Effect of lead on the sorption of phenol onto montmorillonites and organo-montmorillonites

Liang-guo Yan, Xiao-quan Shan^{*}, Bei Wen, Shuzhen Zhang

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

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Abstract

The effect of lead (Pb) on the sorption of phenol onto montmorillonite-based sorbents was studied using a batch equilibration method when phenol and Pb were sorbed simultaneously and either Pb or phenol was previously sorbed. The sorbents were Na⁺-, Ca²⁺-, hexadecyl trimethylammonium (HDTMA)-Na⁺-, and HDTMA-Ca²⁺-montmorillonites. Pb diminished the sorption of phenol largely onto Na⁺- or Ca²⁺-montmorillonites, while phenol had little effect on the sorption of Pb onto all sorbents. Pb had no effect on the sorption of phenol onto HDTMA-Na⁺- or HDTMA-Ca²⁺-montmorillonites either. The sorption capacity of phenol followed the order HDTMA-Na⁺ > HDTMA-Ca²⁺ > Na⁺ > Ca²⁺-montmorillonites. The pseudo-second-order equation described the kinetics of phenol sorption well. Sorption isotherms of phenol followed the Freundlich equation. Phenol sorption on HDTMA-Na⁺- and HDTMA-Ca²⁺-montmorillonites was linear, while that on Na⁺- and Ca²⁺-montmorillonites was nonlinear.

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Keywords: Na⁺-, Ca²⁺-, HDTMA-Na⁺-, and HDTMA-Ca²⁺-montmorillonites; Sorption; Sorption kinetics; Phenol; Pb

1. Introduction

Phenol and its derivatives are common pollutants of petroleum and petrochemical and coal conversion industries. They are considered as priority pollutants since they are harmful to organisms at low concentrations.

In recent years, there has been an increasing interest in utilizing natural clay minerals and organoclays for the removal of phenol and phenolic compounds from aqueous solutions [1–7]. Banat et al. [1] examined the feasibility of using natural bentonite (mainly montmorillonite) for the sorption of phenol from aqueous solution. Treatment of clays with quaternary amine cationic surfactants could increase sorption capacity of phenol greatly [8–12]. Quaternary ammonium cations may be retained by both the outer and interlayer surfaces of an expandable clay particle via an ion-exchange, which are not easily displaced by smaller cations, such as H⁺, Na⁺, or Ca²⁺. The exchanged

mineral surfaces become more organophilic, thus increase their sorption of nonionic organic solutes from water. Sorption of nonionic organic contaminants from water by organoclays such as hexadecyl trimethylammonium (HDTMA)-smectite was originally viewed as a partition process involving the organic cation-derived organic phase [13–17]. Sorption of phenol, *p*-nitrophenol and aniline to the synthesized dual-cation and anion–cation organobentonites was dominated by adsorption at low concentrations and by partition at high concentrations [18,19].

Lead (Pb) is one of hazardous heavy metals. It tends to be accumulated in organisms and enter the food chains. Pb content in the environment can be accumulated to a very high level through the application of fertilizers, sewage sludge or irrigation with wastewater. Clay minerals, such as montmorillonite, are potential adsorbents for heavy metals as they have a large specific surface area and a high cation-exchange capacity. X-ray absorption fine structure spectroscopic study indicated that the formation of inner- and outer-sphere complexes is responsible for the adsorption of Pb onto montmorillonite, and the adsorption of Pb depended on ionic strength and pH [20].

^{*} Corresponding author. Fax: +86 10 62923563.

E-mail address: xiaoquan@rcees.ac.cn (X.-q. Shan).

At low ionic strength and pH the adsorption is primarily ascribed to the formation of outer-sphere complex and most likely occurs on the basal planes existing in the interlayer regions of the montmorillonite. As pH and ionic strength increases, the formation of inner-sphere complex becomes more important. It occurs on the edges of the montmorillonite and includes the formation of Pb polymers. The data from such study also suggested that adsorbed Pb existed as a mixture of inner- and outer-sphere complexes under appropriate ionic strength and pH conditions.

It is realized that under field conditions both heavy metals and organic chemicals may coexist. Compared with the extensive separate studies on the sorption of heavy metals and organic chemicals onto clays and organoclays, there is little information on the effect of heavy metals on the sorption of organic chemicals and vice versa [21–24]. Generally, clays are known to effectively sorb mostly heavy metals, while organoclays are adsorbents of organic contaminants. It has been assumed that there exists an optimal coverage of cationic surfactant on the clay particles to sorb both heavy metals and organic contaminants [25,26].

Adsorption and desorption of Cu on montmorillonite were affected by the presence of a cationic pesticide chlordimeform [24]. Cu adsorption decreased when both adsorbates were adsorbed simultaneously, indicating a competition between Cu and chlordimeform for interlamellar positions. Morillo et al. [22,23,27,28] studied the mutual influence of glyphosate and Cu adsorption on montmorillonite and soil. Glyphosate adsorption on montmorillonite decreased in the presence of Cu in solution. This was attributed to the formation of Cu–glyphosate complexes that have a lower tendency to be adsorbed on montmorillonite than the free glyphosate. These works also found that the presence of Cu enhanced the sorption of glyphosate on soil.

It is very important to study the sorption behaviors of heavy metals and toxic organic pollutants and the relevant mechanisms, which may help to uphold environmental standards for complex pollutants. There are few reports available in this field [29,30]. In the present study, Pb and phenol were chosen as representatives of heavy metals and toxic organic pollutants, respectively. We studied the sorption of phenol as affected by Pb using Na^+ -, Ca^{2+} -, HDTMA- Na^+ -, and HDTMA- Ca^{2+} -montmorillonites as sorbents and vice versa. The sorption kinetics was also evaluated.

2. Materials and methods

2.1. Materials

Natural montmorillonite used in this study was purchased from Beijing Youlichuangjia Science and Technology Development Company (Beijing, China). According to the supplier, the natural montmorillonite contains 98% montmorillonite, 0.5% kaolinite, and 1.0% quartz. The chemical compositions are 50.90% SiO_2 , 18.36% Al_2O_3 , 1.03% Fe_2O_3 , 3.97% CaO , 4.14% MgO , 0.02% TiO_2 , 0.72% K_2O , 1.18% Na_2O , and 2.15% P_2O_5 .

All chemicals, such as phenol, HDTMA, $\text{Pb}(\text{NO}_3)_2$, NaNO_3 , NaOH , and HNO_3 were of analytical reagent grade or better quality.

2.2. Preparation of sorbents

Natural montmorillonite was used just as received without further purification. A portion of 10 g montmorillonite was enriched with 1.0 L of 1.0 mol L^{-1} NaCl or CaCl_2 solution in beaker. The montmorillonite suspension was shaken for 24 h and fresh chloride salt solutions were used to replace the original solutions obtained after sedimentation. This process was repeated three times to ensure complete cation saturation. The excess chloride salts were removed by repeatedly washing with deionized water until chloride-free as indicated by the AgNO_3 test. The product was dried at 80 °C and gently ground in an agate mortar. Such treated montmorillonites were designated as Na^+ - and Ca^{2+} -montmorillonites.

The organo-montmorillonites were prepared by adding 10 g Na^+ - or Ca^{2+} -montmorillonite to 1.0 L appropriate amount of HDTMA solution in a 1:1 molar ratio to their CEC (89.6 cmol kg^{-1} for Na^+ -montmorillonite and 72.4 cmol kg^{-1} for Ca^{2+} -montmorillonite), respectively. The mixtures were subjected to a mechanical stirring for 24 h. The suspensions were then separated by centrifugation, washed with deionized water several times until no Br^- was detected from the supernatant and dried at 80 °C. The two prepared sorbents were designated as HDTMA- Na^+ - and HDTMA- Ca^{2+} -montmorillonites.

2.3. Effect of pH on the sorption of phenol

Phenol was dissolved in 0.01 mol L^{-1} NaNO_3 /0.1 g L^{-1} NaN_3 solutions for the sorption experiment of Na^+ - and HDTMA- Na^+ -montmorillonites, and in a 0.01 mol L^{-1} $\text{Ca}(\text{NO}_3)_2$ /0.1 g L^{-1} NaN_3 solution for the sorption experiment of Ca^{2+} - and HDTMA- Ca^{2+} -montmorillonites. The batch sorption equilibration was done in triplicate in 50-ml glass centrifuge tubes by mixing 0.400 g Na^+ -montmorillonite (or Ca^{2+} -montmorillonite) or 0.100 g HDTMA- Na^+ - (or HDTMA- Ca^{2+} -montmorillonite) with 20 ml 10.0 mmol L^{-1} phenol solutions. Due to the large sorption ability of HDTMA- Na^+ - or HDTMA- Ca^{2+} -montmorillonite, only 0.100 g HDTMA- Na^+ - or HDTMA- Ca^{2+} -montmorillonite was used in this study. The pH was adjusted from 3.0 to 12.0 by addition of 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} NaOH . The suspension was shaken by end-over-end continuously for 24 h at room temperature. During the shaking, the pH values were measured at certain intervals and readjusted if necessary. The suspension was centrifuged at 1667g for 20 min to separate liquid and solid phases, and then a portion of supernatant was used for spectrophotometric determination of phenol at 269.5 nm.

2.4. Sorption kinetics of phenol

Sorption kinetics was performed by a batch equilibration method at room temperature. Briefly, 0.100 g of HDTMA- Na^+ -

or HDTMA- Ca^{2+} -montmorillonite or 0.400 g of Na^{+} - or Ca^{2+} -montmorillonite with 20 ml of phenol solutions was added to 50-ml glass centrifuge tubes sealed by Teflon-lined screw caps. The pH value of the system was kept at 6.0. The initial phenol concentration added was 10.0 or 4.0 mmol L^{-1} . After the suspension was shaken by end-over-end for the target contact time, the suspension was centrifuged. The sorbed phenol was measured by the differences between the initial and final phenol concentrations in the equilibrium solutions. The sorption kinetic experiments were performed in triplicate.

2.5. Sorption isotherms of phenol

The experiments were carried out in triplicate by mixing 0.100 g of HDTMA- Na^{+} - or HDTMA- Ca^{2+} -montmorillonite or 0.400 g of Na^{+} - or Ca^{2+} -montmorillonite with 20 ml of various concentrations of phenol in 0.01 mol L^{-1} NaNO_3 (or $\text{Ca}(\text{NO}_3)_2$)/0.1 g L^{-1} NaN_3 background electrolyte solution. The pH of phenol-sorbent suspension was adjusted to 6.0. The pH value was measured at certain intervals and readjusted if necessary. The suspension was shaken by end-over-end continuously for 24 h to ensure complete sorption.

2.6. Effect of Pb on the sorption of phenol

The batch equilibration sorption experiments were carried out in triplicate by mixing 0.100 g of HDTMA- Na^{+} - or HDTMA- Ca^{2+} -montmorillonite or 0.400 g Na^{+} - or Ca^{2+} -montmorillonite with 20 ml 0.01 mol L^{-1} NaNO_3 (or $\text{Ca}(\text{NO}_3)_2$)/0.1 g L^{-1} NaN_3 solution containing various concentrations of phenol and Pb (0, 0.5, 1.0, and 2.0 mmol L^{-1}) in 50-ml glass centrifuge tubes sealed by Teflon-lined screw caps. The pH of suspensions was adjusted to 6.0. The suspensions were shaken by end-over-end continuously for 24 h at room temperature. After centrifugation at 1667g for 20 min, phenol and Pb in the supernatant were determined, respectively. The concentrations of Pb were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA2000DV, Perkin-Elmer, USA).

Effect of Pb on the sorption of phenol was also conducted when either phenol or Pb was previously sorbed. The procedure outlined above for simultaneous sorption of both sorbates was followed. The only exception was that either Pb or phenol was previously sorbed for 24 h, and then the suspension was shaken for extra 24 h again after the solution containing various concentrations of phenol or Pb was added.

2.7. Sorption isotherms of Pb in the absence or presence of phenol

A portion of 0.100 g of Na^{+} - or Ca^{2+} -montmorillonite or HDTMA- Na^{+} - or HDTMA- Ca^{2+} -montmorillonite with 20 ml of various concentrations of Pb in the absence and presence of 10.0 mmol L^{-1} phenol in 0.01 mol L^{-1} NaNO_3 /0.1 g L^{-1} NaN_3 (or $\text{Ca}(\text{NO}_3)_2$ /0.1 g L^{-1} NaN_3) background electrolyte solution was added together to glass centrifuge tubes. The pH

of all sorbate-sorbent solutions was adjusted to 6.0. The sorption equilibration time was 24 h. After reaching equilibrium the suspensions were centrifuged at 1667g for 20 min to separate liquid and solid phases, and then Pb in supernatants was determined by ICP-AES. The sorption experiments were carried out in triplicate.

2.8. Sorption models

2.8.1. Sorption kinetics models

The kinetics of sorption is important from the point of view that it controls the sorption efficiency. Two kinetics models, pseudo-first- and pseudo-second-order equations, were applied to our experimental data.

A simple kinetic analysis of sorption is the pseudo-first-order equation in the form [31]:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303}t, \quad (1)$$

where q_t (mmol kg^{-1}) is the amount of sorbed at time t (h), q_e (mmol kg^{-1}) is the amount of sorbed at equilibrium, and k_1 (1/h) is the rate constant of the first-order sorption.

The sorption kinetics may also be described by a pseudo-second-order reaction [31]. The linear form of this model is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t, \quad (2)$$

where k_2 ($\text{kg mmol}^{-1} \text{h}^{-1}$) is the rate constant of pseudo-second-order sorption.

2.8.2. Sorption isotherms models

The widely used equilibrium-based isotherm models are Freundlich and Langmuir equations. Their linear forms are listed below:

$$\ln q_e = n \ln C_e + \ln K_f, \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}, \quad (4)$$

where q_e (mmol kg^{-1}) is the amount of sorption, C_e (mmol L^{-1}) is the equilibrium concentration; n is a constant indicating the Freundlich isotherm curvature, and K_f ($(\text{mmol kg}^{-1})/(\text{mmol L}^{-1})^n$) is the Freundlich sorption coefficients; q_m (mmol kg^{-1}) is the maximum adsorption capacity of Langmuir, b is Langmuir constants.

3. Results and discussion

3.1. Effect of pH on phenol sorption

The sorption of phenol by Na^{+} -, Ca^{2+} -, HDTMA- Na^{+} -, and HDTMA- Ca^{2+} -montmorillonites was studied at various pH levels. As shown in Fig. 1, the sorption capacities of phenol showed no systematic variations between pH 3.0 and 10.0, while it declined dramatically between 10.0 and 12.0. This observation is consistent with Juang et al. [2], Li et al. [32], and Yang et al. [11]. However, phenol sorption to montmorillonite, kaolinite, and organobentonite decreased when pH was higher

Fig. 1. Effect of equilibrium solution pH on the sorption of phenol on (■) HDTMA-Na⁺, (●) HDTMA-Ca²⁺, (▲) Na⁺, and (◆) Ca²⁺-montmorillonites.

than 8 [1,3,33], and to organo-montmorillonite increased when pH was higher than its pK_a 9.89 [4,34]. It seems that the extent of sorption of phenol to montmorillonites varies as a function of solution pH, since pH governs both the fraction of phenol in deprotonated form and charges of sorbent surfaces. Phenol is present in neutral form when pH was lower than 2 units of its pK_a 9.89. When pH was higher than 2 units of its pK_a 9.89, deprotonated phenol is predominated. At higher pH, the decreased phenol sorption may be caused by the electrostatic repulsion between the reactive surface sites and the negatively charged phenol molecules [11,30]. Moreover, the sorbent is a key factor since the charge density on a given solid is dependent on the surrounding conditions. Solution ionic strength and composition also affect the sorption of phenol.

3.2. Sorption kinetics of phenol

The results of the sorption kinetics experiments are presented in Fig. 2. The plots represent the amount of phenol sorbed q_t onto montmorillonites versus time t . For an initial phenol concentration of 10 mmol L⁻¹, it was shown that the equilibrium time was almost 18 h for all types of montmorillonites. However, the equilibrium time was slightly different for the initial concentration of 4.0 mmol L⁻¹. The decrease in initial phenol concentration influenced the contact time necessary to reach equilibrium and decreased the sorption capacity on Na⁺, Ca²⁺, HDTMA-Na⁺, and HDTMA-Ca²⁺-montmorillonites, respectively. In order to ensure equilibrium, the subsequent experiments were performed for 24 h.

Many studies have pointed out that the majority of sorption kinetics can be represented as a pseudo-first-order rate mechanism [35]. A detailed sorption studies on the phenol and three chlorophenols by carbonaceous adsorbent have indicated that the sorption process is a first-order kinetics and is pore diffusion control [36]. Akçay [37] found that the sorption rate of *p*-chlorophenol by organophilic bentonite fit the pseudo-first-order kinetics. However, it was clearly found that the pseudo-second-order equation, which agrees with chemisorption as the rate-control mechanism, was able to better describe the sorption

Fig. 2. Sorption kinetics of phenol for (■) HDTMA-Na⁺, (●) HDTMA-Ca²⁺, (▲) Na⁺, and (◆) Ca²⁺-montmorillonites. The initial phenol concentrations were 10 mmol L⁻¹ (a) and 4.0 mmol L⁻¹ (b).

of phenolic compounds onto organoclays [2,6,38] and other sorbents [39,40].

To evaluate the differences in the sorption kinetics rate, the kinetics of phenol sorption was described with pseudo-first- and pseudo-second-order models. The kinetics data are plotted as the linear form of the models (Fig. 3), and the resultant parameters are given in Table 1. By comparing the amount of phenol sorbed q_e at equilibrium, the following order is observed: HDTMA-Na⁺ > HDTMA-Ca²⁺ > Na⁺ > Ca²⁺-montmorillonites. The rate constant k_1 of pseudo-first-order sorption and k_2 of pseudo-second-order sorption ranged from 0.07478 to 0.2739 h⁻¹ and 9.629×10^{-4} to 3.367 kg mmol⁻¹ h⁻¹, respectively. The correlation coefficients of the linear fit are all higher than 0.97 with 99% confidence level (Table 1). As shown in Fig. 3 and Table 1, whatever the kinetic equation used, the description of the sorption kinetics was satisfactory.

The validity of the pseudo-first- and pseudo-second-order equations can be checked by studying the kinetics under different initial concentrations, because in the case of a first-order kinetic reaction, the half-life time is constant whatever the initial sorbate concentration [41]. The initial concentration of phenol was varied from 10 to 4.0 mmol L⁻¹, as shown in Fig. 2. Furthermore, the calculated half-life time based on k_1 values (Table 1) decreased from 3.1, 6.7, 3.0, and 4.4 to 2.8, 3.8,

Fig. 3. Pseudo-first- (a, b) and pseudo-second-order equation (c, d) fit of phenol sorption on (■) HDTMA- Na^+ -, (●) HDTMA- Ca^{2+} -, (▲) Na^+ -, and (◆) Ca^{2+} -montmorillonites. The initial phenol concentrations were 10 mmol L^{-1} (a, c) and 4.0 mmol L^{-1} (b, d).

Table 1
Kinetics parameters and correlation coefficients for the sorption of phenol

Sorbent	C_0 (mmol L^{-1})	Pseudo-first-order equation			Pseudo-second-order equation		
		q_e (mmol kg^{-1})	k_1 (h^{-1})	R^2	q_e (mmol kg^{-1})	k_2 ($\text{kg mmol}^{-1} \text{h}^{-1}$)	R^2
Na^+ -Mt ^a	10	184.3	0.1769	0.9979 ^b	261.1	1.614×10^{-3}	0.9981 ^b
	4.0	107.9	0.1636	0.9632 ^b	156.7	3.367	0.9892 ^b
Ca^{2+} -Mt ^a	10	32.70	0.1306	0.9789 ^b	56.37	1.262×10^{-2}	0.9996 ^b
	4.0	15.97	0.07478	0.9724 ^b	20.88	1.809	0.9980 ^b
HDTMA- Na^+ -Mt ^a	10	528.7	0.2739	0.9873 ^b	862.1	1.170×10^{-3}	0.9984 ^b
	4.0	51.44	0.1673	0.9797 ^b	271.7	0.2594	0.9999 ^b
HDTMA- Ca^{2+} -Mt ^a	10	439.1	0.2174	0.9965 ^b	636.9	9.629×10^{-4}	0.9980 ^b
	4.0	65.52	0.1148	0.9915 ^b	182.5	0.6149	0.9992 ^b

^a Mt, montmorillonite.

^b Indicates the statistical significance at probability level of $p < 0.01$.

1.8, and 2.3 h on Na^+ -, Ca^{2+} -, HDTMA- Na^+ -, and HDTMA- Ca^{2+} -montmorillonites when the initial phenol concentration improved from 4.0 to 10 mmol L^{-1} . Thus the sorption of phenol seemed to be best described by the pseudo-second-order equation. The tendency of the pseudo-first-order equation underestimated the quantity of the phenol sorption.

3.3. Sorption isotherms of phenol

Sorption isotherms of phenol from water by HDTMA- Na^+ -, HDTMA- Ca^{2+} -, Na^+ -, and Ca^{2+} -montmorillonites were per-

formed. The equilibrium sorption data were evaluated by Langmuir and Freundlich models.

The linear plots of phenol sorption on montmorillonites and the resulted parameters are shown in Fig. 4 and Table 2, respectively. It is found that the best fitting was obtained by the Freundlich model ($R^2 > 0.96$ with 99% confidence level). This is in agreement with other works on the sorption of phenolic pollutants by clays and organoclays [4,5,8,9,38]. When the Langmuir model was applied to these data, a good fit was obtained on the sorption of phenol by homoionic montmorillonites. How-

Table 2
Freundlich and Langmuir constants and correlation coefficients for the sorption of phenol

Model	Parameter	Na ⁺ -Mt ^a	Ca ²⁺ -Mt ^a	HDTMA-Na ⁺ -Mt ^a	HDTMA-Ca ²⁺ -Mt ^a
Freundlich equation	k_f^b	66.89	15.85	99.30	62.50
	n	0.6128	0.5556	1.181	1.1099
	R^2	0.9964 ^c	0.9663 ^c	0.9941 ^c	0.9768 ^c
Langmuir equation	q_m (mmol kg ⁻¹)	480.8	78.19	–2417	–1483
	b (L mmol ⁻¹)	0.1347	2.276	–0.04136	–0.03919
	R^2	0.9569 ^c	0.9857 ^c	0.7217	0.6759

^a Mt, montmorillonite.

^b (mmol kg⁻¹ (mmol L⁻¹)⁻ⁿ).

^c Indicates the statistical significance at probability level of $p < 0.01$.

Fig. 4. Langmuir (a) and Freundlich (b) equation fit of phenol sorption onto (■) HDTMA-Na⁺, (●) HDTMA-Ca²⁺, (▲) Na⁺, and (◆) Ca²⁺-montmorillonites.

ever, deviations of the linear fit were observed on the sorption by HDTMA-Na⁺ and HDTMA-Ca²⁺-montmorillonites. Freundlich model seemed to be more appropriate than Langmuir model.

The Freundlich constant n is also a measure of the deviation from linearity of the sorption. With $1.05 > n > 0.95$, the sorption is practically considered linear. This means that the sorption sites are homogeneous in energy and no interaction occurs between the adsorbed species; when $n < 1$, the isotherm is concave downward and implies that added sorbates are bound with weaker and weaker free energies; finally, when $n > 1$, the isotherm is convex upward and infers that more sorbate presence in the sorbent enhances the free energies of further sorption [42].

The sorption isotherms (Fig. 4) and n values (Table 2) indicate that partition is apparently the dominant mechanism for phenol sorption by HDTMA-Na⁺ and HDTMA-Ca²⁺-montmorillonites. Here, the high degree of sorption into the HDTMA phase substantially changed the composition of the phase. This caused the solvency (i.e., the solubilization capability) of HDTMA phase for phenol to increase, so that the isotherms became convex to the abscissa. A similar phenomenon was observed for the partition of trichloroethylene and chlorobenzene by HDTMA-clays [43]. On the other hand, phenol sorption by homoionic montmorillonites is due to specific sorption to the negatively charged surface of clays and the sorption capacity is much lower than that by partition to HDTMA-montmorillonites.

Sorption was affected by the type of exchanged cations on montmorillonite (Table 2). Between the cations tested, Na⁺ and HDTMA-Na⁺-montmorillonites were much more effective than the corresponding Ca²⁺ and HDTMA-Ca²⁺-montmorillonites for phenol sorption. The comparatively lower sorption by Ca²⁺-montmorillonite is attributed to the larger enthalpy of hydration of Ca²⁺ as compared with Na⁺. Larger hydration sphere around Ca²⁺ obscured a greater portion of the neutral siloxane surface, thereby reducing hydrophobic interactions between these surfaces and phenol [44]. For HDTMA-exchanged montmorillonites, Na⁺-montmorillonite sorbed more HDTMA than Ca²⁺-montmorillonite due to its higher CEC (89.6 cmol kg⁻¹ for Na⁺-montmorillonite and 72.4 cmol kg⁻¹ for Ca²⁺-montmorillonite), thus more phenol was partitioned into the surfactant derived organic matter.

3.4. Effect of Pb on phenol sorption

Effect of Pb on the sorption of phenol was evaluated when both sorbates were sorbed simultaneously on Na⁺ and Ca²⁺-montmorillonites and the corresponding HDTMA-exchanged montmorillonites (Fig. 5). For Na⁺ and Ca²⁺-montmorillonites the sorption of phenol decreased clearly when 1.0 mmol L⁻¹ Pb was added simultaneously. In contrast, Pb had almost insignificant effect on the sorption of phenol on HDTMA-Na⁺ and HDTMA-Ca²⁺-montmorillonites. Compared with homoionic montmorillonites, HDTMA-montmorillonites sorbed more phenol due to its surfactant derived organic matter. When Pb was added, it was sorbed on the surface of

Fig. 5. Sorption isotherms of phenol onto (a) Na⁺-, (b) Ca²⁺-, (c) HDTMA-Ca²⁺-, and (d) HDTMA-Na⁺-montmorillonites in the absence (■) and presence (●) of Pb.

HDTMA-Na⁺- and HDTMA-Ca²⁺-montmorillonites, while phenol was partitioned into surfactant derived organic matter, indicating that they were sorbed by different domains. In order to determine Pb remaining in solid phase its concentration in the supernatant solution was also determined simultaneously. However, the sorbed Pb on solid-phase sorbents varied slightly. Obviously, Pb sorption was independent on the presence of phenol, suggesting the higher affinity of lead for the sorbents.

To determine the effect of Pb on the sorption of phenol onto homoionic montmorillonites, a series of experiments were conducted. Figs. 6a and 6b show the sorption isotherms of phenol on Na⁺- and Ca²⁺-montmorillonites when phenol and different Pb concentrations (0, 0.5, 1.0, and 2.0 mmol L⁻¹) were sorbed simultaneously. The sorbed phenol decreased with increasing Pb concentrations from 0 to 2.0 mmol L⁻¹, suggesting that Pb decreased the sorption of phenol. The effect of Pb on the sorption of phenol was also conducted when phenol or Pb was previously sorbed. The sorbents were equilibrated with phenol first for 24 h, and then a certain amount of Pb solution was added to the equilibrated suspension to make the initial Pb concentrations of 0.5, 1.0, and 2.0 mmol L⁻¹, respectively. The

suspension was further equilibrated for an additional 24 h. The results are shown in Figs. 6e and 6f. Figs. 6c and 6d show the sorption isotherms of phenol when Pb was previously sorbed. These results indicated that the suppression effect of Pb on the phenol sorption was quite similar to that when both sorbates were sorbed simultaneously (Figs. 6a and 6b). This is due to the fact that Pb with positive charge has stronger sorption affinity than phenol for sorption sites of montmorillonites. The results suggested that Pb was able to compete with phenol for the same sorption sites, even when phenol was previously sorbed. This implies that the addition of Pb would release the sorbed phenol from clays, and this phenomenon has its important environmental consequence.

3.5. Sorption isotherms of Pb in the absence or presence of phenol

Sorption of Pb in the absence and presence of 10.0 mmol L⁻¹ phenol was performed. The sorption data were analyzed by a linear fit of the Freundlich and Langmuir isotherm models (Table 3). They fit the Freundlich and Langmuir equations well with correlation coefficients higher than 0.93 ex-

Fig. 6. Sorption isotherms of phenol on Na^+ - (a, c, e) and Ca^{2+} -montmorillonites (b, d, f) when phenol and no (■), 0.5 (●), 1.0 (▲), 2.0 mmol L^{-1} Pb (◆) were sorbed simultaneously (a, b), and when Pb (c, d) or phenol (e, f) was previously sorbed.

cept the data of HDTMA- Na^+ -montmorillonite. The sorption capacity of Pb decreased as follows: $\text{Na}^+ > \text{Ca}^{2+} > \text{HDTMA-Ca}^{2+} > \text{HDTMA-Na}^+$ -montmorillonites. More Pb was sorbed onto homoionic montmorillonites than HDTMA-montmorillonites mainly due to the relatively higher cation-exchange capacity of Na^+ -montmorillonite ($89.6 \text{ cmol kg}^{-1}$) and Ca^{2+} -montmorillonite ($72.4 \text{ cmol kg}^{-1}$) and hydrophobic-

ity of HDTMA-montmorillonites. However, the presence of phenol had little effect on Pb sorption.

Generally, the sorption of Pb on montmorillonites was very rapid and reached equilibrium within about 1 h. However, the diffusion velocity of phenol was slower than that of Pb and the sorption equilibrium time was about 18 h. Furthermore, the intensity of coordination bonds between Pb and montmo-

Table 3

Freundlich and Langmuir constants and correlation coefficients of sorption of Pb in the absence and presence of phenol

Model	Parameter	Na ⁺ -Mt ^a		Ca ²⁺ -Mt ^a		HDTMA-Ca ²⁺ -Mt ^a		HDTMA-Na ⁺ -Mt ^a	
		Absence	Presence	Absence	Presence	Absence	Presence	Absence	Presence
Freundlich equation	K_f^b	483.8	474.5	387.2	391.3	285.6	279.4	154.2	149.2
	n	0.3338	0.3221	0.2869	0.2852	0.3834	0.3894	0.7774	0.7950
	R^2	0.9825 ^c	0.9784 ^c	0.9633 ^c	0.9688 ^c	0.9609 ^c	0.9592 ^c	0.9874 ^c	0.9883 ^c
Langmuir equation	q_m (mmol kg ⁻¹)	615.0	601.3	514.7	517.1	451.5	447.2	647.7	672.9
	b (L mmol ⁻¹)	6.583	6.929	6.110	6.341	2.873	2.744	0.3571	0.3657
	R^2	0.9811 ^c	0.9823 ^c	0.9528 ^c	0.9598 ^c	0.9325 ^c	0.9337 ^c	0.7773 ^c	0.7140 ^c

^a Mt, montmorillonite.^b (mmol kg⁻¹ (mmol L⁻¹)⁻ⁿ).^c Indicates the statistical significance at probability level of $p < 0.01$.

illonites was also stronger than that of hydrogen bonds and van der Waals force between phenol and sorbents. This may be the reason why the phenol sorption was influenced by addition of Pb, while the sorption of Pb was independent of phenol on montmorillonites. For HDTMA-montmorillonites, Pb and phenol were sorbed by different domains, thus their sorption interactions were insignificant.

4. Conclusions

The sorption of phenol onto Na⁺- and Ca²⁺-montmorillonites was largely decreased in the presence of Pb, while phenol had little effect on the sorption of Pb. For HDTMA-Na⁺- and HDTMA-Ca²⁺-montmorillonites, Pb had little effect on the sorption of phenol and vice versa. The kinetic data can be best described by the pseudo-second-order equation. Sorption of phenol and Pb onto homoionic and HDTMA-exchanged montmorillonites followed Freundlich equation well. Sorption of phenol on Na⁺- and Ca²⁺-montmorillonites was non-linear and the sorption capacity was relatively low. Due to the interlayer cation exchanging by HDTMA cation surfactant, the sorption of phenol to HDTMA-Na⁺- and HDTMA-Ca²⁺-montmorillonites was greatly increased and the sorption isotherms were linear. However, HDTMA-Na⁺- and HDTMA-Ca²⁺-montmorillonites had lower sorption capacity of Pb than that of Na⁺- and Ca²⁺-montmorillonites.

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