

# Effect of quaternary ammonium cation loading and pH on heavy metal sorption to Ca bentonite and two organobentonites

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## Abstract

Sorption of four heavy metals (Pb, Cd, Zn and Hg) to calcium bentonite (Ca bentonite), hexadecyltrimethylammonium bentonite (HDTMA bentonite) and benzyltriethylammonium bentonite (BTEA bentonite) was measured as a function of the quaternary ammonium cation (QAC) loading at 25, 50 and 100% of the clay's cation-exchange capacity (CEC). The effects of pH on the surface charge of the clays and heavy metal sorption were also measured. Sorption of Cd, Pb, and Zn was non-linear and sorption of all three metals by HDTMA and BTEA bentonites decreased as the QAC loading increased from 25 to 100%. In most cases, sorption of these metals to 25% BTEA and 25% HDTMA bentonite was similar to or greater than sorption to Ca bentonite. Hg sorption was linear for both HDTMA and BTEA bentonite. No significant effect on Hg sorption was observed with increasing QAC loading on BTEA bentonite. However, an increase of Hg sorption was detected with increasing QAC loading on HDTMA bentonite. This behavior suggests that a process different than cation exchange was the predominant Hg sorption mechanism. Cd, Pb, and Zn sorption decreased with pH. However, this effect was stronger for Cd and Pb than Zn. Hg sorption varied inversely with pH.

QAC loading affected the surface charge of the clays. Twenty-five and 50% loading of BTEA cations increased the negative charge on the clay's surface relative to the untreated clay, without affecting the zero point of charge (ZPC) of the clay. Increased QAC loading on HDTMA bentonite causes the surface charge to become more positive and the ZPC increased. One hundred percent of HDTMA bentonite maintained a positive surface charge over the range of pH values tested.

The organoclays studied have considerable capacity for heavy metal sorption. Given that prior studies have demonstrated the strong sorption capacity of organoclays for nonionic organic pollutants, it is likely that organoclays can be useful sorbents for the treatment of effluent streams containing both organic contaminants and heavy metals.

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**Keywords:** Organoclay; Metals; Sorption; pH; Zero point of charge

## 1. Introduction

Organoclays are produced by the exchange of organic quaternary ammonium cations (QACs) for inorganic cations (e.g.  $\text{Ca}^{+2}$ ,  $\text{Na}^{+}$ ) that naturally occur on the internal and external mineral surfaces of the clay. Compared to natural clays, organoclays are organophilic and have increased sorption capacity for relatively nonpolar organic solutes [1,2]. Depending on the molecular structure of the QAC, sorption of organic solutes occurs by either a partition or adsorption process [2–5]. Environmental engineering applications of organoclays include their use in compacted

earthen landfill liners [6–9] and slurry walls [10], as a component of geosynthetic clay liners [11,12], as liners for gasoline storage tanks [13–15], as a component of sediment caps [16], as a sorbent for sampling airborne organic contaminants [17] and removing oil from wastewater streams [18]. Because of their unique organic solute sorption properties, the interest in applications of organoclays has increased significantly over the last decade.

Although numerous studies have focused on the sorption of nonionic organic compounds to organoclays as a function of QAC type and loading [1–5,9,19–22], relatively few studies have investigated the sorption of metals to organoclays. Lee et al. [23] quantified Pb sorption to hexadecyltrimethylammonium (HDTMA) bentonite and found that sorption capacity decreased with increasing substitution (loading) of HDTMA

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cations for inorganic cations. Yoo et al. [24] reported that sorption of Cd to HDTMA bentonite and conventional bentonite was similar, suggesting that QAC treatment of bentonite does not adversely impact metal sorption. Most recently, Tillman et al. [25,26] studied the removal of heavy metals by column-flow and batch systems containing organoclays and several other proprietary sorbents. They observed that the organoclays were able to sorb significant quantities of metals, but their investigation provided little mechanistic interpretation of the sorption mechanism. None of these studies have considered the effect of pH on sorption.

Wastewater effluents frequently are composed of both organic and inorganic pollutants. Heavy metals are of particular concern because of their harmful effects on human health and the environment. The combination of metals and organic pollutants ranked fifth (based on frequency of occurrence) among the 51 pairs of compounds found in soil and sediments at contaminated Department of Energy sites [27]. Leachates coming from industrial or municipal landfills also present a wide range of heavy metal and xenobiotic organic compounds simultaneously [28]. Remediation of sites contaminated with mixed wastes is generally more difficult than for sites contaminated with a single contaminant, since metals and organic compounds have a different fate and transport in soil and water [29]. If organoclays can sorb heavy metals at a variety of environmental pH values, they could be effective sorbents for mixed-waste systems containing relatively nonpolar organic pollutants and heavy metals.

Heavy metal sorption by clays and organoclays is influenced by the surface properties of these sorbent materials. ZPC is one of the most relevant parameters for characterizing the electrochemical state of soil surfaces in solution and is defined as the pH where the net surface charge, resulting from the sorption of  $H^+$  and  $OH^-$ , is zero. If the pH of a soil is above its ZPC, the soil surface will have a net negative charge and will exhibit an ability to exchange cations. On the other hand, if the pH is below the ZPC, anion exchange predominates. A few studies determined the ZPC of organoclays [30,31]; however, these studies did not quantify heavy metal sorption.

The objective of this research is to determine the optimal mass of BTEA and HDTMA on the clay mineral in order to effectively remove heavy metals from an aqueous solution. To meet this objective, the sorption of heavy metals to organoclays with different masses of QACs and at different pH values was quantified. Also, the effect of different QAC loadings on the ZPC of the organoclays was determined.

## 2. Experimental methodology

### 2.1. Materials

The six organobentonites used in this study were synthesized from Wyoming bentonite (American Colloid Company). The base bentonite was composed of 3.6% sand, 7.3% silt and 89.1% clay.

Two quaternary ammonium compounds were used to synthesize the clays: HDTMA bromide  $[(CH_3)_3NC_{16}H_{33}Br]$  and BTEA chloride  $[(C_2H_5)_3NCH_2C_6H_5Cl]$ . Both compounds were

obtained from Aldrich Chemical Company, had a chemical purity of 99%, and were used as received.

The aqueous-metal solution was prepared using the following salts:  $CdCl_2$ ,  $ZnCl_2$ ,  $PbNO_3$  and  $HgCl_2$  (Acros Organics). The salts were >97% purity and were used as received.

### 2.2. Preparation of organobentonites

Homoionic clays were prepared in order to avoid differences in QAC exchange and/or competition between the sorbing metal and the ions originally present, and thus the final metal-sorbing capacities.  $Ca^{+2}$  was selected as the exchange ion due to its usual presence in natural water. Exchangeable inorganic cations on the base bentonite were primarily Na with a small percentage of Mg and Ca. The detailed procedure for homoionic clay preparation is given by Boyd et al. [32]. Briefly the Wyoming bentonite was treated with aqueous  $CaCl_2$  in a five-fold excess of the CEC of the clay (0.691 mmol/g). The Ca-saturated clay was washed several times with distilled water and then dried.

The organoclays were prepared by replacing  $Ca^{+2}$  on the surface of the homoionic clay with either of the two quaternary ammonium cations at 25, 50 and 100% of the clay CEC according to the procedure described by Bartelt-Hunt et al. [9]. Briefly, the quantity of organic cation added to the bentonite was determined by

$$f = \frac{M_{\text{cation}}}{\text{CEC} \times M_{\text{clay}} \times \text{GMW}_{\text{cation}} \times Z} \quad (1)$$

where  $f$  is the fraction of CEC satisfied by the organic cation,  $M_{\text{cation}}$  the mass of organic cation required to achieve the desired fraction of CEC,  $M_{\text{clay}}$  the mass of the homoionic clay,  $\text{GMW}_{\text{cation}}$  the gram molecular weight of the organic cation, and  $Z$  is the moles of charge per equivalent.

### 2.3. Surface area determination

The surface area of the sorbents was measured using a multi-point BET method (Gemini 2360 surface analyzer, Micromeritics) with  $N_2$  as the adsorbate. The  $N_2$  BET surface area determination is a widely accepted method for quantifying the specific surface area of soil.  $N_2$  is a small, inert probe that does not alter the physical structure of the sorbent. However, this method does not quantify surfaces in the interlamellar space of Ca bentonite that may be available for metal sorption from water. These surfaces become available in aqueous solution as water is intercalated into the interlamellar space. Polar solvents (such as ethylene glycol or ethylene glycol monoethyl ether) used in other methods of surface area determination can potentially access these internal surfaces and would likely yield higher surface areas. These alternate methods may also partition into soil organic matter by dissolution and give erroneously large values of surface area [33,34]. BET analysis with a  $N_2$  probe was chosen for this analysis because the measurement process does not change the physical structure of the sorbent in a vacuum. For the organobentonites studied, the substituted quaternary ammonium cations exchanged onto surfaces in the interlamellar space

act as props that allow penetration of N<sub>2</sub>. Therefore, alternate surface area analysis methods would not likely differ from the BET results reported here for these organobentonites.

#### 2.4. Zero point of charge measurements

The zeta potential of the sorbents was measured without pre-treatment using a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchwsky equation:

$$ZP = 113000 \frac{V_t}{D_t} \times EM \quad (2)$$

where ZP is the zeta potential in millivolts,  $V_t$  the viscosity of the suspending liquid in poises at temperature  $t$ ,  $D_t$  the dielectric constant, and EM is the electrophoretic mobility at solution temperature.

Zeta potential measurements were carried out as a function of pH in order to determine the ZPC of each organoclay. The voltage applied for pH values between 3 and 10 was 1000 mV. For pH 2 the applied voltage was increased to 4000 mV due to the high specific conductance of the samples.

#### 2.5. Speciation of heavy metals

MINTEQA2 [35], an equilibrium speciation model, was used to estimate the speciation of the metals in solution as a function of pH.

#### 2.6. Sorption of heavy metals

Cd, Zn, Pb and Hg sorption to untreated Ca bentonite and the different organobentonites was quantified using equilibrium batch sorption experiments. Batch sorption experiments for each individual metal on each of the seven organoclays at three different pH values were performed by combining sorbent, aqueous-metal solution, and organic-free deionized (DI) water in 15-mL polypropylene tubes. Sorbent mass used in each isotherm experiment was 1 g. The aqueous-metal solutions were prepared at concentrations of 1000 mg/L for Cd, Zn and Hg and 5000 mg/L for Pb. These concentrations and sorbent masses were used to ensure that 30–90% of the added heavy metals were sorbed at equilibrium. The aqueous-metal solution was mixed with DI water prior to contacting the sorbent materials in the following ratios: 100% (v/v) metal solution; 80% metal solution/20% DI water; 50% metal solution/50% DI water; 20% metal solu-

Table 1  
Specific surface area (m<sup>2</sup>/g ± 1 standard deviation) for BTEA bentonite and HDTMA bentonite

% of CEC modified	BTEA	HDTMA
0	22.5 ± 1.6	22.5 ± 1.6
25	30.90 ± 0.89	10.88 ± 0.36
50	28.65 ± 0.96	10.28 ± 1.98
100	21.52 ± 0.07	4.57 ± 0.01

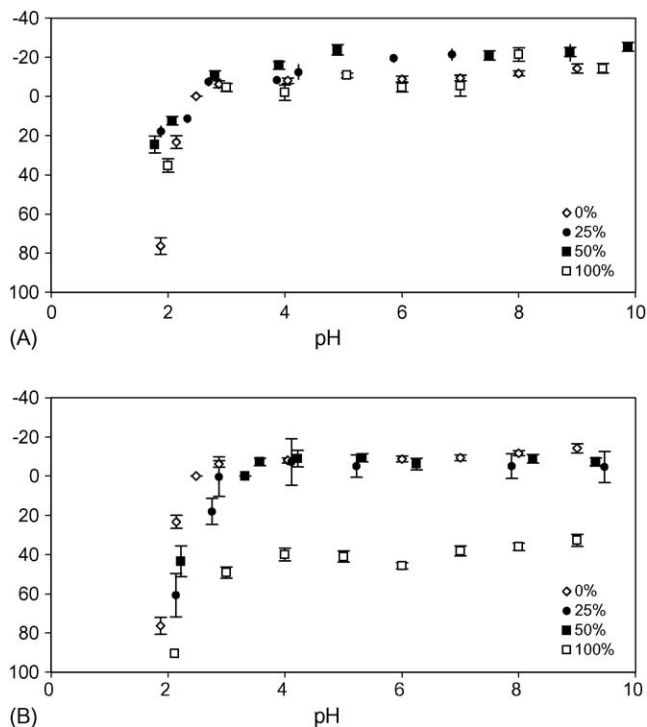


Fig. 1. Dependence of zeta potential on pH for benzyltriethylammonium bentonite (graph A) and hexadecyltrimethylammonium bentonite (graph B) at different organic cation loadings. Error bars represent the standard deviation of the 15 measurements for every point.

tion/80% DI water. Immediately after combining the DI water and aqueous-metal solution in the above ratios, the solvent phase of each reactor was buffered in order to obtain the desired pH. The following three values of pH were selected: 2.0, 3.0 and 5.0. Values of pH above 5.0 were not considered because they lead to Pb and Hg precipitation.

Tubes containing the diluted metal solution and no sorbent were carried through the experiment and analyzed to determine the losses due to contact with the tubes or caps. No significant losses were measured, and recovery in all tubes was determined

Table 2  
Speciation of heavy metals as a function of pH

Metal	Species	Percentage		
		pH 2	pH 3.5	pH 5
Hg	HgCl(OH) (aq)	0.142	2.590	16.27
	HgCl <sup>+</sup>	1.707	0.917	0.182
	HgCl <sub>2</sub> (aq)	98.12	96.47	82.81
	HgCl <sub>3</sub> <sup>-</sup>	0.013	0.021	0.076
	Hg(OH) <sub>2</sub> (aq)	0.000	0.014	0.641
Pb	Pb <sup>+</sup>	98.54	98.27	98.05
	Pb(NO <sub>3</sub> ) <sup>+</sup>	1.454	1.711	1.721
Cd	Cd <sup>+</sup>	94.95	94.26	94.23
	CdCl <sup>+</sup>	4.990	5.660	5.692
	CdCl <sub>2</sub> (aq)	0.058	0.071	0.071
Zn	Zn <sup>+</sup>	99.42	99.34	99.33
	ZnCl <sup>+</sup>	0.578	0.650	0.653

to be greater than 97%. The difference between the initial and final (equilibrium) metal mass in the aqueous phase was considered equal to the mass sorbed to the solid phase.

The tubes were capped and shaken for 1 day at  $23 \pm 1$  °C. Several previous studies investigating sorption of metals to modified clays found 24 h to be a sufficient time to reach equilibrium [23,36].

Samples were analyzed for aqueous-metal species using Acetylene-Air Flame/Atomic Adsorption (Perkin-Elmer Model 5100PC) with single-element hollow cathode lamps. Calibration curves were prepared from stock solutions for each element.

Samples were diluted with water to bring the concentration within the linear range of the instrument. Check standards were used periodically (two to three times) throughout sample analysis to ensure quality control.

### 3. Results and discussion

#### 3.1. Surface area determination

The surface area measurements are given in Table 1. For BTEA bentonite, surface area increased as organic cation sub-

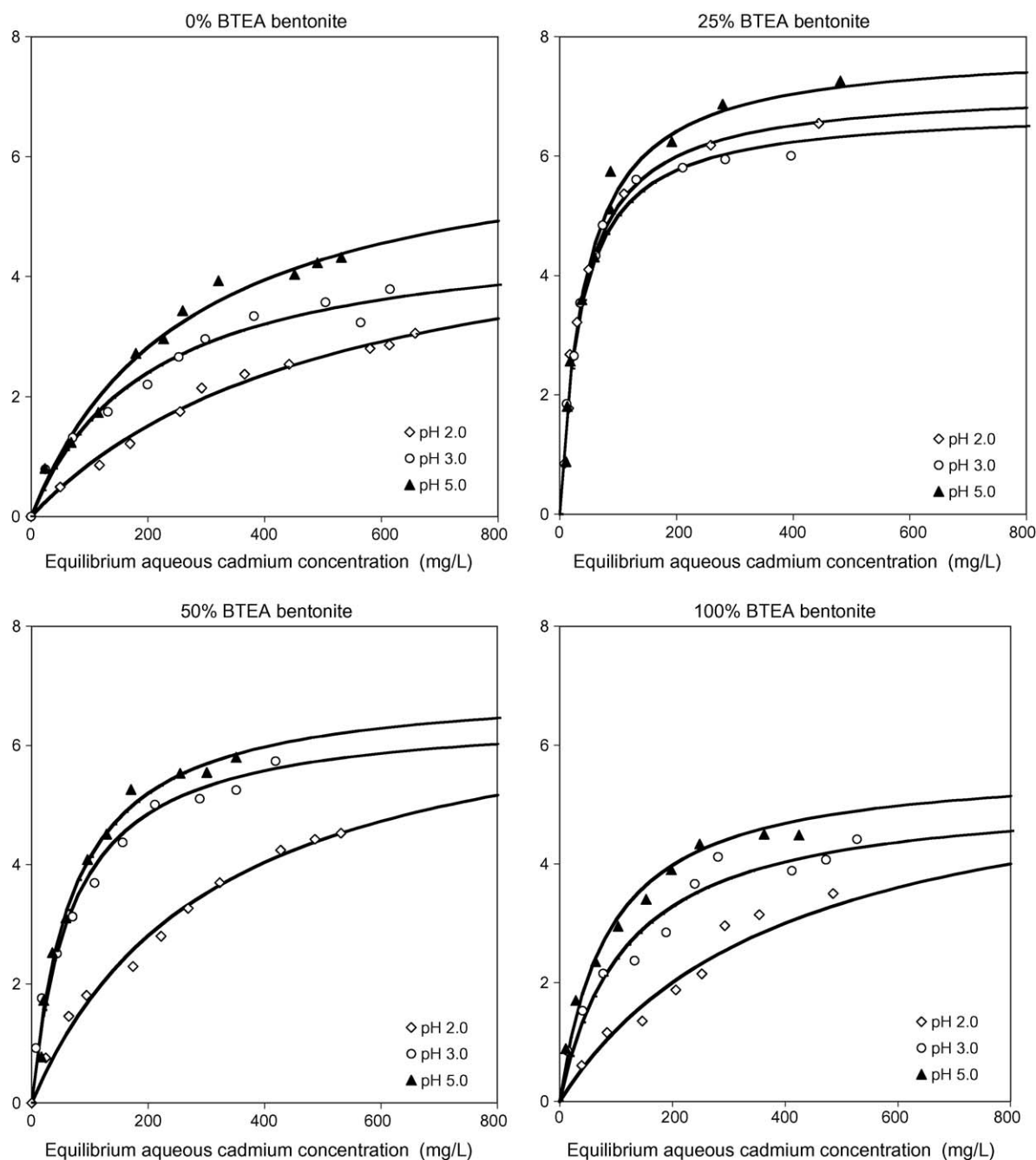


Fig. 2. Isotherms for the sorption of Cd to bentonite exchanged with BTEA cations at 0, 25, 50 and 100% of its CEC. Lines represent Langmuir model fits.

stitution increased from 0 to 25%. This result can be attributed to the “propping” open of the interlamellar space by the exchanged BTEA cations and thereby allowing the  $N_2$  probe to access interlamellar surfaces. This effect was not observed with 0 and 25% HDTMA bentonite. Surface areas obtained for BTEA bentonite were larger than those obtained for HDTMA bentonite. These results are similar to those obtained by Bartelt-Hunt et al. [9] at similar QAC loading. Larger HDTMA cations may be subject to relatively compact packing in the interlamellar space, causing steric hindrance of the nitrogen probe [37,38]. Smaller BTEA ions may be isolated from each other and hydrated water molecules when adhering to the interlamellar surfaces of bentonite. Similar behavior was observed

by Wang et al. [30] using tetramethylammonium instead of BTEA [23,30]. For both clays, the measured surface area generally decreased as QAC loading increased in the range of 25–100%. This result is likely caused by the increased packing density of the BTEA and HDTMA cations in the interlamellar space and the corresponding steric hindrance of the  $N_2$  probe.

### 3.2. ZPC measurements

Although electrokinetic measurements of fine clay suspensions is a common practice, this step requires a certain theoretical idealization of the system under study such as: (a)

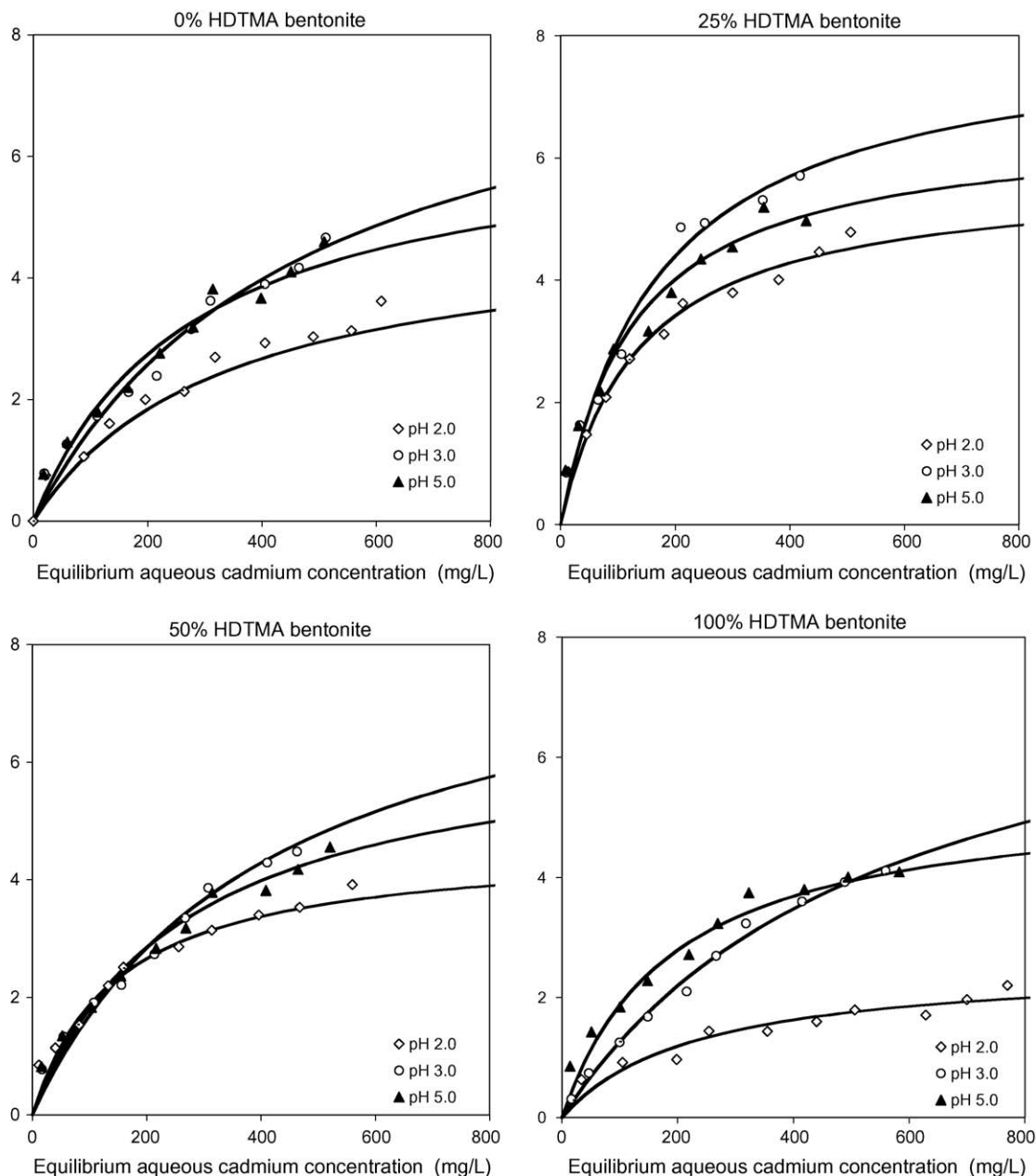


Fig. 3. Isotherms for the sorption of Cd to bentonite exchanged with HDTMA cations at 0, 25, 50 and 100% of its CEC. Lines represent Langmuir model fits.

the solid particles are assumed to be spheres and (b) electric charges on the particles are uniformly distributed on the particle surface. However, this method has been successfully used to determine the ZPC of soil by several groups of investigators [39–41].

Zeta potential–pH curves are shown in Fig. 1. Ca bentonite (0% QAC loading) has a ZPC around pH 2.4 and values of  $\zeta$  between  $-8$  and  $-11$  mV in the pH range 2.4–9.0, when its surface charge is negative. For BTEA-bentonite clays, regardless of the amount of CEC exchanged by the QAC, the ZPC is around pH 2.3 and is similar to Ca bentonite. An HDTMA loading equal to 100% of the CEC of bentonite results in a

positively charged surface at the examined pH range. This is likely caused by tail–tail interactions between HDTMA cations such that the charged moiety is oriented outwards towards the bulk solution. Li and Bowman [42] hypothesized this organic cation orientation to explain the sorption of chromate to an organo-clinoptilolite. Similar results were also reported by Wang et al. [30] for HDTMA bentonite. Xu and Boyd [37] found that HDTMA was initially sorbed by cation exchange in the interlayer, which caused extensive clay aggregation. As loading increased, HDTMA sorbed to the external surfaces of aggregates via cation exchange and hydrophobic bonding, the latter causing positive charge development on surfaces. On the other

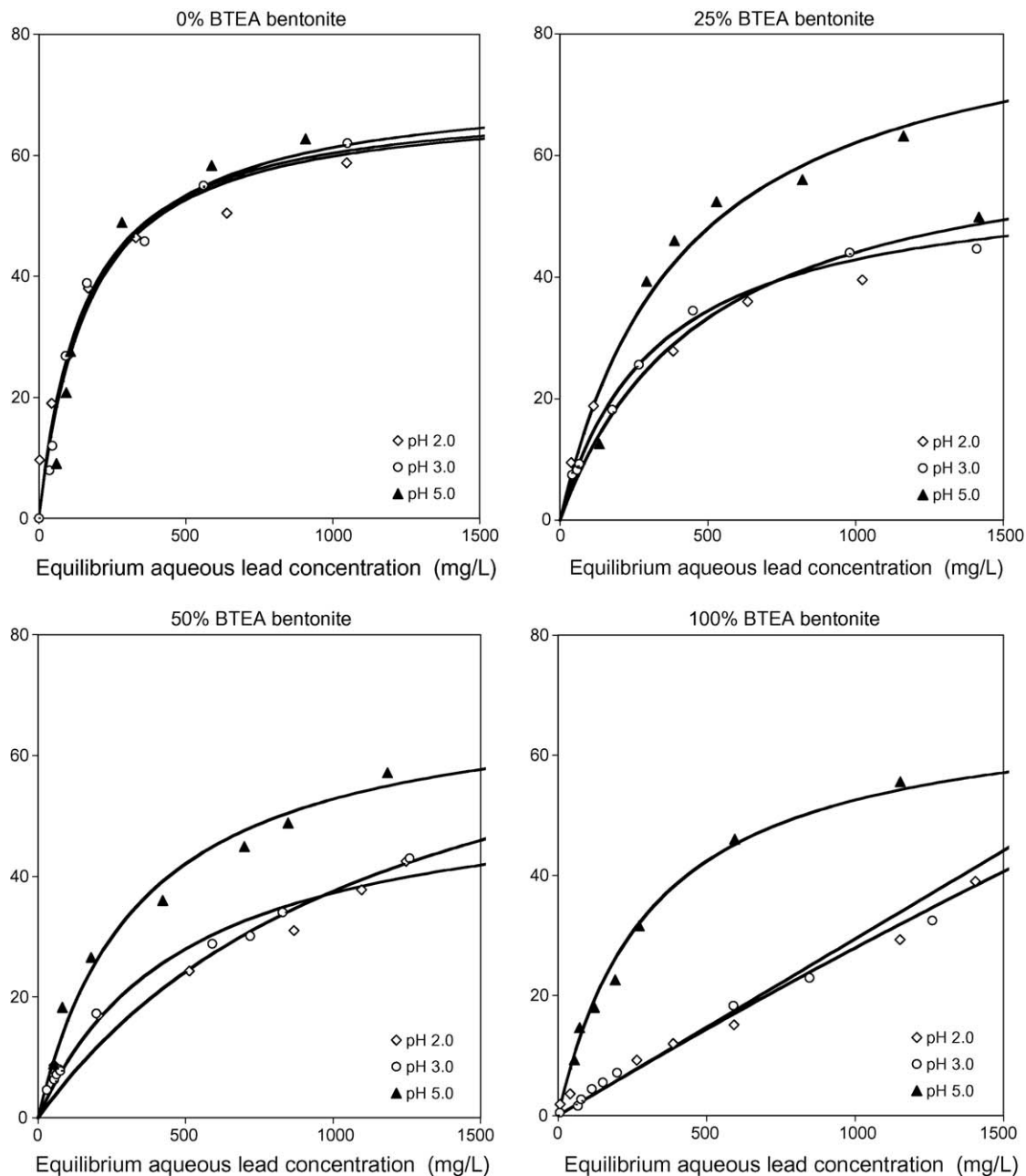


Fig. 4. Isotherms for the sorption of Pb to bentonite exchanged with BTEA cations at 0, 25, 50 and 100% of its CEC. Lines represent Langmuir model fits.

hand, the sorption of smaller BTEA cations is mainly caused by a cation-exchange reaction with negligible hydrophobic bonding. Similar behavior was observed by Wang et al. [30] using tetramethylammonium (TMA) instead of BTEA.

### 3.3. Speciation of heavy metals

Table 2 shows the speciation of the different metals obtained using MINTEQA2 [35]. For the three pH values tested, Cd, Pb and Zn are predominantly present in their divalent form (e.g.  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{Zn}^{+2}$ ). Mercury predominantly exists as  $\text{HgCl}_2$  at the pH studied.

### 3.4. Sorption of heavy metals

Batch isotherm experiments were performed for each metal/sorbent/pH combination (Figs. 2–7). For sorption of Cd, Pb, and Zn onto each sorbent, sorption is non-linear. The mechanism of metal uptake on the organoclays occurs in part by cation exchange with  $\text{Ca}^{+2}$  ions on the clay surface and also by formation of inner-sphere complexes with silanol and aluminol groups at the clay edges [43]. This latter process would explain the sorption of the heavy metals when 100% of the  $\text{Ca}^{+2}$  ions on the clay surface were modified with QAC and ion exchange is likely minimal. Isotherm data were fit to a Langmuir model using ISOFIT

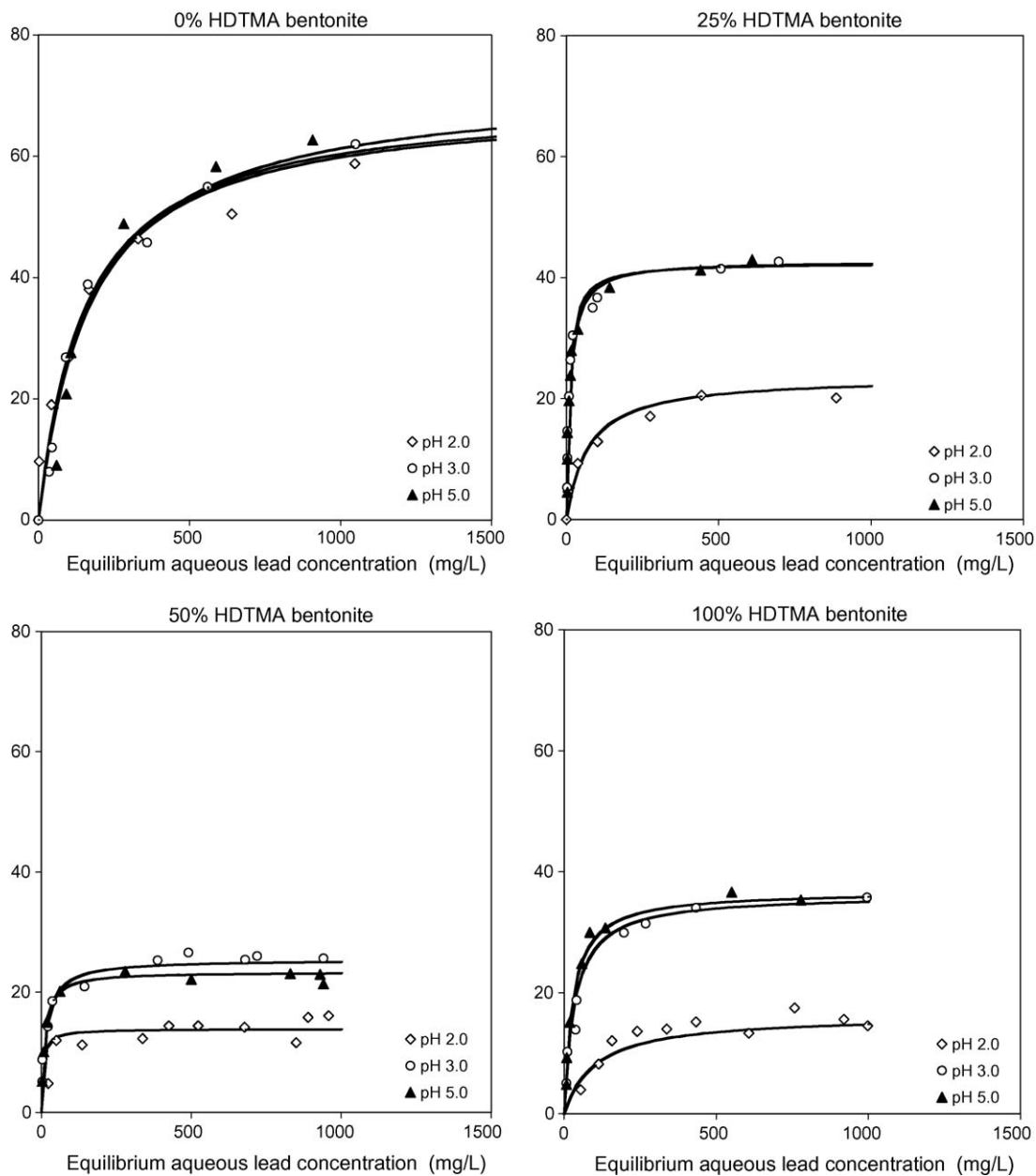


Fig. 5. Isotherms for the sorption of Pb to bentonite exchanged with HDTMA cations at 0, 25, 50 and 100% of its CEC. Lines represent Langmuir model fits.

software [44]:

$$C_s = \frac{bC_e Q}{1 + bC_e} \quad (3)$$

where  $C_s$  is the equilibrium sorbed metal concentration (mg/g),  $b$  (1/mg) and  $Q$  (mg/g) the fitted isotherm parameters, and  $C_e$  (mg/L) is the equilibrium aqueous solute concentration. Isotherm parameters and model fits are given in Table 3.

For Cd and Pb, the magnitude of sorption onto HDTMA and BTEA bentonites decreases with increased QAC loading up to 100%. Similar results were reported by Yoo et al. [24] and Lee et al. [23]. The decrease in metal sorption is likely caused by the inability of the metal ions to exchange with the larger quaternary

ammonium ions on the clay's external and interlamellar surfaces. This reduction in sorption with QAC loading is more pronounced with Pb than Cd. Greater sorption of both metals was observed on BTEA bentonite in comparison with HDTMA bentonite, possibly due to the higher surface area of BTEA bentonite relative to HDTMA bentonite. Higher surface area of BTEA bentonite implies a higher number of silanol and aluminol groups available for the sorption of heavy metals [36]. Sorption of Cd and Pb was at a minimum at pH 2, which is below the ZPC of the organoclay. At that pH, the organoclays have a more positively charged surface, which likely reduces sorption of like-charged metals. Furthermore, at lower pH, aluminol and silanol groups are more protonated and are unable to retain cations. This effect is strong for Pb and Cd and less pronounced for Zn. The rea-

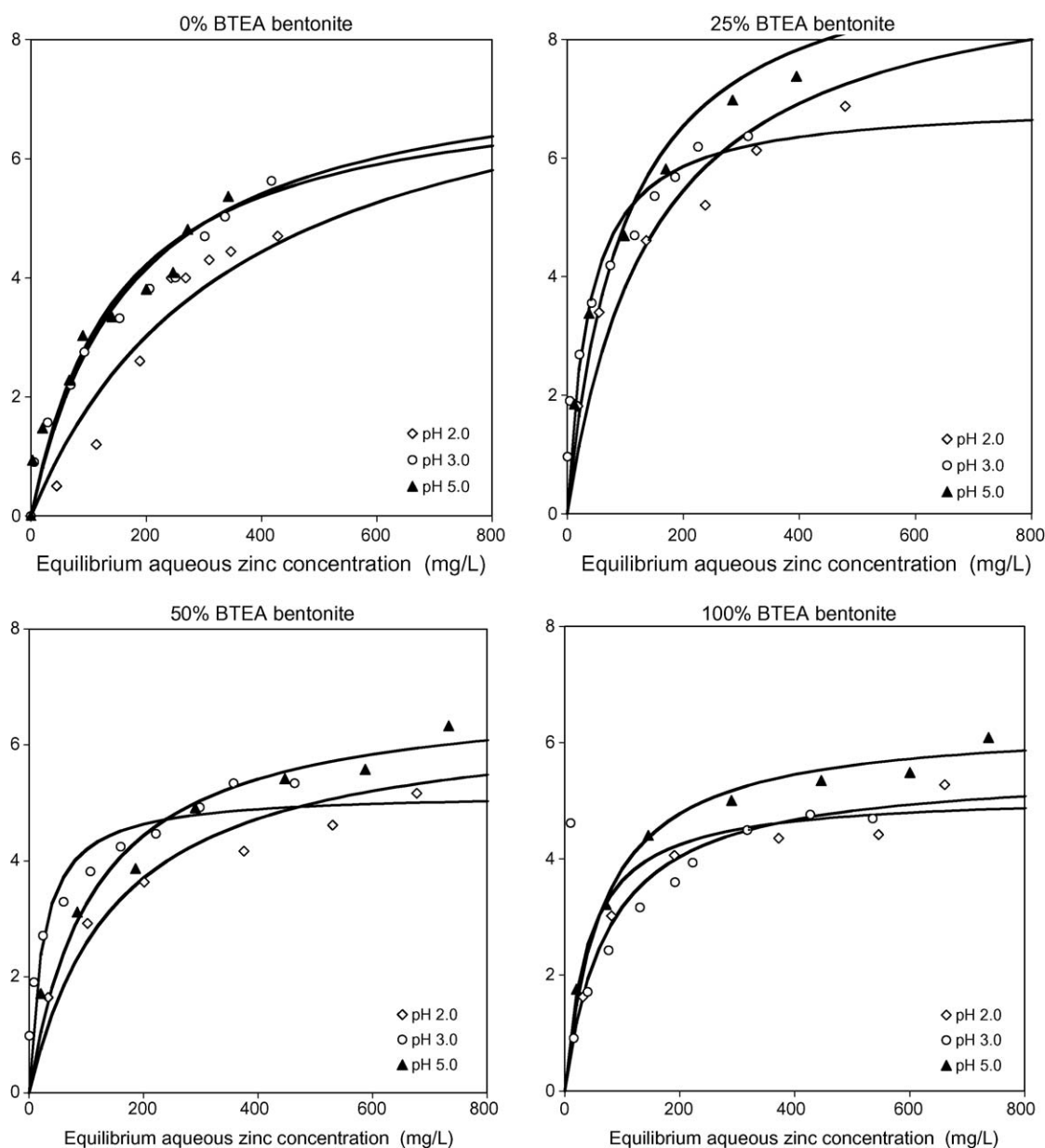


Fig. 6. Isotherms for the sorption of Zn to bentonite exchanged with BTEA cations at 0, 25, 50 and 100% of its CEC. Lines represent Langmuir model fits.



son for this behavior is that the surface complexation reactions are influenced by an electrostatic attraction between the surface charge and the dissolved ions. Since Cd and Pb have relatively large radii (0.97 and 1.2 Å, respectively), they have lower charge densities and, therefore, are more affected by protonation of the surface groups [45].

Zn sorption at different QAC loadings on each organoclay was similar to the sorption of Pb and Cd. However, the pH influence for Zn sorption was lower than that observed for Pb and Cd. Zn has a smaller atomic radius (0.64 Å) and a higher charge density, so its sorption is less affected by protonation of surface groups.

Sorption of Hg on BTEA and HDTMA bentonites is shown in Figs. 8 and 9, respectively. These data were fit to a linear

model of the form:

$$C_s = K_d C_e \quad (4)$$

where  $C_s$  is the equilibrium sorbed concentration (mg/g),  $C_e$  the equilibrium aqueous concentration (mg/L), and  $K_d$  is the sorption distribution coefficient (L/g). Isotherm parameters and model fits are given also in Table 3.

Hg sorption was distinctly different compared to the other three metals. Hg sorption to HDTMA and BTEA bentonite was linear. QAC loading on BTEA bentonite did not affect Hg sorption. Hg sorption increased with the QAC loading on HDTMA bentonite and showed higher sorption than the corresponding BTEA bentonites. On the other hand, decreased pH increased sorption; in general, the maximum sorption was

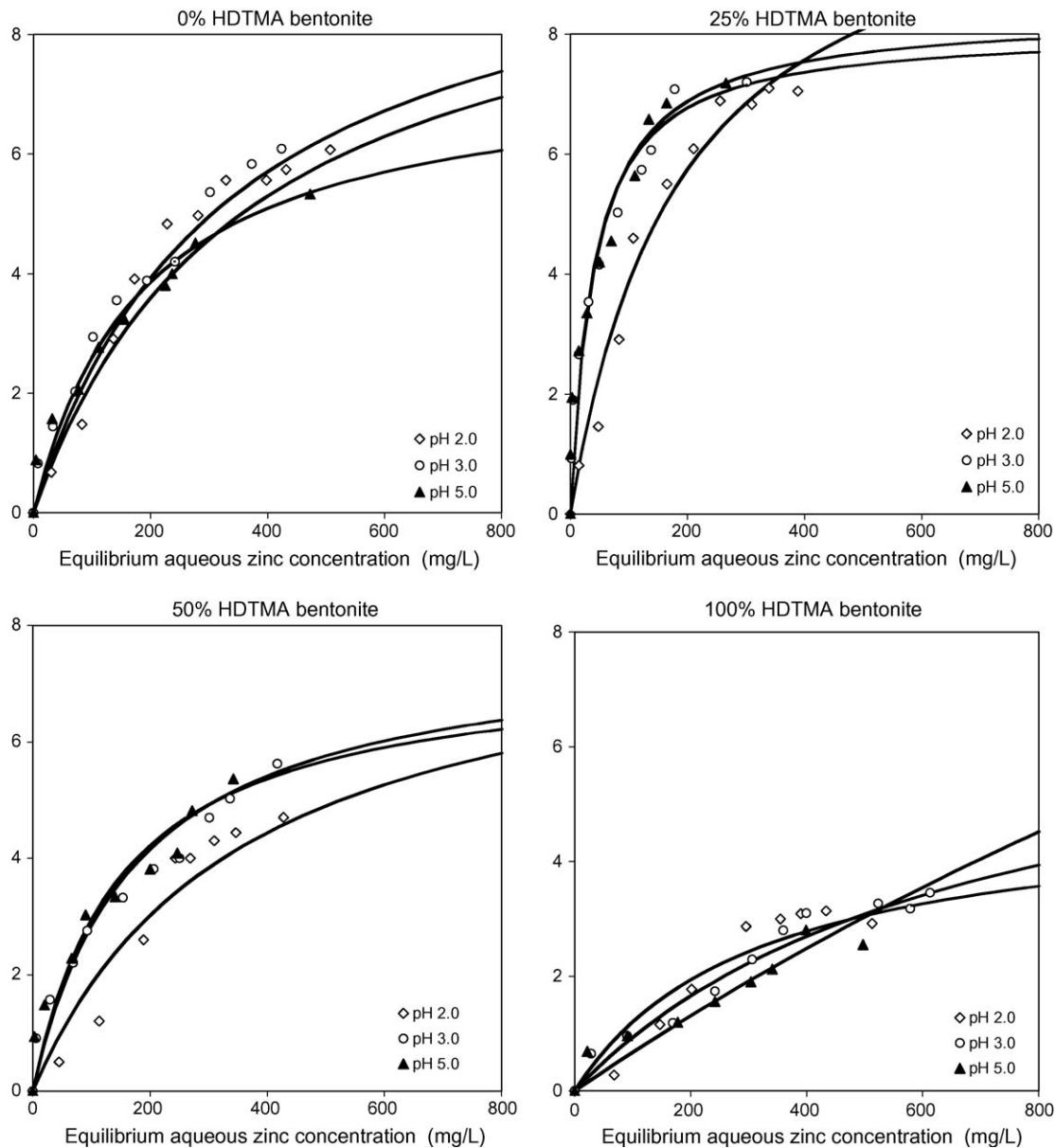


Fig. 7. Isotherms for the sorption of Zn to bentonite exchanged with HDTMA cations at 0, 25, 50 and 100% of its CEC. Lines represent Langmuir model fits.

Table 3  
Isotherm parameters for the sorption of heavy metals on BTEA bentonite and HDTMA bentonite with varying organic-carbon contents

	pH	Sorbent	$Q$ (mg/g)	$b$ (1/mg)	$R^2$	Sorbent	$Q$ (mg/g)	$b$ (1/mg)	$R^2$
Zn	2.0	0 BTEA	15.6	0.001	0.972	0 HDTMA	10.4	0.003	0.978
		25 BTEA	9.47	0.006	0.965	25 HDTMA	11.0	0.005	0.978
		50 BTEA	6.52	0.006	0.966	50 HDTMA	8.38	0.003	0.936
		100 BTEA	5.54	0.013	0.978	100 HDTMA	4.96	0.003	0.943
	3.0	0 BTEA	6.23	0.010	0.985	0 HDTMA	10.1	0.003	0.955
		25 BTEA	6.94	0.026	0.957	25 HDTMA	8.34	0.023	0.977
		50 BTEA	5.17	0.042	0.953	50 HDTMA	7.38	0.007	0.964
		100 BTEA	5.12	0.024	0.969	100 HDTMA	24.6	0.001	0.961
	5.0	0 BTEA	9.23	0.004	0.978	0 HDTMA	7.48	0.005	0.976
		25 BTEA	9.78	0.010	0.984	25 HDTMA	8.06	0.026	0.944
		50 BTEA	6.93	0.008	0.982	50 HDTMA	7.74	0.006	0.968
		100 BTEA	6.34	0.015	0.980	100 HDTMA	7.28	0.002	0.977
Cd	2.0	0 BTEA	5.43	0.002	0.991	0 HDTMA	4.90	0.003	0.972
		25 BTEA	7.13	0.026	0.986	25 HDTMA	5.72	0.007	0.965
		50 BTEA	7.17	0.003	0.992	50 HDTMA	4.60	0.006	0.966
		100 BTEA	6.01	0.003	0.974	100 HDTMA	2.57	0.004	0.975
	3.0	0 BTEA	4.81	0.005	0.979	0 HDTMA	4.79	0.002	0.981
		25 BTEA	6.73	0.028	0.982	25 HDTMA	8.08	0.005	0.985
		50 BTEA	6.50	0.014	0.989	50 HDTMA	8.71	0.002	0.986
		100 BTEA	5.21	0.009	0.969	100 HDTMA	8.31	0.001	0.975
	5.0	0 BTEA	6.55	0.003	0.986	0 HDTMA	6.51	0.003	0.910
		25 BTEA	7.82	0.023	0.983	25 HDTMA	6.54	0.007	0.985
		50 BTEA	7.53	0.014	0.987	50 HDTMA	6.63	0.003	0.986
		100 BTEA	5.64	0.012	0.982	100 HDTMA	5.43	0.005	0.971
Pb	2.0	0 BTEA	69.2	0.006	0.944	0 HDTMA	65.9	0.014	0.936
		25 BTEA	65.2	0.002	0.985	25 HDTMA	23.5	0.014	0.955
		50 BTEA	83.6	0.001	0.912	50 HDTMA	13.8	0.017	0.976
		100 BTEA	36.4	0.002	0.948	100 HDTMA	16.2	0.010	0.959
	3.0	0 BTEA	72.0	0.005	0.986	0 HDTMA	50.4	0.034	0.967
		25 BTEA	56.7	0.003	0.995	25 HDTMA	42.4	0.103	0.987
		50 BTEA	55.9	0.003	0.988	50 HDTMA	25.3	0.065	0.989
		100 BTEA	36.8	0.004	0.991	100 HDTMA	36.7	0.037	0.972
	5.0	0 BTEA	69.6	0.007	0.987	0 HDTMA	55.9	0.031	0.987
		25 BTEA	87.8	0.002	0.995	25 HDTMA	42.7	0.085	0.979
		50 BTEA	70.8	0.002	0.988	50 HDTMA	23.3	0.098	0.995
		100 BTEA	69.1	0.003	0.966	100 HDTMA	36.1	0.023	0.981
			$K_d$ (mg/g)	$R^2$		$K_d$ (mg/g)	$R^2$		
Hg	2.0	0 BTEA	0.0023	0.937	0 HDTMA	0.0021	0.902		
		25 BTEA	0.0028	0.981	25 HDTMA	0.0021	0.937		
		50 BTEA	0.0021	0.979	50 HDTMA	0.0083	0.971		
		100 BTEA	0.0306	0.999	100 HDTMA	0.0271	0.911		
	3.0	0 BTEA	0.0021	0.963	0 HDTMA	0.0029	0.927		
		25 BTEA	0.0026	0.983	25 HDTMA	0.0041	0.913		
		50 BTEA	0.0017	0.968	50 HDTMA	0.0061	0.924		
		100 BTEA	0.0027	0.975	100 HDTMA	0.0268	0.919		
	5.0	0 BTEA	0.0014	0.913	0 HDTMA	0.0015	0.953		
		25 BTEA	0.0013	0.945	25 HDTMA	0.0029	0.924		
		50 BTEA	0.0013	0.918	50 HDTMA	0.0038	0.901		
		100 BTEA	0.0021	0.941	100 HDTMA	0.0242	0.995		

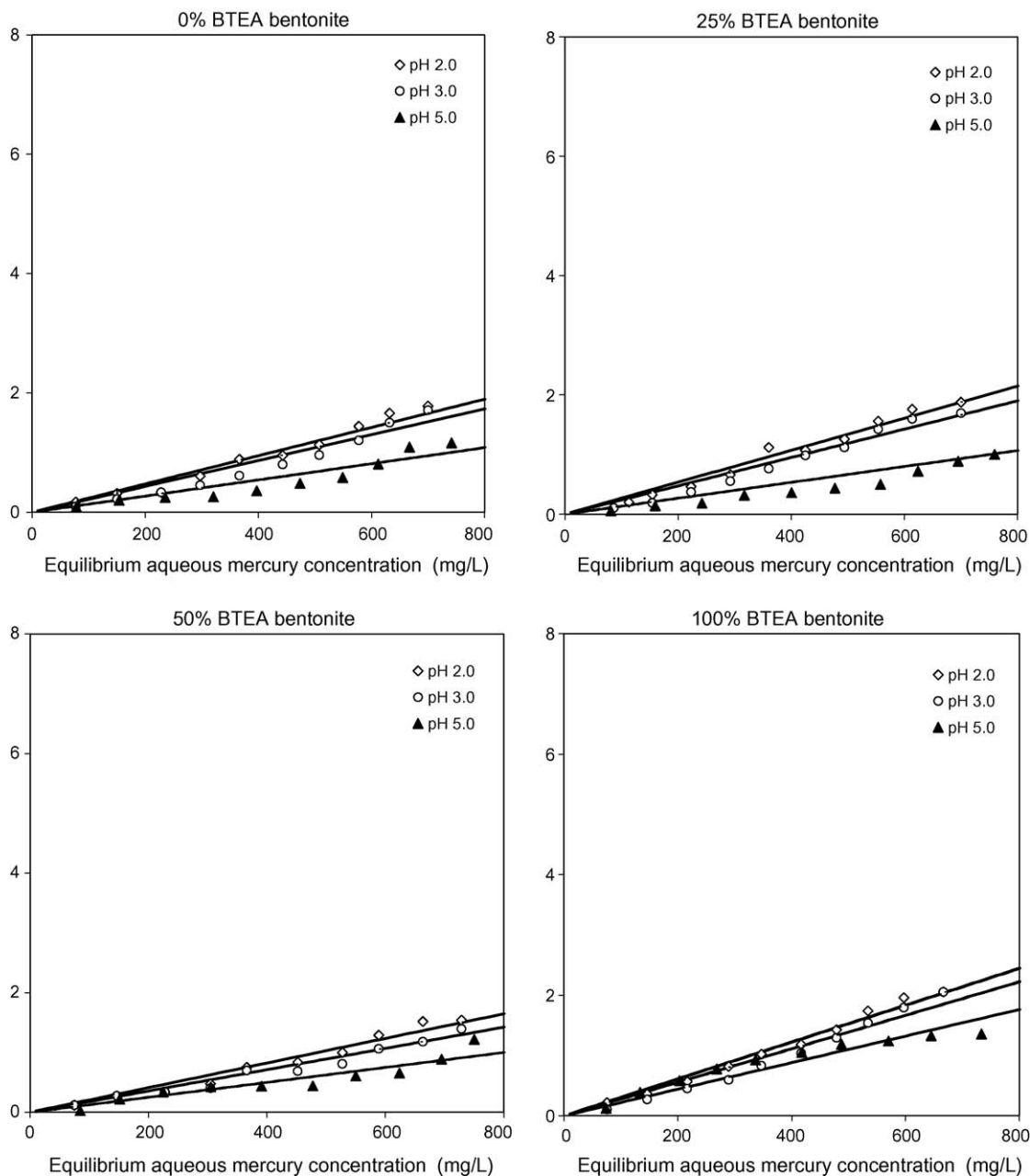


Fig. 8. Isotherms for the sorption of Hg to bentonite exchanged with BTEA cations at 0, 25, 50 and 100% of its CEC. Lines represent linear model fits.

achieved at pH 2.0. Hg was present in solution mainly as a non-charged species and the neutrality of the surface at pH close to the ZPC may increase the sorption of this species. On the other hand, Hg sorption to 100% HDTMA bentonite was greater than sorption of any other metal–organoclay combination, implying that Hg could be sorbed by process other than ion exchange. The linearity of the Hg isotherm with HDTMA bentonite and its increased sorption with HDTMA cation loading supports the idea that sorption occurs by partition between the aqueous solution and the organic medium created by the alkyl chains. This observation is also in concert with observa-

tions of nonionic organic solute uptake to HDTMA clays that indicate solute uptake occurs by partition [2,32]. For BTEA bentonite, the linearity of the Hg isotherm may be caused primarily by the relatively low concentration of positively charged Hg species in solution. Because sorption does not increase with BTEA cation loading and because previous research has shown that nonionic solute sorption to BTEA bentonite is caused by physical adsorption [2], it is possible that Hg sorption to BTEA bentonite is also caused by physical adsorption. Additional research will be required to better elucidate this sorption mechanism.

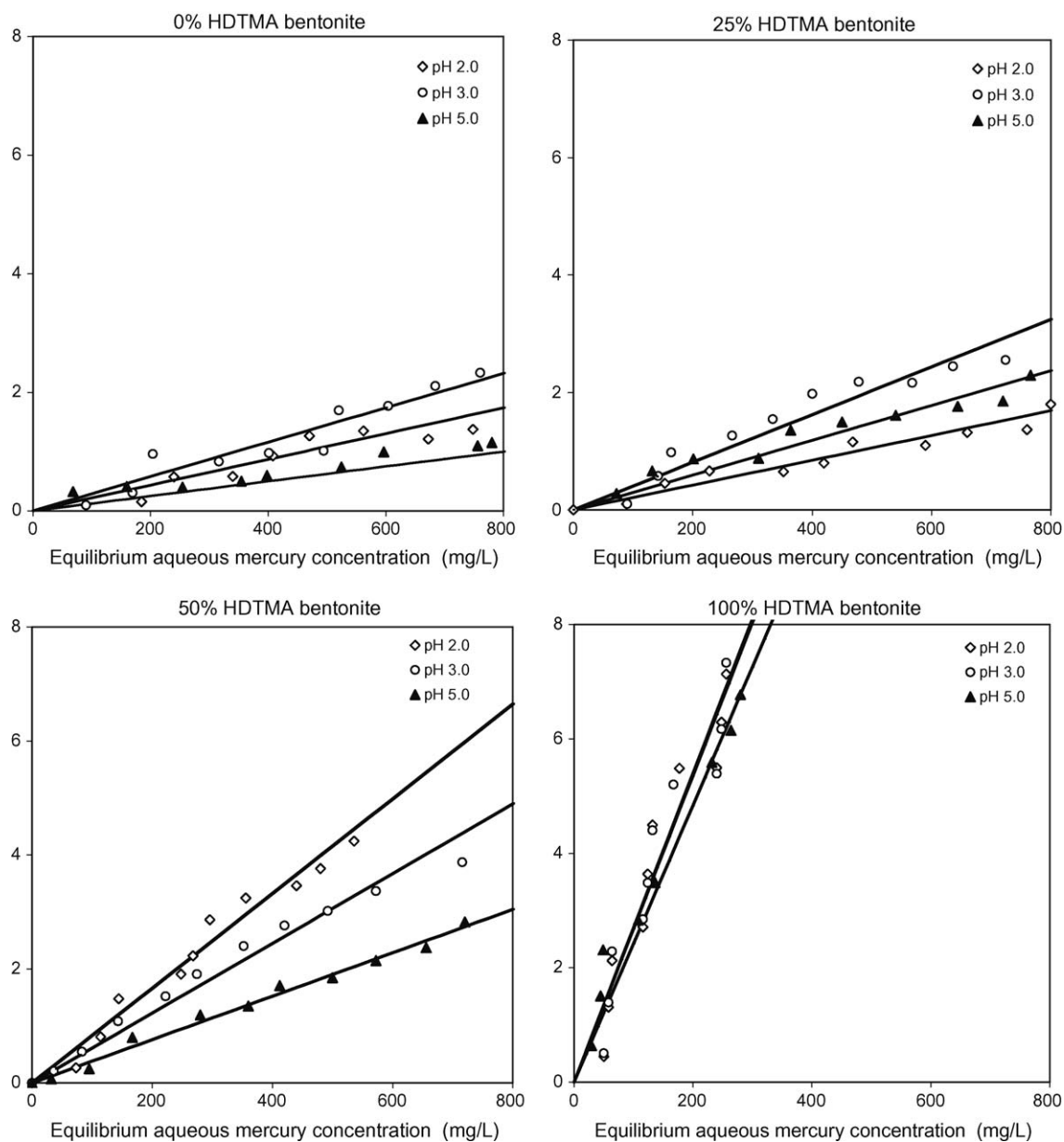


Fig. 9. Isotherms for the sorption of Hg to bentonite exchanged with HDTMA cations at 0, 25, 50 and 100% of its CEC. Lines represent linear model fits.

#### 4. Conclusion

Organoclays can effectively remove heavy metals from aqueous solution. Their capacity to sorb Pb, Cd and Zn decrease with increasing QAC loading, presumably because the metal cations cannot effectively exchange with the larger, quaternary ammonium cations. Hg, due to its different speciation, exhibits different sorption behavior, suggesting that the sorption mechanism is partition instead of ion exchange on HDTMA bentonite. Pb and Cd sorption showed higher dependence on pH than Zn and Hg. Values of pH close to the ZPC of the clays reduce sorption for Pb, Cd and Zn due to the protonation of the surface groups. The results of this study indicate that organobentonites are effective sorbents for both heavy metals and nonionic organic solutes. Additional research is needed to characterize any competitive

sorption effects between these different groups of environmental pollutants.

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