



# Remediation of hexavalent chromium through adsorption by bentonite based Arquad® 2HT-75 organoclays

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## ABSTRACT

Unlike hydrophobic organic pollutants, the potential of organoclays to adsorb inorganic ionic contaminants is relatively underexplored. The present study attempts to characterise bentonite (QB) based organoclays synthesised from a commercially available, low-cost alkyl ammonium surfactant Arquad® 2HT-75 (Aq) and test their ability to adsorb hexavalent chromium (Cr (VI)) in aqueous solution. XRD, FTIR and TGA characterisation techniques prove successful modification of the bentonite structure and reveal that higher surfactant loadings gives rise to more ordered surfactant conformation in the organoclays. The zeta potential values indicate that higher surfactant loadings also create positive charges on the organoclay surfaces. Detailed isothermal and kinetic studies show that the organoclays effectively remove hexavalent chromium (Cr (VI)) from aqueous solution by both physical and chemical adsorption processes. Higher surfactant loadings provide better adsorption efficiency. The adsorption performance is reasonably efficient under the levels of pH, temperature, electrolyte concentration and natural organic matter concentration that generally prevail in contaminated soil and water. This study shows that organoclay sorbents offer good potential for remediating Cr (VI) under real environmental conditions.

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## 1. Introduction

The use of chromium in industries is widespread and economically important. It is widely used in industries such as electroplating, alloy and steel manufacturing, leather tanning, metal finishing, pigment and dye synthesis and many others. Chromium commonly enters the environment in the effluents from these industries. Once released into soil and water, it is considered a major cause of environmental pollution. Chromium is listed among the 126 priority pollutants by the US EPA. It is also listed among the 25 most hazardous substances posing the greatest risk to human and ecosystem health at the priority superfund sites [1]. Chromium exists in the environment in two major oxidation states, trivalent (Cr (III)) and hexavalent chromium (Cr (VI)). Of the two, Cr (III) is an essential microelement for living organisms at low concentrations. However, its hexavalent form, which is the most dominant ox-

idation state in natural systems, is seriously toxic when present at concentration as low as 50 ppb in drinking water. Being a cation, Cr (III) is less mobile in the soil environment, whereas anionic Cr (VI) is highly mobile and poses a tremendous risk of ground water pollution. Cr (VI) is a known mutagen and carcinogen, shown to cross the cell membrane readily and convert to forms that can adduct with DNA causing permanent damage to the cells, leading to cancer [2]. Due to its serious environmental and health impact, industrial effluents containing Cr (VI) must be treated as a rule. Several chemical, physio-chemical and biological treatment methods have been developed and implemented for this purpose. Sorption is one of the most popular methods where an engineered sorbent material acts as a sink for the contaminant and so reduces its mobility.

Natural materials such as clays are cost-effective for immobilising toxic environmental contaminants as they are inexpensive, readily available, environmentally stable and have high adsorptive and ion exchange properties. Clay materials can also be modified using a variety of chemical/physical treatments to achieve the desired surface properties for best immobilisation of contaminants. For example, when surfaces of these clays are modified with organic molecules, the resulting products are called organoclays [3–5]. The organic modifiers used for this purpose are generally cationic quaternary amine compounds which are commonly known as surfactants.

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Organoclays have extensively been studied for their unique sorption behaviour towards various hydrophobic organic contaminants in the environment [6–9]. However, these clay-based modified materials can also be used for the remediation of ionic contaminants such as heavy metals [10–14] and metalloids [15–18]. For example, Lin and Juang [12] reported that sodium dodecylsulphate (SDS; an anionic surfactant) modified montmorillonite showed a much more negative zeta potential and exhibited higher affinity for Cu and Zn as compared to the naturally available montmorillonite. In another study, Oyanedel-Craver and Smith [13] found that the sorption of Cd, Pb and Zn by hexadecyltrimethylammonium (HDTMA) and benzyltrimethylammonium modified bentonite was non-linear and the adsorption of metals decreased with the increase in surfactant loadings in the organoclays from 25% to 100% of the CEC of the bentonite. Normally, naturally occurring clays are not efficient sorbents for anions because of their intrinsic negative charge. Although a very small amount of anion sorption can take place with natural clays through physical sorption, anion exchange or electrostatic binding mechanisms, it is neither significant in terms of sorption quantity nor binding strength. So, in order to immobilise anions like chromate and arsenate effectively using these materials, their surfaces are modified to possess enough positively charged sites to bind with the anions. In addition, another mechanism can come into action if the weakly held counter ions of the modifying surfactants are replaced by more strongly held adsorbate counter ions. Some specific alkyl ammonium surfactant cations may impart such favourable surface properties to natural clays to enhance their ability to hold anions. For example, Krishna et al. [16] reported improved adsorption of chromate oxyanion by HDTMA modified kaolinite, montmorillonite and pillared montmorillonite as compared to the unmodified clays. The authors [16] found that the amount of adsorption decreased with increasing pH of the solution. Atia [15] also observed similar results when they used cetylpyridinium modified bentonite to adsorb chromate and molybdate. However, the potential for remediating anionic pollutants using organoclays has yet to be fully explored. There is also a need to study the mechanism of sorption of anionic metalloids onto organoclays and the associated process parameters, so as to predict the performance of the sorbents under field conditions.

This study attempts to characterise bentonite based organoclays synthesised from a commercially available, relatively cheaper alkyl ammonium surfactant Arquad® 2HT-75 and test their adsorption abilities towards hexavalent chromium (Cr (VI)) in aqueous solution. Organic modification of the bentonite clay is established and characterised by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and zeta potential measurement. The resulting sorbents have been tested for sorption of hexavalent chromium from an aqueous solution. Sorption isotherm, kinetics and effect of process parameters such as pH, ionic strength, temperature and dissolved organic carbon (DOC) on sorption have been investigated in details. This study will help in developing novel remediation materials for removing Cr (VI) from various industrial waste waters as well as *in situ* immobilisation of Cr (VI) in contaminated soils and sediments.

## 2. Experimental

### 2.1. Materials and synthesis

The clay used in the present study is a locally available bentonite (QB). The cation exchange capacity (CEC) value of this clay determined by the ammonia electrode method [19] is 66.7 cmol ( $p^+$ )  $kg^{-1}$ . The clay was passed through a 300  $\mu m$  sieve and used without any further purification.

Two organoclays, QB-Aq1 and QB-Aq2, were prepared by modifying Queensland bentonite (QB) with a commercially available, relatively inexpensive surfactant, Arquad® 2HT-75 (Aq). Chemically this surfactant is di(hydrogenated tallow) dimethylammonium chloride (~75%) having 2-propanol (~14%) and water (~11%) as impurities. The surfactant was purchased from Sigma–Aldrich, Australia. Since this surfactant does not have an accurate molecular weight because of the impurities and homologs present, loadings for modification were adjusted as 2.38:1 and 4.75:1 clay–surfactant (w/w) ratio for QB-Aq1 and QB-Aq2, respectively. The organoclays were synthesised in a hydrothermal cation exchange reaction [20]. The required quantity of surfactant was dissolved in 500 mL Milli-Q water on a magnetic stirrer heated to 80 °C. Then 30 g clay ( $\leq 300 \mu m$  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 Milli-Q 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

#### 2.2.1. X-ray diffraction (XRD)

The powdered clay samples, including the organoclays (QB-Aq1 and QB-Aq2) and the starting bentonite clay mineral (QB), were pressed in stainless steel sample holders for XRD analysis. XRD patterns were obtained using Cu K $\alpha$  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° ( $2\theta$ ) at a step size of 0.016°. The basal spacing was calculated from the  $2\theta$  value using Bragg's equation.

#### 2.2.2. Fourier transformed infrared spectroscopy (FTIR)

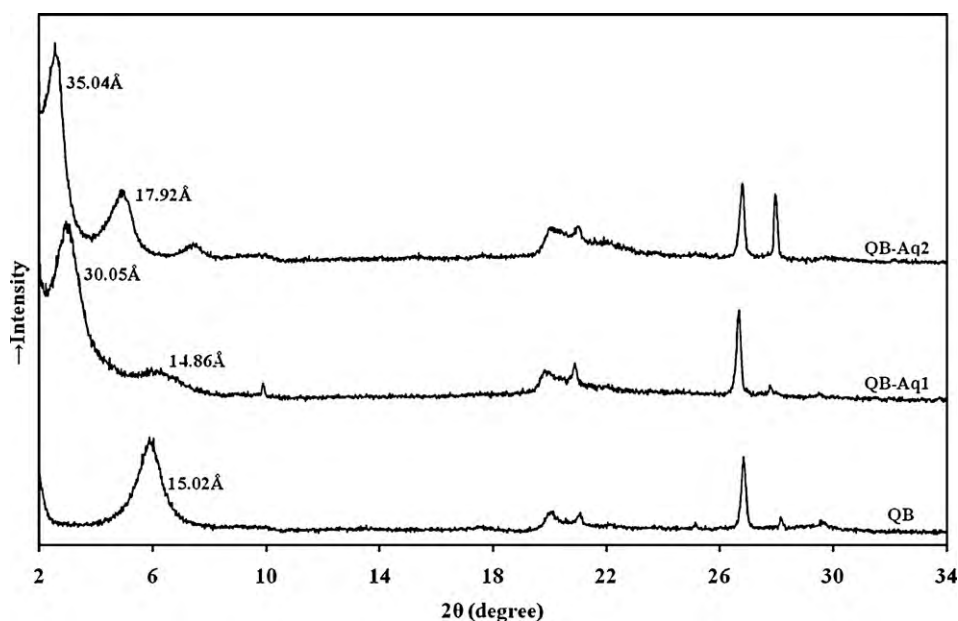
Infrared (IR) spectra were obtained using a Magna-IR™ spectrometer 750 (Nicolet Instrument Corp., USA) equipped with liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector and DRIFT (Diffuse Reflectance Infra-red Fourier Transform) accessories. Spectra over the 4000–400  $cm^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of 4  $cm^{-1}$  and a mirror velocity of 0.6329  $cm s^{-1}$ . PeakFit v4.12 software package (Hearne Scientific Software) was used to undertake band component analysis that enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Gauss–Lorentz cross-product function with the minimum number of component bands was used for band fitting. The fitting was undertaken until reproducible results were obtained with squared correlations ( $r^2$ ) greater than 0.98.

#### 2.2.3. Thermal analysis

The organoclays were characterised by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) on a TGA 2950 Thermal Analysis instrument (Thermal Analysis Inc., USA). The temperature range for TGA was raised at a rate of 10 °C  $min^{-1}$  ranging from 25 to 1000 °C with a resolution of 6.0 °C. Approximately 50 mg of finely ground sample was heated in open platinum crucible. Inert atmosphere was maintained inside the furnace with pure  $N_2$  flowing at 70  $mL min^{-1}$ .

#### 2.2.4. Measurement of zeta potential

Zeta potential of the organoclays (QB-Aq1 and QB-Aq2) and the starting bentonite clay mineral (QB) were measured by a Malvern



**Fig. 1.** X-ray diffraction patterns of the unmodified bentonite (QB) and its organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio).

Zetasizer Nano instrument (Malvern Instruments, USA). Clay samples were suspended in Milli-Q water (0.01%, w/v) for zeta potential measurement.

### 2.3. Adsorption

Batch experiments were carried out to test the adsorption capabilities for Cr (VI) by the synthesised organoclays. The kinetic study was done by equilibrating 0.1 g of sorbent with 20 mL of 50 mg L<sup>−1</sup> aqueous Cr (VI) solution in 50 mL plastic centrifuge tube. The mixture was continuously agitated on a rotary shaker (Ratek Instrument Pty. Ltd., Victoria, Australia) for variable times (5–180 min). The kinetic experiment was carried out at 23 °C temperature. Similarly, adsorption isotherms were also established at concentration of Cr (VI) ranging from 10 to 200 mg L<sup>−1</sup> having a sorbent dose of 5 g L<sup>−1</sup> and an equilibration time of 180 min. All adsorption experiments were carried out in Milli-Q water without any background electrolyte except in the case where effect of electrolyte concentrations was studied. The pH of Cr (VI) solutions in Milli-Q water was around 4.7.

The effect of temperature on the adsorption of Cr (VI) onto organoclays was investigated by carrying out isotherm studies at 18, 23 and 37 °C temperature in a constant temperature room. The influence of pH on the adsorption of Cr (VI) by the organoclays was studied for a fixed concentration of Cr (VI), 50 mg L<sup>−1</sup>, equilibration time of 180 min and sorbent dose of 5 g L<sup>−1</sup>. The experiment was conducted at pH values ranging from 4.0 to 9.0 adjusted with dilute HCl or KOH (0.1 M). Similarly, the effect of electrolyte concentration on the adsorption was studied at ionic strength values ranging from 0.01 to 1.0 adjusted with KNO<sub>3</sub>. Also, the influence of dissolved organic matter (DOM) on the adsorption of Cr (VI) was investigated at dissolved organic carbon (DOC) concentrations ranging from 2 to 23 mg L<sup>−1</sup> supplied as reagent grade humic acid (Sigma–Aldrich). In another experiment, adsorption of Cr (VI) by the organoclays was carried out in the presence of dissolved organic matter in soil (SDOM) extracted from soil in 1:1 soil–water extraction ratio for 24 h. The DOC concentration in the soil extract that had been used in the experiment was 71.30 mg L<sup>−1</sup>.

In all experiments, the solute–sorbent mixture was centrifuged at 11000 rpm for 8 min to separate the sorbent from the liquid. Then the concentration of Cr (VI) or DOC in the supernatant was analysed.

The quantity of Cr (VI) or DOC adsorbed was calculated from the following equation:

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

where,  $q_e$  is the amount of solute adsorbed on the sorbent (mg g<sup>−1</sup>),  $C_i$  is the initial liquid phase concentration of the solute (mg L<sup>−1</sup>),  $C_e$  is the equilibrium liquid phase concentration of the solute (mg L<sup>−1</sup>),  $V$  is the volume of liquid phase (mL) and  $M$  is the mass of the sorbent (g).

### 2.4. Analytical method

Hexavalent chromium (Cr (VI)) in the supernatant was estimated by spectrophotometric methods [21]. In short, 2 mL of the aliquot (after proper dilution) was reacted with 2 mL of 1N H<sub>2</sub>SO<sub>4</sub> and 0.8 mL of the colour developing reagent (4.0 g of phthalic acid and 0.25 g of 1,5-diphenyl carbazide (DPC) in 100 mL of 95% ethanol). The colour intensity was measured at 540 nm wavelength by an Agilent 8453 UV-VIS Spectrophotometer (Agilent Technologies, Japan). DOC in the aliquot was quantified by an OI Analytical 1010 total organic carbon (TOC) analyser (OI Corporation, USA).

### 2.5. Statistical analysis

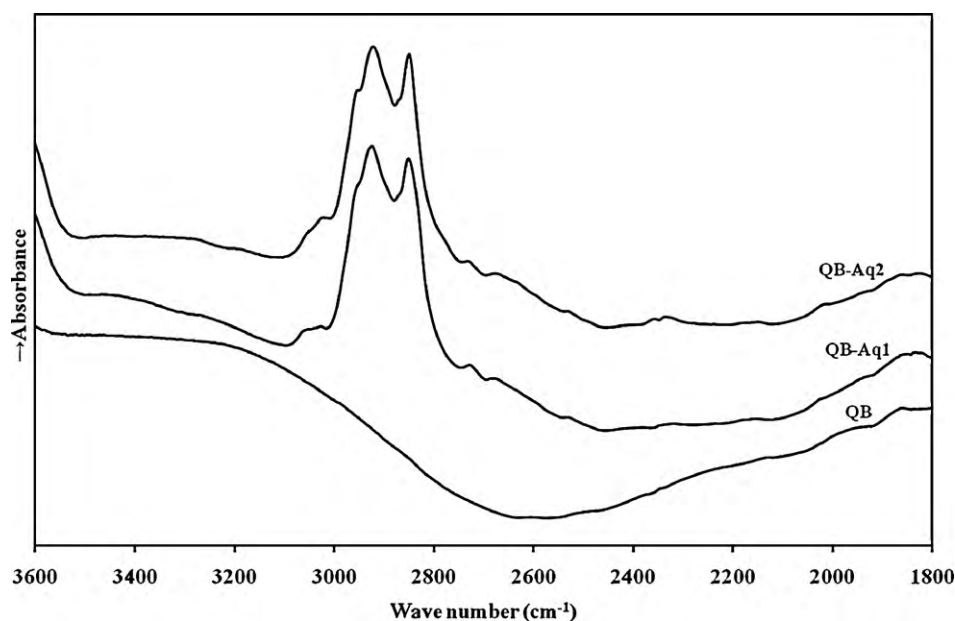
The adsorption data were fitted into a linear regression model to find the regression coefficient ( $r^2$ ) and the corresponding value of  $F$  (degree of reduction of heterogeneity in a population) and  $p$  (probability) using Statistix 8.0 statistical package.

## 3. Results and discussion

### 3.1. Characterisation of the sorbents

#### 3.1.1. X-ray characterisation of the organoclays

The X-ray diffraction patterns of the unmodified bentonite (QB) and the synthesised organoclays are shown in Fig. 1. The main primary diffraction peaks attributed to (001) planes are observed at 15.02, 30.05 and 35.04 Å, respectively, for QB, QB-Aq1 and QB-Aq2. Additionally, the clay products show intense XRD peak at  $2\theta$  value



**Fig. 2.** FTIR spectra of the unmodified bentonite (QB) and its organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio) in the region 3600–1800  $\text{cm}^{-1}$ .

of  $26.8^\circ$ , which is attributed to the presence of quartz as impurity. In the present study, the  $d(001)$  spacing of the unmodified QB is slightly higher ( $15.02 \text{ \AA}$ ) than the value usually reported for natural bentonite ( $\sim 10.0$  to  $12.0 \text{ \AA}$ ), which might be due to excess moisture adsorption during sample storage and the exchangeable cations. The results clearly show that modification of QB with Arquad® 2HT-75 causes large primary expansion of the  $d(001)$  spacing. This expansion is greater when QB is modified with higher doses of the surfactant. The  $d(001)$  spacing for QB-Aq1 at 2.38:1 clay–surfactant (w/w) ratio is almost double the value of  $d(001)$  spacing for QB. However, the basal spacing for QB-Aq2 is higher by only  $5 \text{ \AA}$  compared to QB-Aq1 which implies the increase in basal spacing is almost reaching a plateau at 4.75:1 clay–surfactant (w/w) ratio. The  $d(001)$  spacing of  $30.05 \text{ \AA}$  shown by QB-Aq1 reflects evolution of paraffin type monolayer arrangement of the surfactant molecules in the clay interlayer [22], whereas  $d(001)$  spacing value of  $35.04 \text{ \AA}$  shown by QB-Aq2 could be due 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 [23,24]. In addition to the primary XRD peaks assigned to  $(001)$  planes, the XRD patterns of QB-Aq1 and QB-Aq2 also have weak peaks at  $14.86$  and  $17.92 \text{ \AA}$ , which are assigned to  $(002)$  planes. The presence of  $d(002)$  spacing in the XRD patterns of organoclays, synthesised with surfactant doses greater than 100% CEC of the starting clay, were earlier reported [22]. Presence of higher orders of diffraction peaks, such as  $d(002)$  and  $d(003)$ , in the XRD patterns of synthesised organoclays clearly indicates regular stacking of surfactant alkyl chains in the interlayers of QB.

### 3.1.2. FTIR characterisation of the organoclays

The FTIR spectral regions between  $3600$  and  $1800 \text{ cm}^{-1}$  for the unmodified bentonite and its two organoclays are shown in Fig. 2. The IR peaks that appear at the  $3000$ – $2800 \text{ cm}^{-1}$  region are the signature of  $\text{CH}_2$  infrared absorption bands. These bands are indicative of the ordering (*gauche/trans* conformer ratio), packing density of the surfactants in organoclays and the interactions between the alkyl chains [25–27]. As shown in Fig. 2, the  $\text{CH}_2$  asymmetric stretching vibration ( $\nu_{\text{asy}}$ ) and  $\text{CH}_2$  symmetric stretching vibration

( $\nu_{\text{sy}}$ ) for QB-Aq1 appear at  $2926$  and  $2852 \text{ cm}^{-1}$ , respectively. In case of QB-Aq2, ( $\nu_{\text{asy}}$ ) and ( $\nu_{\text{sy}}$ ) they appear at  $2922$  and  $2850 \text{ cm}^{-1}$ , respectively. It is evident that there is a shift for these bands towards a lower frequency as the surfactant loading rate increase from 2.38:1 clay–surfactant (w/w) ratio to 4.75:1 clay–surfactant (w/w) ratio. In general, band shifts to higher wavenumber are characteristic of disorder *gauche* conformations, whereas band shifts to lower wavenumber are characteristic of highly ordered all-*trans* conformations [25–28]. It is also evident from the XRD results in this study that increasing surfactant packing density causes additional expansion of the clay interlayer spaces. So, these results are attributable to the progressively developing conformation of the adsorbed surfactant molecules from low packing density and ordering (liquid like) to high packing density and ordering (solid like) [25–28]. Peaks due to ( $\nu_{\text{asy}}$ ) and ( $\nu_{\text{sy}}$ ) do not appear in case of unmodified QB due to the absence of any organic molecule therein.

### 3.1.3. Thermal characterisation of the organoclays

Thermal characterisation is a useful tool for exploring the structure of organoclays. Earlier reports have shown that the thermal behaviour of surfactant modified clays correlate well with the conformation of the surfactant molecules within the organoclay structure [4,25,29,30]. The TG and DTG patterns of the unmodified QB show three characteristic weight loss steps, as illustrated in Fig. 3. The first weight loss occurs at  $81^\circ\text{C}$  due to desorption of water, a second relatively less intense step at  $140^\circ\text{C}$  is due to dehydration of the hydrated cations in the interlayer and the third at  $679^\circ\text{C}$  is a result of dehydroxylation [25,31]. On the other hand, weight losses happen in four steps for the organoclays (Fig. 4 and 5). In case of QB-Aq1, the four different DTG peaks appear at  $50$ ,  $320$ ,  $431$  and  $713^\circ\text{C}$ , respectively (Fig. 4). The first peak at  $50^\circ\text{C}$  is due to desorption of water, the second at  $320^\circ\text{C}$  corresponds to decomposition of the surfactants bound to their neighbouring molecules, the third peak at  $431^\circ\text{C}$  results from loss of surfactants bound to the silica surface of the bentonite and the final peak at  $713^\circ\text{C}$  is due to dehydroxylation of bentonite [4,5,25,29–31]. The DTG curve of QB-Aq2 also shows similar patterns with four notable peaks (Fig. 5). However, the four different peaks appear at slightly reduced temperatures as compared to QB-Aq1, which can be attributed to higher



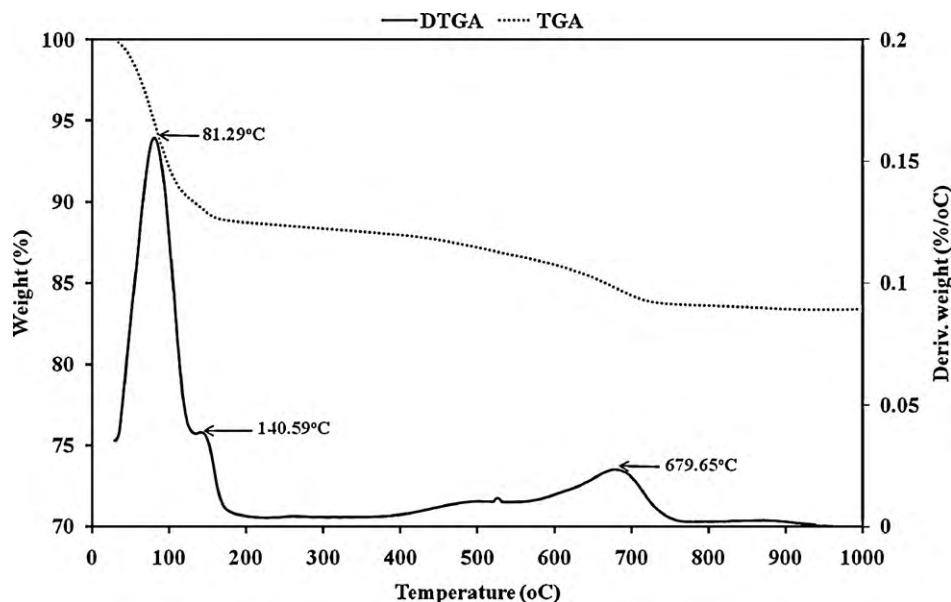


Fig. 3. TG and DTG patterns of bentonite (QB).

surfactant loading in QB-Aq2 [5,25,29,30]. This is indicative of conformational changes of the surfactant molecules in the organoclays with incremental surfactant loading. The QB-Aq2 synthesised at 4.75:1 clay–surfactant (w/w) ratio evolves more ordered ‘solid like’ surfactant conformation, which supports the XRD and FTIR characterisation results.

### 3.2. Adsorption of Cr (VI) by the organoclay sorbents

#### 3.2.1. Adsorption isotherm

The adsorption data of Cr (VI) by the organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio) best fit to the Langmuir isothermal model (Fig. 6). The Langmuir model is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (2)$$

where,  $C_e$  is the concentration of Cr (VI) at equilibrium ( $\text{mg L}^{-1}$ ),  $q_e$  is the amount of Cr (VI) adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_m$  is the maximum adsorption capacity of Cr (VI) by the organoclays ( $\text{mg g}^{-1}$ ) and  $K_L$  is the Langmuir adsorption constant ( $\text{L mg}^{-1}$ ) related to the free energy of adsorption. The corresponding model fitting parameters are shown in Table 1. The Langmuir model actually explains saturated monolayer adsorption without any transmigration of the adsorbate molecules on the sorbent surface [32]. Since QB-Aq2 adsorption data fit better to this model than QB-Aq1 (Table 1) in this study, it is evident that a higher degree of modification makes the clay surface more homogeneous and improves adsorption. The FTIR and TGA characterisation data has also shown that organoclay synthesised at wider surfactant clay ratio results into highly ordered homogeneous type of surfactant conformation. From the Langmuir model, the maximum monolayer Cr (VI) adsorption ( $q_m$ ) by QB-Aq2 and QB-Aq1 are calculated and presented in Table 1. The  $q_m$  values for QB-Aq1 and QB-Aq2 at 37 °C

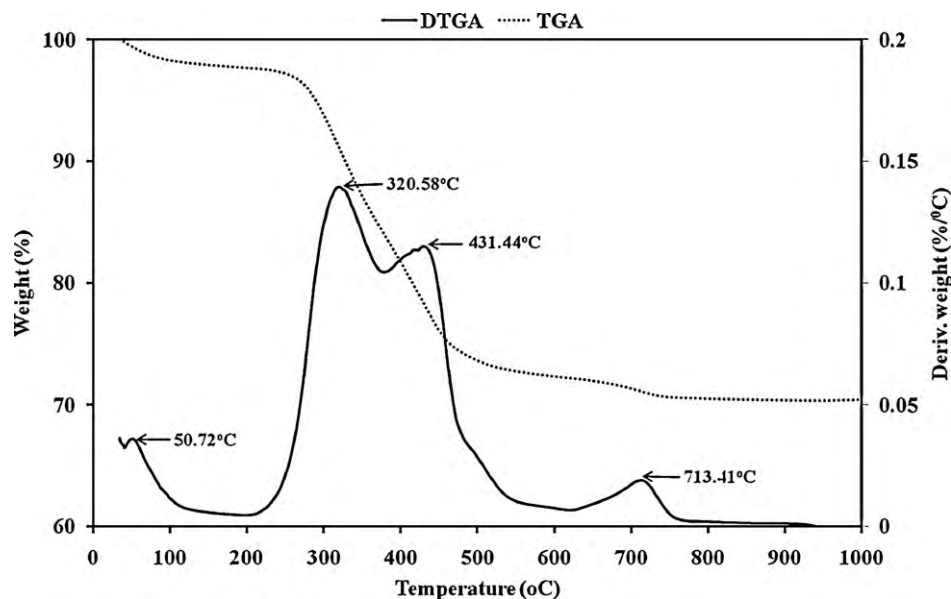


Fig. 4. TG and DTG patterns of bentonite organoclay QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio).

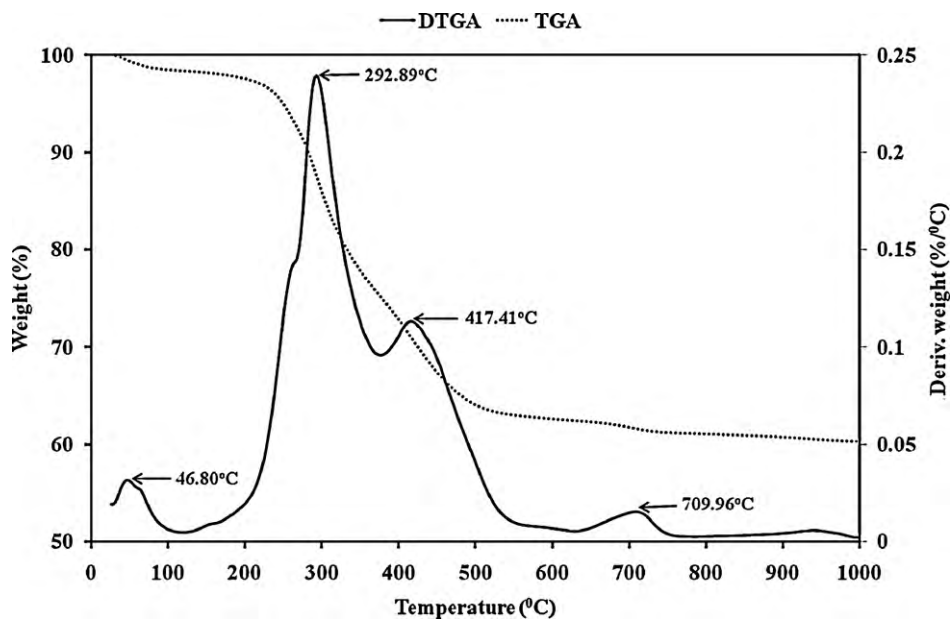


Fig. 5. TG and DTG patterns of bentonite organoclay QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio).

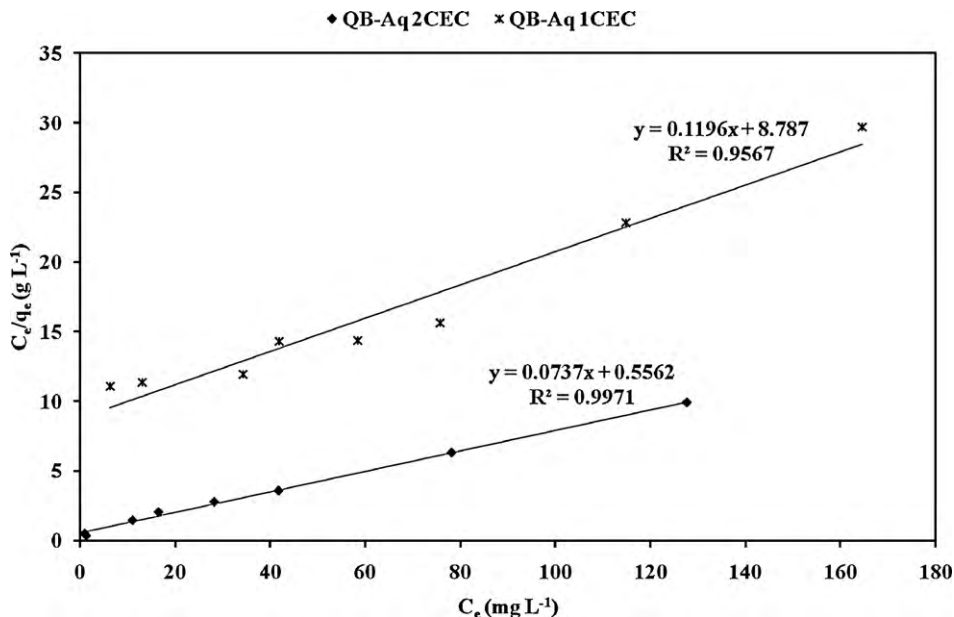


Fig. 6. Langmuir isotherm for the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay-surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio) at 18 °C temperature.

temperature are 8.51 and 14.64 mg g<sup>-1</sup>, respectively. This result is attributable to the creation of greater numbers of cationic adsorption sites for Cr (VI) in QB-Aq2 due to higher surfactant loadings. The  $q_m$  value for QB-Aq2 (14.64 mg g<sup>-1</sup>) at pH value around 5.0 in our study is comparable with that of HDTMA modified montmorillonite (21.05 mg g<sup>-1</sup>) at pH 4.2 as reported by Krishna et al. [16].

Moreover, Aq modified bentonite holds promise over other organoclays due to cheaper market price of Aq as compared to other pure surfactants such as HDTMA. The current study also shows that the unmodified bentonite (QB) adsorbs almost negligible amounts of Cr (VI) in comparison to the Aq modified hybrids. One possible mechanism for adsorption of hexavalent chromate anion (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) by

**Table 1**  
Langmuir isotherm parameters for the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay-surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio) at 18 and 37 °C temperatures.

Sample	18 °C					37 °C				
	$q_m$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$r^2$	$F$	$p$	$q_m$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$r^2$	$F$	$p$
QB-Aq1	8.36	0.0136	0.9567	132	<0.0001	8.51	0.0093	0.8945	51	0.0004
QB-Aq2	13.57	0.1325	0.9971	2060	<0.0001	14.64	0.0922	0.9826	338	<0.0001

the organoclays could be the electrostatic attraction forces working between the  $\text{Cr}_2\text{O}_7^{2-}$  anions and positively charged sites that were evolved in the organoclays through surfactant modification. This assumption is supported by the measured zeta potential values of the used sorbents. The zeta potential values for QB, QB-Aq1 and QB-Aq2 were measured to be  $-21.3$ ,  $0.49$  and  $51.1$  mV, respectively. However, anion exchange is another possible mechanism where the weakly held counter anions (halide) of the modifying surfactants are replaced by more strongly held  $\text{Cr}_2\text{O}_7^{2-}$  counter ions [16,33,34].

### 3.2.2. Thermodynamic favourability of the adsorption isotherm

Whether an adsorption process is thermodynamically favourable or unfavourable can be predicted by a dimensionless constant called separation parameter or factor. The separation parameter ( $R_L$ ) is calculated from the Langmuir adsorption constant using the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where,  $R_L$  is the separation factor,  $K_L$  is the Langmuir adsorption constant ( $\text{L mg}^{-1}$ ) and  $C_0$  is the initial Cr (VI) concentration ( $\text{mg L}^{-1}$ ). An adsorption isotherm is considered favourable if  $0 < R_L < 1$ , unfavourable if  $R_L > 1$ , linear if  $R_L = 1$  and irreversible if  $R_L$  is zero [35,36]. The calculated  $R_L$  values for the adsorption of Cr (VI) by QB-Aq1 and QB-Aq2 at 18 and 37 °C temperatures are listed in Table 2. It is evident from the results that over the Cr (VI) concentration range tested ( $10\text{--}80 \text{ mg L}^{-1}$ ), the  $R_L$  values lie between  $0 < R_L < 1$  in all the cases. It indicates that both the organoclays perform favourable Cr (VI) adsorption at the studied temperatures in this concentration range. Having lesser  $R_L$  values, QB-Aq2 performs more favourable Cr (VI) adsorption compared to QB-Aq1. It is also observed that the adsorption process becomes less favourable at higher temperature.

### 3.2.3. Effect of temperature on the adsorption of Cr (VI) by organoclays

The influence of temperature on the adsorption of Cr (VI) by the Aq-bentonite organoclays was studied by establishing the adsorption isotherms at two different temperatures (18 and 37 °C). The

**Table 2**

Values of separation parameters,  $R_L$ , based on the Langmuir isotherm constants ( $K_L$ ), for the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay-surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio) at 18 and 37 °C temperatures.

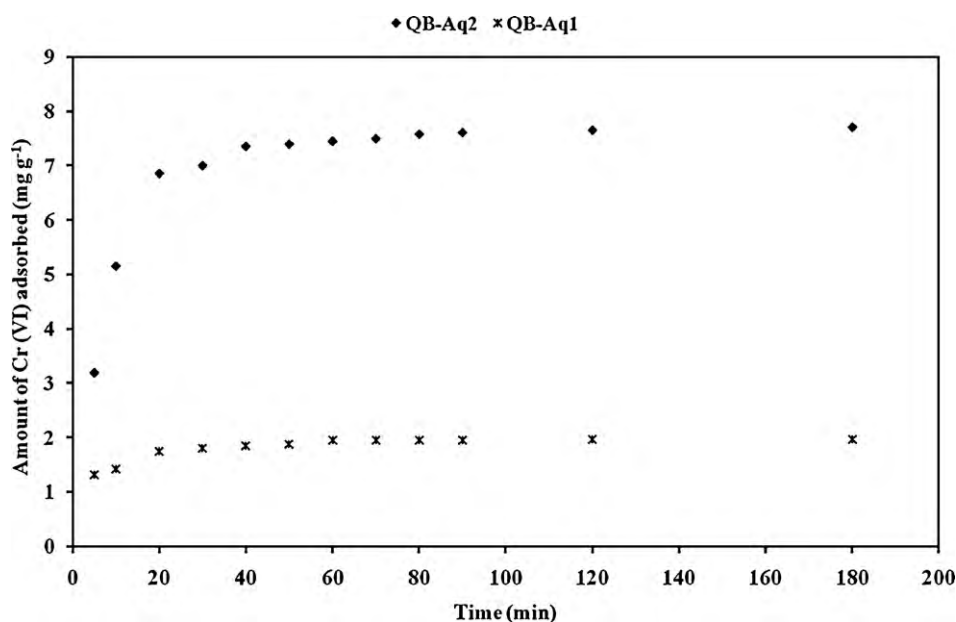
Initial Cr (VI) concentration ( $\text{mg L}^{-1}$ )	$R_L$ at 18 °C		$R_L$ at 37 °C	
	QB-Aq1	QB-Aq2	QB-Aq1	QB-Aq2
10	0.8802	0.4301	0.9145	0.5202
20	0.7860	0.2740	0.8425	0.3515
30	0.7101	0.2010	0.7809	0.2654
40	0.6475	0.1587	0.7278	0.2132
50	0.5950	0.1311	0.6814	0.1782
60	0.5505	0.1117	0.6406	0.1530
70	0.5121	0.0973	0.6044	0.1341
80	0.4787	0.0862	0.5721	0.1193

Langmuir model parameters at both these temperatures are listed in Table 1. It is apparent from the data that the  $q_m$  values for both the organoclays are relatively higher at 37 °C than at 18 °C. At the same time, the  $K_L$  values show a reduction at higher temperature. The data indicate that the adsorption reaction between Aq-bentonite organoclays and chromate anion is endothermic in nature. However, from the calculated  $R_L$  values it is found that the adsorption process is less favourable at higher temperatures irrespective of the organoclays and concentrations of Cr (VI) studied (Table 2).

### 3.2.4. Adsorption kinetics

The batch kinetic studies indicate that both the organoclays reach equilibrium for Cr (VI) adsorption within about 1 h of agitation (Fig. 7). Throughout the experiment duration, QB-Aq2 adsorbs higher amounts of Cr (VI) compared to QB-Aq1. The rate of adsorption is much higher at the initial stage, and then it slows down and gradually reaches a plateau. It appears in Fig. 7 that QB-Aq1 reaches adsorption equilibrium quicker than QB-Aq2 because higher surfactant loading in QB-Aq2 may cause pore blockage and so prevent rapid migration of the adsorbate in its inner structure through the pores [37].

Fitting the kinetic data into various mechanistic models, it appears that a pseudo second order kinetic equation best fits the adsorption data of QB-Aq1 ( $R^2 = 0.9998$ ,  $F = 45622$ ,  $p < 0.0001$ ) and QB-Aq2 ( $R^2 = 0.9994$ ,  $F = 17427$ ,  $p < 0.0001$ ) (Table 3) (fitting param-



**Fig. 7.** Influence of agitation time on the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay-surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio) at 23 °C temperature.

**Table 3**  
Pseudo second order kinetic parameters for the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio) at 23 °C temperature and 50 mg L<sup>−1</sup> initial Cr (VI) concentration.

Sample	$q_t$ (mg g <sup>−1</sup> )	$k$ (g mg <sup>−1</sup> min <sup>−1</sup> )	$q_e$ (mg g <sup>−1</sup> )	$h$ (mg g <sup>−1</sup> min)	$r^2$	$F$	$p$
QB-Aq1	1.97	0.166	2.01	0.671	0.9998	45622	<0.0001
QB-Aq2	7.70	0.028	7.94	1.790	0.9994	17427	<0.0001

eters for other models not presented). The linear form of pseudo second order kinetics [38] is described by the following expression:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (4)$$

where,  $q_e$  and  $q_t$  are the amount of Cr (VI) adsorbed at equilibrium and at time  $t$  (mg g<sup>−1</sup>), respectively, and  $k$  is the pseudo second order kinetic rate constant (g mg<sup>−1</sup> min<sup>−1</sup>). In Eq. (4), if  $t \rightarrow 0$ , the initial adsorption rate ( $h$ ) (mg g<sup>−1</sup> min), can be obtained from the following equation:

$$h = kq_e^2 \quad (5)$$

The pseudo second order kinetic plots for the adsorption of Cr (VI) by QB-Aq1 and QB-Aq2 at 50 mg L<sup>−1</sup> initial Cr (VI) concentration and 23 °C temperature are presented in Fig. 8. The corresponding kinetic parameters are listed in Table 3. The results show that the theoretical amount of Cr (VI) adsorption by the two organoclays ( $q_e$ ) calculated from the pseudo second order model is reasonably consistent with the experimental amount of Cr (VI) adsorption ( $q_t$ ). Attainment of faster adsorption equilibrium by QB-Aq1 compared to QB-Aq2 is further supported by the calculated pseudo second order rate constant ( $k$ ) which is higher for QB-Aq1 (0.166 g mg<sup>−1</sup> min<sup>−1</sup>) than QB-Aq2 (0.028 g mg<sup>−1</sup> min<sup>−1</sup>). However, the initial adsorption rate ( $h$ ) is more for QB-Aq2 (1.79 mg g<sup>−1</sup> min) than QB-Aq1 (0.67 mg g<sup>−1</sup> min) due to the presence of greater numbers of adsorption sites in QB-Aq2 which can readily hold Cr<sub>2</sub>O<sub>7</sub><sup>2−</sup> anions. After the readily available adsorption sites are fully occupied, the adsorbate anions need to migrate in the inner pores of the organoclays. Thus, adsorption at the later stage may be slower due to the effect of pore blocking arising from higher surfactant loadings [37]. From the viewpoint of adsorption mechanisms, best fitness of the pseudo second order model for Cr (VI) adsorption onto the sorbents confirms that adsorption is controlled by both

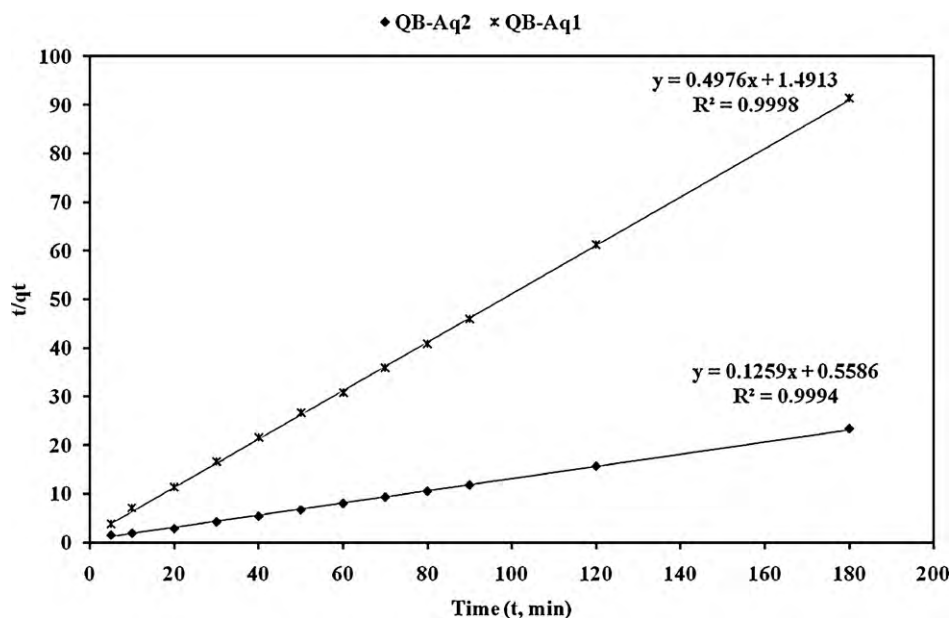
physical and chemical processes over the whole range of adsorbate concentrations studied [38].

### 3.2.5. Effect of initial pH on the adsorption of Cr (VI) by organoclays

The influence of initial pH on the adsorption of Cr (VI) by QB-Aq1 and QB-Aq2 was examined at a pH range from 4.0 to 9.0 which better represents the pH of contaminated waters and soils. As shown in Fig. 9, a decrement in the amount of Cr (VI) adsorption takes place with increasing initial pH values and is more drastic in case of QB-Aq2 at pH > 5.0. The reduction in adsorption with increasing initial pH values may be explained by the aqueous chemistry of chromium. At pH values ranging from 4.0 to 6.0, the predominant species of Cr present in the system is Cr<sub>2</sub>O<sub>7</sub><sup>2−</sup> with a small quantity of HCrO<sub>4</sub><sup>−</sup> whereas at pH > 7.0 CrO<sub>4</sub><sup>2−</sup> dominates [39]. For this reason, at pH < 6.0 adsorption of chromium occurs mainly through salt formation [(Aq)HCrO<sub>4</sub><sup>−</sup> and (Aq)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub><sup>2−</sup>] and to some extent by anion exchange where the counter anion of Aq (Cl<sup>−</sup>) is displaced by HCrO<sub>4</sub><sup>−</sup> from the exchange sites forming bentonite-Aq-HCrO<sub>4</sub><sup>−</sup> [16,33,34]. At pH > 6, the dominant mechanism for sorption is probably only salt formation [(Aq)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub><sup>2−</sup> and (Aq)<sub>2</sub>CrO<sub>4</sub><sup>2−</sup>] [16,33]. Another reason for this is the changes in the surface charge of organoclays with changing pH of the reaction system (data not presented). We have observed that the zeta potential values of QB, QB-Aq1 and QB-Aq2 in pure water suspension are about −21.3, 0.49 and 51.1 mV, respectively.

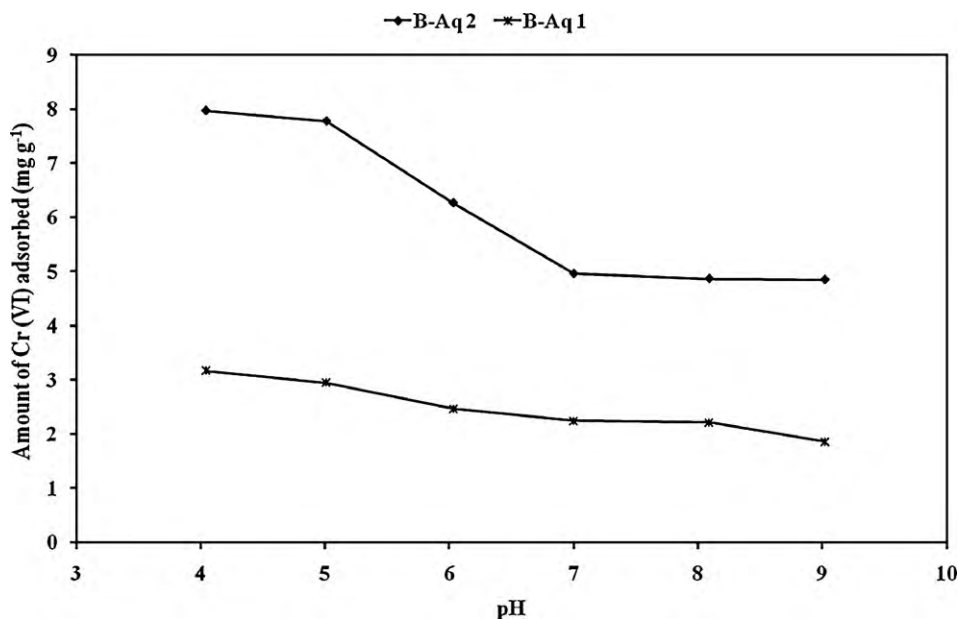
### 3.2.6. Effect of electrolyte concentration on the adsorption of Cr (VI) by organoclays

As shown in Fig. 10, increasing electrolyte concentration, i.e. ionic strength, causes a reduction in the amount of Cr (VI) adsorbed by QB-Aq1 and QB-Aq2. Increasing electrolyte concentration actually relates to changes in the surface potential of the organoclays



**Fig. 8.** Pseudo second order kinetic plots for the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio) at 23 °C temperature.





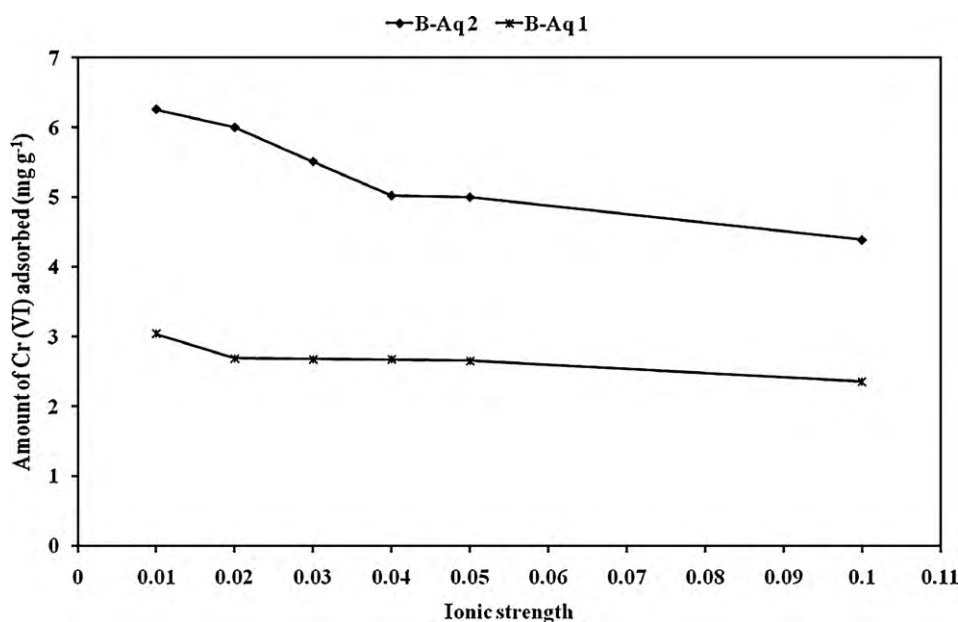
**Fig. 9.** Influence of initial pH on the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay-surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio) at 23 °C temperature.

[40] and hence reduces their adsorption performance. It is noteworthy that the influence of ionic strength on the adsorption of Cr (VI) by QB-Aq2 is more prominent than for QB-Aq1 probably because the former contains more variable potential sites than the later. Higher surfactant loadings might have created more variable potentials in QB-Aq2 as compared to QB-Aq1. However, the sorbents show consistently good Cr (VI) adsorption performance at ionic strength value 0.03 which is the one most frequently encountered in contaminated soil environments.

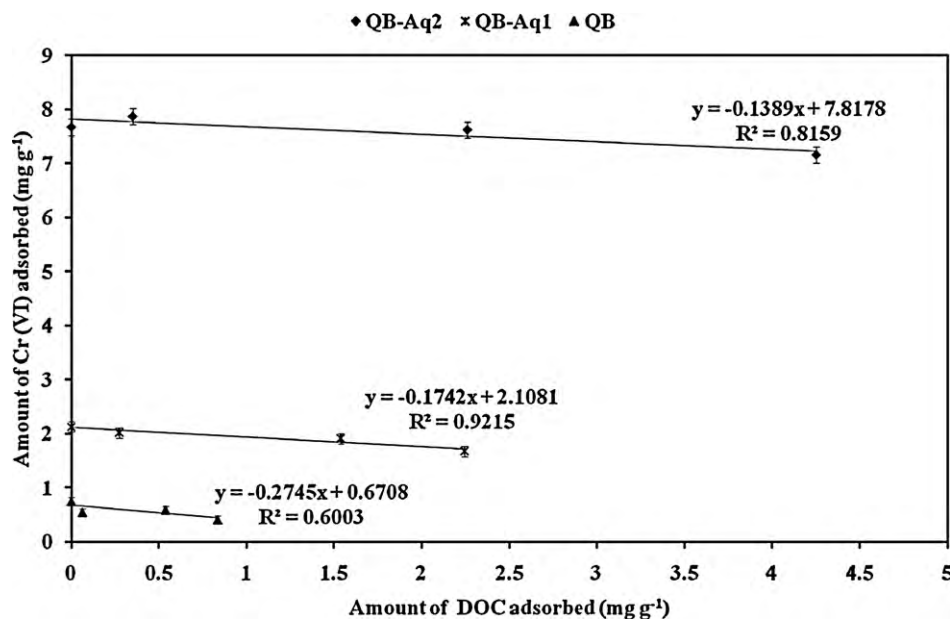
### 3.2.7. Effect of DOM on the adsorption of Cr (VI) by organoclays

Reagent grade humic acid was used in the experiment to investigate the influence of DOM on the adsorption of Cr (VI) by QB-Aq1 and QB-Aq2 and the concentration of DOM in the system was expressed as DOC. Fig. 11 presents the relationship between the

adsorbed amounts of DOC ( $\text{mg g}^{-1}$ ) and Cr (VI) ( $\text{mg g}^{-1}$ ). The bentonite clay mineral (QB) used in the present study could adsorb very little Cr (VI) probably due to presence of some impurities. The regression analysis between the adsorbed amounts of DOC and Cr (VI) indicates that DOC competes with Cr (VI) for adsorption sites in the organoclays (Fig. 11). It can be predicted from the negative slopes of the regression analyses that the extent of competition follows the order QB > QB-Aq1 > QB-Aq2. This indicates that the higher the degree of surfactant loadings in organobentonite, the less the influence of DOM on Cr (VI) adsorption. Information about the effects of natural organic matters on the contaminant adsorption capabilities of organoclays is very scarce in the literature. However, this information is of utmost significance in predicting the efficiencies of these sorbents in real field situations.



**Fig. 10.** Influence of electrolyte concentration on the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay-surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay-surfactant (w/w) ratio) at 23 °C temperature.



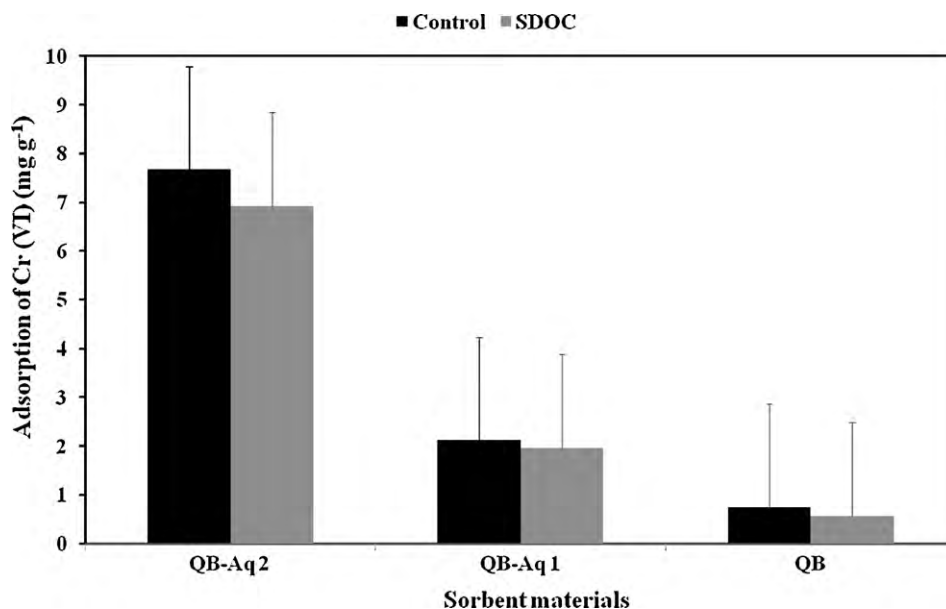
**Fig. 11.** Relationship between the adsorption of Cr (VI) and DOM by the bentonite (QB) and its organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio) at 23 °C temperature; bars represent standard error.

### 3.2.8. Adsorption of Cr (VI) by organoclays in the presence of DOM extracted from soil

In the present study, adsorption of Cr (VI) by the organoclays was also conducted in presence of DOC extracted from soil to simulate the natural organic matter present in the soils. DOC was extracted from soil at 1:1 soil–water ratio and the mixture was agitated for 24 h. Filtered soil extract was used to prepare 50 mg L<sup>−1</sup> Cr (VI) solution and in the adsorption experiment. DOC concentration in the soil extract was 71.30 mg L<sup>−1</sup>. As shown in Fig. 12, soil extracted DOC (SDOC) reduces the amount of Cr (VI) adsorption by QB and its two Aq organoclays. As discussed in the previous section, this reduction in the adsorption efficiency of the organoclays is due to competition for adsorption sites between SDOC and Cr (VI).

## 4. Conclusions

This study concludes that bentonite can effectively be modified by Arquad® 2HT-75, which is a relatively cheaper surfactant, for adsorbing Cr (VI) from aqueous solution. As illustrated by XRD, FTIR and TGA characterisation techniques, more ordered solid like conformation of surfactant molecules is obtained in the organoclay as the surfactant loading increases. As apparent from the measured zeta potential values, positive charge formation takes place on the bentonite surface due to surfactant modification. All these result in a remarkable improvement in the adsorption capacity of the bentonite-Aq organoclays for anionic Cr (VI). Even greater sorption is achieved when bentonite is modified with higher surfactant



**Fig. 12.** Influence of soil extracted DOC on the adsorption of Cr (VI) by organoclays QB-Aq1 (2.38:1 clay–surfactant (w/w) ratio) and QB-Aq2 (4.75:1 clay–surfactant (w/w) ratio) at 23 °C temperature; bars represent standard error.

doses. The adsorption of Cr (VI) by the organoclays is best explained by the Langmuir isothermal model and pseudo second order kinetic model. The sorption mechanism for Cr (VI) by the bentonite-Aq organoclays is both physical and chemical in nature. The adsorption process is influenced by initial pH and electrolyte concentration in the system. The organoclay sorbents perform reasonably well under environmental pH and ionic strength conditions and in the presence of natural organic matter, although natural organic matter may compete to some extent with Cr (VI) for adsorption sites in the organoclays. This study will assist in developing novel remediation materials for removing Cr (VI) from various industrial waste waters as well as *in situ* immobilisation of Cr (VI) in contaminated soils and sediments. This study also provides an insight into the application of organoclay sorbents for remediating contaminants under real environmental conditions. The organoclays reported in this paper may also be helpful to remediate other contaminants such as arsenate, selenate, antimonate, molybdate, nitrate, phosphate, anionic dyes, herbicides, etc in contaminated soil and water.

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