and then coated with platinum under vacuum in argon atmosphere for the SEM studies. The surface charge behaviour of the organoclays was determined

from their zeta potential values in aqueous suspension (0.01% w/v) at pH values ranging from 2 to 12. Zeta potential was measured on a Malvern Zetasizer Nano instrument (Malvern Instruments, USA). Total organic carbon (TOC) in the organoclays was determined by high temperature combustion in an atmosphere of oxygen using a Leco CNS-2000. Carbon was converted to CO_2 and determined by infrared detection [8].

2.3. Adsorption study

To test the adsorption of phenol and *p*-nitrophenol onto organoclays, batch experiments were conducted by equilibrating 0.1 g of adsorbent with 10 mL of aqueous phenol and *p*-nitrophenol solution separately in 40 mL centrifuge tube. The initial concentration of phenol and *p*-nitrophenol in the reaction mixture ranged from 50 to 700 mg L^{-1} and 50– 1500 mg L^{-1} , respectively. The mixture was continuously agitated on an end-over-end shaker for 4 h. Preliminary experiment showed that the adsorption of phenol and *p*-nitrophenol onto these organoclays reach equilibrium within 2 h of agitation. The batch adsorption was started at an initial pH value very close to neutral (pH 6.7–7). However, after 2 h of agitation the pH of the adsorption mixtures varied from 6.9 to 7.5. The increase in pH was not affected by the concentration of *p*-nitrophenol in the adsorption mixtures, but was more prominent for the organoclays prepared with surfactant concentration greater than the CEC of the bentonite. All adsorption experiments were carried out in triplicate in deionised water without any background electrolyte. The solute-adsorbent mixture was centrifuged at 11,000 rpm for 10 min to separate the sorbent from the liquid. Then the concentration of phenol and *p*-nitrophenol in the supernatant was analysed on an Agilent 8453 UV–vis Spectrophotometer (Agilent Technologies, Japan) at 270 and 317 nm wavelength, respectively. The pK_a of *p*-nitrophenol at 25°C is 7.15. Above pH 7.15, molecular *p*-nitrophenol dissociates into *p*-nitrophenol anion and gives yellow colour which causes a shift of the absorption peak (K_{max}) from 317 nm to 400 nm [6]. For this reason, all the aliquots (following separation of the adsorbents by centrifugation) including the standards were mildly acidified with a drop of 0.5 M HCl immediately before spectrophotometric measurement of *p*-nitrophenol at 317 nm [9]. The quantity of phenol and *p*-nitrophenol adsorbed was calculated using the following equation:

$$q_e = V \frac{(C_i - C_e)}{(M \times 1000)} \quad (1)$$

where, q_e is the amount of solute adsorbed on the adsorbent (mg g^{-1}), C_i the initial liquid phase concentration of the solute (mg L^{-1}), C_e the equilibrium liquid phase concentration of the solute (mg L^{-1}), V the volume of liquid phase (mL) and M the mass of the adsorbent (g).

2.4. Statistical analysis

The fitness of the adsorption data into isothermal model was tested by SPSS version 18 (SPSS Inc., Chicago, USA) packages. The distribution of residues after model fitting was checked as described by Draper and Smith [10].

3. Results and discussion

3.1. Characterisation of the organobentonites

3.1.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction patterns of the unmodified bentonite and its organoclays. The basal spacing of unmodified bentonite was 15.03 \AA . As observed in Fig. 1, the X-ray diffraction reflections of the organoclays shifted towards lower 2θ values

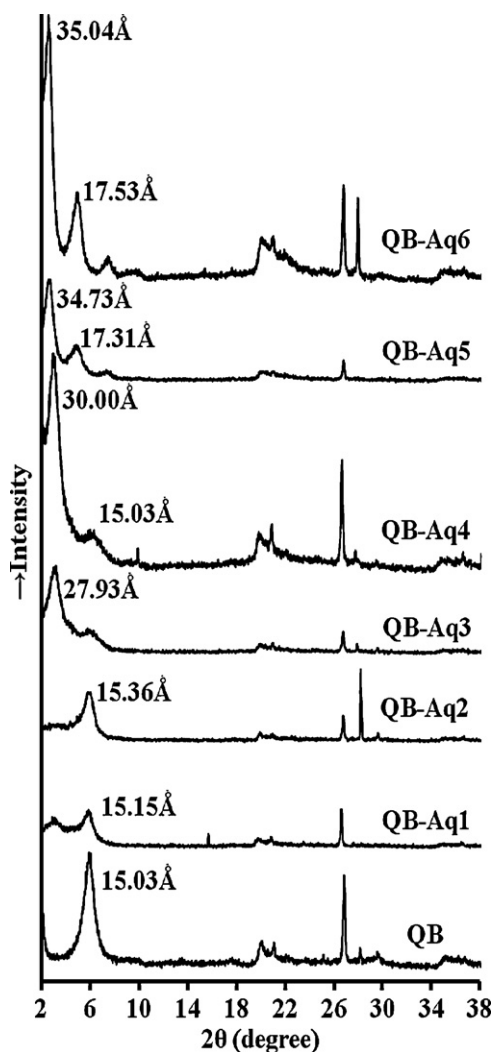


Fig. 1. X-ray diffraction patterns of bentonite and the Arquad® 2HT-75-modified organobentonites.

as the loadings of surfactant in the organoclays increased. The corresponding d values of all the organobentonites are shown in Fig. 1. It is apparent from Fig. 2 that the gradual increase in surfactant density in the clay interlayer resulted in a corresponding increase in the basal spacing from 15.15 Å to 35.04 Å for QB-Aq1, QB-Aq2, QB-Aq3, QB-Aq4, QB-Aq5 and QB-Aq6. We modified QB with Arquad® 2HT-75 which does not have an accurate molecular weight due to the presence of impurities and homologs. For this reason, the calculation of exact loadings of the surfactant in the QB interlayer was not possible to explain in terms of clay CEC. Rather we used the surfactant–clay (w/w) ratio of 0.60:1, 1.2:1, 1.79:1, 2.38:1, 3.57:1 and 4.75:1 to obtain organoclays QB-Aq1, QB-Aq2, QB-Aq3, QB-Aq4, QB-Aq5 and QB-Aq6, respectively. The corresponding TOC contents of the organoclays were 6.9%, 12.5%, 17.4%, 21.7%, 28.1% and 30.6%, respectively. Fig. 2 also shows that the basal spacing for QB-Aq2 (12.5% TOC) was slightly higher than QB-Aq1 (6.9% TOC). Thereafter, for QB-Aq3 (17.4% TOC) and QB-Aq4 (21.7% TOC) the basal spacing increased sharply and then arrived to almost a plateau for QB-Aq5 (28.1% TOC) and QB-Aq6 (30.6% TOC). The basal spacing (d_{001}) give details of arrangement of surfactant molecules in the organoclays [11–14]. Xi et al. [11] described that (a) at surfactant concentrations equivalent to 0.2–0.4 CEC of the bentonite clay mineral, lateral monolayer and lateral bilayer conformation is formed, (b) at 0.6–0.8 CEC modifications, lateral bilayer

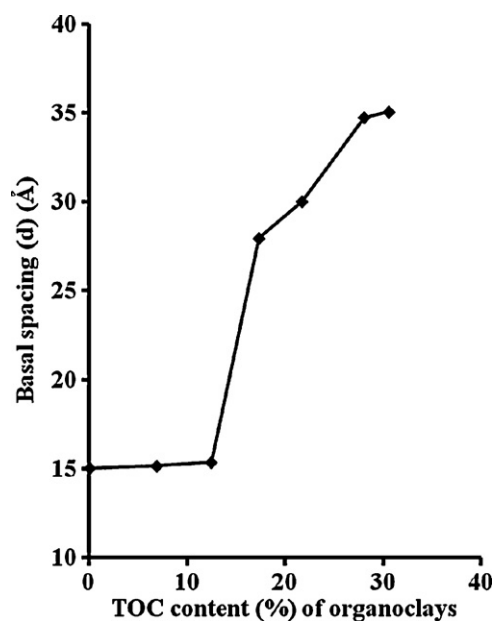


Fig. 2. Changes in the basal spacings (d) of bentonite and the Arquad® 2HT-75-modified organobentonites with increasing TOC contents (%).

arrangement is obtained and (c) above 1 CEC, pseudo-trilayer or paraffin layer orientation is formed. However, this model is applicable for the structure of organoclays prepared with surfactants having only single alkyl tail. Arquad® 2HT-75 used in the present study contains di(hydrogenated tallow) dimethylammonium chloride which has two long alkyl chains. Xu and Zhu [14] observed the typical d spacing of 15.1 Å (0.1–0.5 CEC) and 37.1 Å (0.5–0.7 CEC) for organobentonites prepared with two alkyl tail containing surfactant dioctadecyl dimethylammonium (DODMA). They [14] suggested formation of a flat monolayer arrangement for DODMA⁺ chains in the organobentonite at low surfactant loadings where the two alkyl chains linked to the same N-atom of DODMA⁺ both laid parallel to the silicate plane. They also proposed that a paraffin-type bilayer with a tilt angle of 33° to the silicate planes was the predominant arrangement of adsorbed DODMA⁺ at high surfactant contents [14]. In the present study, QB-Aq1 and QB-Aq2 might produce lateral monolayer conformation, whereas QB-Aq3 and QB-Aq4 might reflect formation of lateral bilayer conformation [14–16]. QB-Aq5 might produce paraffin type bilayer in the clay interlayer [14–16]. At further higher surfactant concentration, QB-Aq6 could give rise to more flattened plate formation resulting from interactions between surfactant alkyl chain–silicate surface and the alkyl chain–alkyl chain of the alkyl ammonium cation [11–13,15]. Such regular stacking of the surfactant molecules in the clay interlayer is further supported by the appearance of higher order of peaks (002 and 003 planes) in the XRD patterns [4,12]. Fig. 1 clearly shows that QB-Aq4, QB-Aq5 and QB-Aq6 produce 002 peaks at 15.03, 17.31 and 17.53 Å, respectively. Given a double chain cationic surfactant was used to prepare organoclay, evolution of two expansions at each of the surfactant loading levels was proposed due to the existence of two structural arrangements of the surfactant molecules in the clay interlayer [15,17]. Although Xu and Zhu [14] used a surfactant (DODMA) with well defined chain length (double chain) and accurately known molecular weight (630.95) to propose the above mentioned organoclay structure, the organobentonites prepared with Arquad® 2HT-75 would also produce a similar arrangement pattern of the surfactant molecules in the clay minerals due to the fact that Arquad® 2HT-75 is also a double chain surfactant having comparable equivalent mass (576) with DODMA.

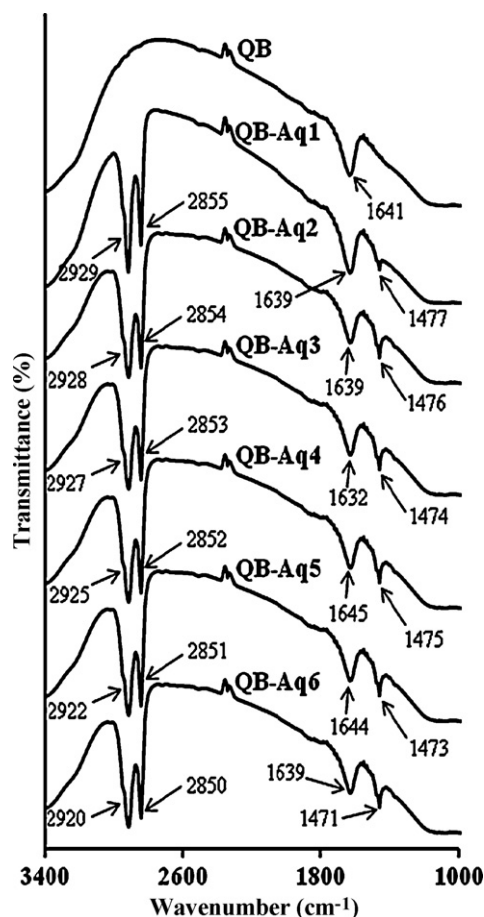


Fig. 3. FTIR spectra of bentonite and the Arquad® 2HT-75-modified organobentonites.

3.1.2. FTIR characterisation of the organoclays

Fig. 3 shows FTIR spectra of QB and the organoclays. The IR spectra were presented in two distinguished regions. The peaks appearing as the signature of CH_2 stretching vibration (both symmetric and asymmetric) and CH_2 bending vibrations are shown in Fig. 3. The bands appearing at $3000\text{--}2800\text{ cm}^{-1}$ region were indicative of the ordering (*gauche/trans* conformer ratio), packing density of the surfactants in organoclays and the interactions between the alkyl chains [4,6,18,19]. As shown in Fig. 3, the CH_2 asymmetric stretching vibration (ν_{asy}) appeared at region ranging $2929\text{--}2920\text{ cm}^{-1}$ wave number for the six organoclays studied, whereas CH_2 symmetric stretching vibration (ν_{sy}) for them appeared at $2855\text{--}2850\text{ cm}^{-1}$ wave number. Both of these peak regions did not appear in unmodified QB. As the distinctive feature of the spectra it appeared that there was a shift for ν_{asy} and ν_{sy} bands towards a lower frequency as the surfactant loading rate (TOC contents in organoclays) increased, which was indicative of highly ordered all-*trans* conformations of Arquad® 2HT-75 in the QB structure [19–21]. In addition, the CH_2 bending vibration bands for the organoclays appeared at wave numbers $1477\text{--}1471\text{ cm}^{-1}$ and here also the shift of bands towards lower frequency with increasing surfactant loadings (TOC contents in organoclays) was prominently observed. The spectral position of these peaks shown by QB-Aq6, the organoclay prepared with maximum surfactant loading density, had been exactly similar to that of pure Arquad® 2HT-75. It implies that the conformation of the adsorbed surfactant molecules in the organoclays progressively develops from low packing density and ordering (liquid like) to high packing density and ordering (solid like) [4,6]. Fig. 3 also shows an IR peak appearing

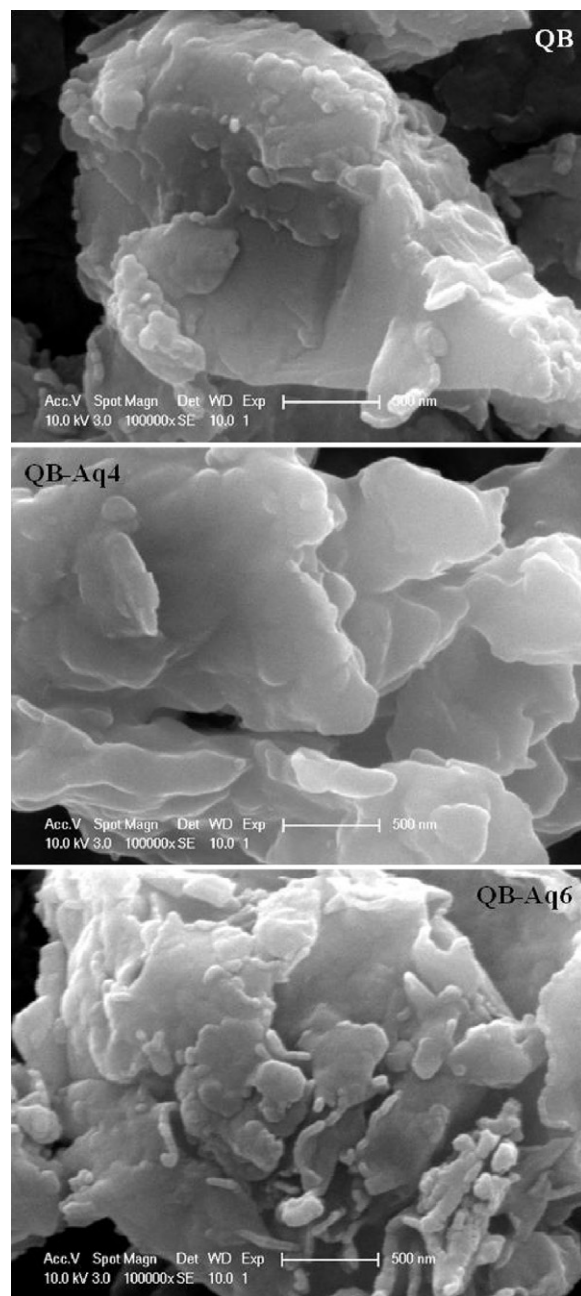


Fig. 4. SEM micrographs of bentonite and the Arquad® 2HT-75-modified organobentonites.

for QB and the organoclays within $1639\text{--}1645\text{ cm}^{-1}$ region which could be attributed to OH deformation vibration [22]. However, no additional structural information of the organoclays could be obtained from this peak as they did not follow any particular trend.

3.1.3. SEM characterisation of the organoclays

SEM study indicated that the morphological differences among the prepared organoclays were not significantly observable. Fig. 4 shows the SEM micrographs of QB, QB-Aq4 and QB-Aq6. It was found that unmodified QB showed massive and aggregated morphology with little number of flakes, whereas the organoclays had less aggregated morphology with large amount of flakes with curled and crumpled structure. As the surfactant density in organoclay increased, the number of flakes also increased, but became more flat in appearance (Fig. 4). The surfactant modification of

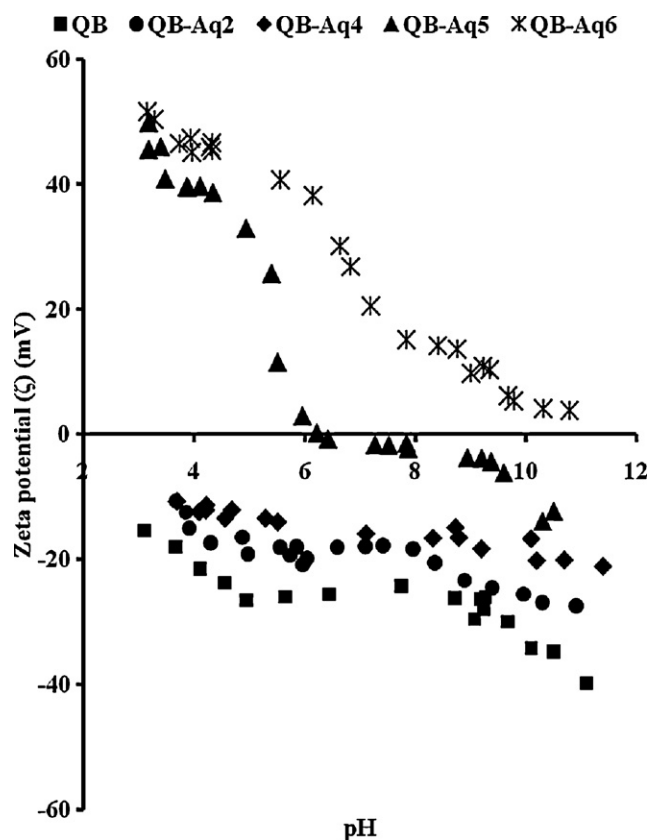


Fig. 5. Changes in the zeta potentials (ζ) of bentonite and the Arquad® 2HT-75-modified organobentonites as a function of pH.

the bentonite might cause fragmentation of the flakes and thus enhance adsorption of contaminants.

3.1.4. Surface charge characteristics of the organoclays

There is limited information in the literature on the relationship between surface charge characteristics of organoclays and contaminant adsorption. In our previous investigations we reported that organopalygorskites prepared with 200% CEC equivalent surfactant concentration could produce positive surface charge and enhance *p*-nitrophenol adsorption [6,23]. We also reported that zeta potential (ζ) values of bentonite modified with Arquad® 2HT-75 at high concentration could reach as high as 51.1 mV at pH ~ 4 as compared to -21.3 mV measured for unmodified QB [4]. In this study we investigated in detail the surface charge behaviour of Arquad® 2HT-75 modified organobentonites as a function of pH. Positive ζ was formed on the surface of organobentonites when the TOC contents were 28.1% and 30.6% (QB-Aq5 and QB-Aq6) (Fig. 5). When the concentration of surfactant in organoclays exceeded the CEC of the clay (as observed from the increasing TOC contents), the excess surfactant molecules adhered to the surface-adsorbed surfactant cations by van der Waal forces [11]. Because of the presence of cationic surfactant molecules in excess to the CEC of the clay mineral covering the total internal and external surface of the bentonite, the resultant organoclays exhibited positive surface charge [6,23,24]. Bate and Burns [25] also reported that the ζ values of organomontmorillonites became less negative as the total organic carbon (surfactant concentration) and the length of attached carbon chain increased. It was attributable to the hydrophobicity of the organoclay, which increased the hydrophobic lateral interaction between surfactant cations giving positive charge within the shear plane [25]. As Arquad® 2HT-75 contains glyceryl esters of oleic, palmitic, and stearic acids (16–18 carbon chains) [1], the longer

chains of the tallow compound led to stronger lateral interaction binding more cations within the shear plane [23–25].

In all the organoclays and unmodified QB, ζ values decreased with increasing pH of the suspension (Fig. 5). Only QB-Aq6 (30.6% TOC) could maintain positive ζ values over the whole range of pH studied (pH 2–12). QB-Aq5 (28.1% TOC) also maintained positive ζ values at pH range 2–6 after which it developed negative surface charge. The ζ values of all other organobentonites were negative over the entire pH range studied and the values became more negative as the pH increased. As indicated by the slope of the ζ vs. pH graphs, the ζ values were less sensitive to the change of pH as the contents of surfactant (TOC) decreased in the organoclays, which is supported by Bate and Burns [25]. The effect of pH on the ζ values of the organoclays might depend on the interactions between surfactant cation and the clay mineral surface. By imparting hydrophobic and van der Waals interactions among themselves, the alkyl tails of the surfactant cation shielded the negative charge on the bentonite surface and developed positive charge when the surfactant addition was in excess to the CEC. With the change in pH from the point of zero charge of the bentonite, the dissolution and subsequent release of metals cations increased that in turn changed the interaction between surfactant cations and bentonite surface [25–28].

3.2. Adsorption of phenol and *p*-nitrophenol

We tested the adsorption efficiency of Arquad® 2HT-75 organobentonites for ionisable organic pollutants such as phenol and *p*-nitrophenol. Among various isothermal models tested, the Freundlich model [29] best fitted the adsorption data.

Freundlich model:

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (2)$$

where, C_e is equilibrium adsorbate concentration, q_e is amount of adsorbate adsorbed at equilibrium, K_F and $1/n$ are the Freundlich constants related to adsorption capacity and intensity of adsorption (n is the heterogeneity factor). The Freundlich model implies the bonding energy of the adsorbate on a given surface decreases with fractional coverage of the surface area and in case of heterogeneous surfaces it is closer to reality than the assumption of constant bonding energy [6,28].

Freundlich plot of phenol adsorption is shown in Fig. 6a. The adsorption data of phenol by Arquad® 2HT-75 modified bentonites fitted very well to Freundlich isothermal model. The r^2 values ranged from 0.985 to 0.997 (Table 1). The corresponding F statistics (the degree of reduction of heterogeneity in a population) and p (probability) values also indicated strong fit of the adsorption data to this model (Table 1). The distributions of the model fitting residues were systematic bell-shaped except for the adsorbent QB-Aq1 (figures not shown). The values of $1/n$ and K_F increased gradually with increasing surfactant loadings in the organobentonites (Table 1). The $1/n$ values were less than unity in case of all the adsorbents which indicated that at higher adsorbate concentrations, the filling of total adsorption capacity occurred without increasing the adsorption intensity [6]. The gradually increasing K_F values indicated the increase in affinity of phenol to the adsorbents [6].

Freundlich plot of *p*-nitrophenol adsorption is shown in Fig. 6b. Similar to phenol, *p*-nitrophenol adsorption data also fitted very well to the Freundlich model (Table 1). The model fitting parameters for *p*-nitrophenol indicated stronger affinity of the adsorbate to the organobentonites surface as compared to phenol (Table 1). The distributions of the model fitting residues were bell-shaped for all the adsorbents (figures not shown). However, compared to phenol, *p*-nitrophenol adsorption data showed slight non-linearity

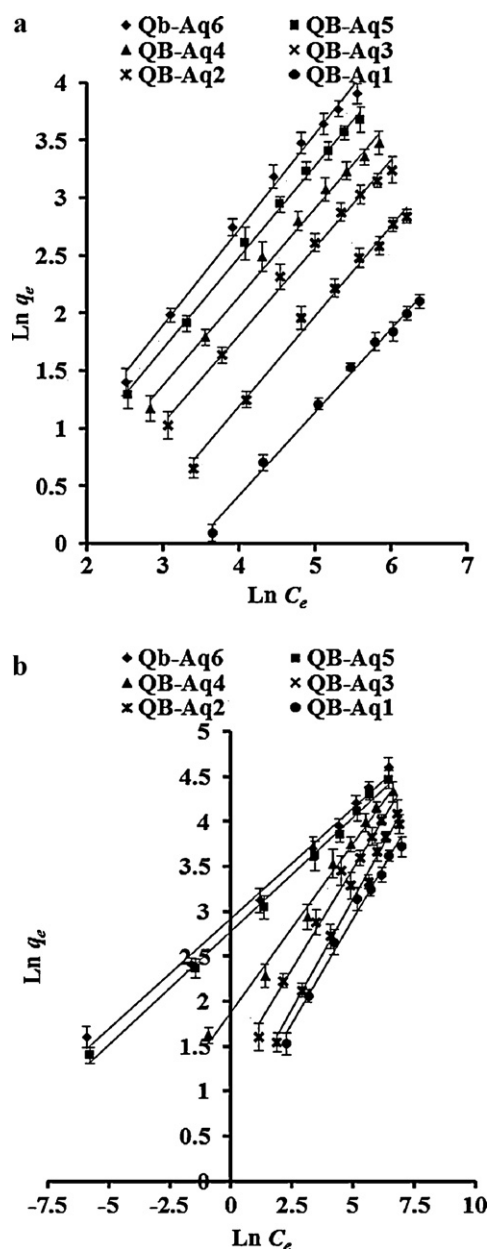


Fig. 6. Freundlich fittings for the adsorption of (a) phenol and (b) *p*-nitrophenol by Arquad® 2HT-75-modified organobentonites. Bars represent standard errors of mean at 95% confidence level ($n=3$).

during model fittings. The K_F values increased remarkably with the increase of surfactant contents (TOC contents) in the adsorbents and reached as high as 19 for QB-Aq6. Such higher K_F value

Table 1
Fitting of the phenol and *p*-nitrophenol adsorption data by the Freundlich model at 95% confidence level.

Sample	Phenol					<i>p</i> -nitrophenol				
	$1/n$	K_F ($L \cdot g^{-1}$)	r^2	F^*	p^*	$1/n$	K_F ($L \cdot g^{-1}$)	r^2	F^*	p^*
QB-Aq1	0.71 ± 0.01^a	0.0913 ± 0.013	0.985	368	<0.0001	0.48 ± 0.008	1.6 ± 0.09	0.978	265	<0.0001
QB-Aq2	0.78 ± 0.006	0.1453 ± 0.019	0.992	715	<0.0001	0.50 ± 0.01	1.9 ± 0.12	0.986	412	<0.0001
QB-Aq3	0.76 ± 0.012	0.2949 ± 0.017	0.993	825	<0.0001	0.45 ± 0.013	3.4 ± 0.23	0.978	271	<0.0001
QB-Aq4	0.77 ± 0.014	0.3953 ± 0.027	0.993	818	<0.0001	0.38 ± 0.016	6.5 ± 0.29	0.993	838	<0.0001
QB-Aq5	0.79 ± 0.017	0.5052 ± 0.025	0.997	2214	<0.0001	0.24 ± 0.027	17.0 ± 0.37	0.986	431	<0.0001
QB-Aq6	0.82 ± 0.013	0.5805 ± 0.033	0.989	525	<0.0001	0.24 ± 0.012	18.8 ± 0.33	0.990	612	<0.0001

* F statistics – the degree of reduction of heterogeneity in a population; p – probability.

^a Standard error at 95% confidence level, $n=3$.

Table 2
Normalized amount of adsorption of phenol and *p*-nitrophenol per percent of carbon incorporated into the organoclays.

Organoclays	TOC content (%)	Normalized adsorption capacity ($mg \cdot g^{-1}$)	
		Phenol	<i>p</i> -Nitrophenol
QB-Aq1	6.9	2.1	6.0
QB-Aq2	12.5	2.5	4.2
QB-Aq3	17.4	2.7	3.4
QB-Aq4	21.7	2.8	3.5
QB-Aq5	28.1	2.9	3.1
QB-Aq6	30.6	3.2	3.3

was indicative of adsorption predominantly through partitioning process [29].

Phenol and *p*-nitrophenol adsorption capacity of the organobentonites was normalized against the TOC content of the modified adsorbents (Table 2). The normalized adsorption capacity of phenol per percent of incorporated carbon gradually increased as the surfactant loadings increased in the organoclays. However, the normalized adsorption capacity of *p*-nitrophenol decreased with increasing surfactant loadings (TOC contents). The relationship between the K_F value and the TOC content in organoclays for phenol adsorption was linear with high correlation coefficient value ($r^2=0.99$ at $p<0.01$). The $1/n$ values also gradually increased (Table 1). However, K_F value for *p*-nitrophenol adsorption maintained a less linear relationship with TOC contents in organoclays ($r^2=0.86$ at $p<0.01$). The results indicated that the mechanism of phenol removal gradually shifted from surface adsorption to partitioning as the TOC contents in the adsorbents increased [30,31], whereas multiple mechanisms such as partitioning, physio-sorption and chemisorption controlled *p*-nitrophenol adsorption [6,22]. Overloading (relative to CEC of the bentonite) of organoclays with surfactants was associated with the appearance of the adsorbed surfactant-anion (halide) pairs such that anion exchange with *p*-nitrophenol anion occurred [6,23]. Evidences exist that the halide counter ions released from the organoclays due to the adsorption of *p*-nitrophenol anion at $pH>7.15$ [6]. This also caused greater non-linearity of the *p*-nitrophenol adsorption isotherms (the reduction of $1/n$ values) as compared to phenol (Table 1).

3.3. Mechanisms of adsorption

QB modified with Arquad® 2HT-75 having long alkyl chain attracted phenol both by adsorption and partition mechanisms [30–32]. Juang et al. [30] proposed adsorption of phenol also by ion exchange on the surfaces of organomontmorillonite. As apparent from the K_F values (Table 1), the affinity of *p*-nitrophenol for the adsorption sites of organobentonites was higher than that of phenol because of the difference in the polarity level of these two contaminants. The adsorption of *p*-nitrophenol to organobentonites

with surfactant contents up to the CEC of the bentonite involved both surface adsorption and partition, whereas its adsorption to organobentonites with surfactant contents in excess to the CEC involved mainly partitioning [11,33]. Adsorption of *p*-nitrophenol by organopalygorskites prepared with surfactant loadings in excess to the CEC of palygorskite occurred through anion exchange also following formation of *p*-nitrophenol anion at higher pH ($\text{pH} > 7.15$) of the adsorption system [6,23]. In one of our previous publication, we reported that *p*-nitrophenol adsorption by organoclays was controlled by multiple mechanisms including hydrophobic bonding, electrostatic attraction and anion exchange (at $\text{pH} > 7.15$) [6,23]. The electrostatic attraction mechanism can come into effect when organoclay possess positive surface charge (ζ) and *p*-nitrophenol anion (after ionisation at $\text{pH} > 7.15$) gets adsorbed thereon [23].

4. Conclusions

Bentonite could be effectively modified with Arquad® 2HT-75. Due to insertion of the surfactant molecule into the clay interlayer the basal spacing of the bentonite gradually increased with increasing surfactant loadings. The arrangement and conformation of surfactant molecules in the bentonite became more regular, ordered and solid-like as the loadings of Arquad® 2HT-75 increased. Positive zeta potential was formed on the surface of organobentonites prepared with 3.57:1 and 4.75:1 surfactant–clay (w/w) ratio where surfactant molecules in excess to the CEC of the clay mineral aggregated on the surface. In all the organoclays and unmodified bentonite the zeta potential values decreased with increasing pH of the suspension. The adsorption capacities of phenol and *p*-nitrophenol improved significantly due to the modification of bentonite with Arquad® 2HT-75. The adsorption data best fitted to Freundlich isothermal model. Predominantly partitioning and adsorption, and to some extent ion exchange and physiosorption were the mechanisms of these contaminants removal by these adsorbents from aqueous solutions. This study illustrates the potential of low cost organobentonite adsorbents for the remediation of ionisable organic contaminants such as phenol and *p*-nitrophenol from contaminated waste water.

Acknowledgement

Binoy Sarkar is thankful to the University of South Australia for the award of University President Scholarship and to the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) for PhD fellowship. The authors would like to acknowledge the financial and infrastructural support from the CRC CARE and the Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia. Suggestions from anonymous reviewers to improve the quality of the manuscript are gratefully acknowledged.

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