Influence of pH, soil humic/fulvic acid, ionic strength, foreign ions and addition sequences on adsorption of Pb(II) onto GMZ bentonite

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ABSTRACT

This work contributed to the adsorption of Pb(II) onto GMZ bentonite in the absence and presence of soil humic acid (HA)/fulvic acid (FA) using a batch technique. The influences of pH from 2 to 12, ionic strengths from 0.004 M to 0.05 M NaNO$_3$, soil HA/FA concentrations from 1.6 mg/L to 20 mg/L, foreign cations (Li$^+$, Na$^+$, K$^+$), anions (Cl$^-$, NO$_3^-$), and addition sequences on the adsorption of Pb(II) onto GMZ bentonite were tested. The adsorption isotherms of Pb(II) were determined at pH 3.6 ± 0.1 and simulated with the Langmuir, Freundlich, and D–R adsorption models, respectively. The results demonstrated that the adsorption of Pb(II) onto GMZ bentonite increased with increasing pH from 2 to 6. HA was shown to enhance Pb(II) adsorption at low pH, but to reduce Pb(II) adsorption at high pH, whereas FA was shown to decrease Pb(II) adsorption at pH from 2 to 11. The results also demonstrated that the adsorption was strongly dependent on ionic strength and slightly dependent on the concentration of HA/FA. The adsorption of Pb(II) onto GMZ bentonite was dependent on foreign ions in solution. The addition sequences of bentonite/Pb(II)/HA had no effect on the adsorption of Pb(II).

1. Introduction

The fate and transport of toxic metal ions in the environment are generally controlled by adsorption reactions, complexation and colloid formation, etc. These interactions may be complicated by the presence of natural organic matter, such as humic substances (HSs), which are not stoichiometric chemical species, but rather macromolecular colloidal phases. Their compositions are variable and differ greatly from one sample to another [1]. HSs are operationally defined from the extraction procedure: (a) humin is the insoluble fraction at whatever pH; (b) humic acids (HAs) are the insoluble fraction in acidic pH; (c) fulvic acids (FAs) are the soluble fraction in whatever pH [2]. Previous works have demonstrated that HSs carry a large number of functional groups that bind strongly with both dissolved metal ions in solution and functional groups at adsorbent surfaces (e.g., carboxylate, phenolate, amino, thiol) [1,3–6]. FAs and HAs represent a major fraction of dissolved organic compounds present in freshwaters. FAs generally have a lower molecular weight and higher acidity than HAs. Hence, FAs are the more water soluble of the two, and therefore generally have larger complexation ability with metal ions than HAs. In the earlier studies [7–10], the adsorptions of Zn(II), Cr(III), Pb(II) and Th(IV) onto bentonite were investigated. The results indicated that the adsorptions of Zn(II), Cr(III), Pb(II) and Th(IV) were strongly dependent on pH values, and HA and FA had a positive effect on Th(IV) adsorption at low pH, but no effect at high pH. With regard to the influence of HSs on metal ion adsorption on mineral and oxide surfaces, it is generally considered that adsorption is enhanced at low pH but reduced at high pH [1]. However, the influence of HSs on the adsorption mechanism of different metal ions in aqueous systems is different and the comparison of the influence of FA and HA on metal ions' adsorption is still scarce [10].

In China, the bentonite in Gaomiaozi county (Inner Mongolia, China) (herein we named it as GMZ bentonite) has been selected as the candidate of backfill material for nuclear waste repository. The use of bentonite as adsorbent has been studied by many authors [7–10]. However, the study of metal ion sorption on GMZ bentonite is still scarce, especially the influence of FA/HA on metal ion sorption on GMZ bentonite. The objectives of the present work are: (a) to compare the different influence of HA and FA, which are extracted from the same soil samples, on Pb(II) adsorption; (b) to determine Pb(II) adsorption isotherms and to simulate experimental data with the Langmuir, Freundlich, and D-R adsorption models; (c) to investigate the influences of HA/FA concentrations (from 1.6 mg/L to 20 mg/L), pH (from 2 to 12), ionic strengths (from 0.004 M to 0.05 M NaNO$_3$), foreign ions and addition sequences on the adsorption of Pb(II) on GMZ bentonite; and (d) to discuss

the adsorption/complexation mechanism of Pb(II) in the ternary systems.

2. Experimental

2.1. Materials

The sample of GMZ bentonite was obtained from Gaomiaozi county (Inner Mongolia, China). The GMZ bentonite was converted to Na-bentonite by treating with 1.0 M NaCl under room temperature for 7 days, then washed with doubly distilled water until they were free from chloride ion, centrifuged at 5000 rpm, dried, and ground to 53 μm. The N_2-BET surface area of the sample was 29.5 m^2/g. The cation exchange capacity (CEC) was 0.65 meq/g by using ammonium acetate method, and the zero point of charge (pH_{zpc}) was 5.5 by using potentiometric titration method. Soil HA and FA were extracted from the soil of Hua-Jia county (Gansu province, China), and had been characterized in detail in an earlier report [11].

All chemicals used in the experiments were purchased in analytical purity. Doubly distilled water was used in the experiments.

2.2. Characterization

The sample of Na-bentonite was characterized using Fourier Transform Infrared (FTIR) (PerkinElmer spectrum 100, America) in pressed KBr pellets. The spectral resolution was set to 1 cm^{-1}, and 150 scans were collected for each spectrum.

The X-ray powder diffraction (XRD) pattern of the Na-bentonite crystal was recorded on a MAC Science Co. M18XHF diffractometer. XRD analysis was performed with CuKα radiation (λ = 0.15406 nm) with a Rigaku. The 2θ-scanning rate was 2° min^{-1}. Patterns were identified by comparison to the JCPD standards.

2.3. Adsorption procedures

All experiments were carried out under ambient conditions using batch technique. The stock suspension of Na-bentonite, $NaNO_3$, lead stock solution and HA/FA were added in the polyethylene tubes to achieve the desired concentrations of different components. The pH values of the solution were adjusted by adding negligible volumes of 0.1 or 0.01 M HNO_3 or NaOH. It is necessary to note that Na-bentonite and $NaNO_3$ were pre-equilibrated for 2 days before the addition of lead stock solution and HA/FA. After the suspensions were shaken for 2 days, the solid and liquid phases were separated by centrifugation at 7500 rpm for 20 min. The concentration of Pb(II) was analyzed by spectrophotometry at wavelength 616 nm by using Pb Chlorophosphonazo-III complex. The amount of Pb(II) adsorbed on Na-bentonite was calculated from the difference between the initial concentration and the equilibrium one.

The tests for the effect of addition sequences of HA/Na-bentonite/Pb(II) were studied, the addition sequence is named by (1) spiking HA and Pb(II) to the Na-bentonite suspension simultaneously (called batch 1); and by (2) spiking HA to the Na-bentonite suspension and then adding of Pb(II) after 2 days (called batch 2). In other tests, if the addition sequence was not noted specially, the addition sequences in the experiments were batch 1.

All experimental data were the average of duplicate or triplicate determinations. The relative errors of the data were about 5%.

3. Results and discussion

3.1. FTIR and XRD characterization

Fig. 1 shows the FTIR spectrum of Na-bentonite sample. The absorption band at 3627 cm^{-1} is due to stretching vibrations of structural –OH groups of bentonite. Water in bentonite gives a broad band at 3437 cm^{-1} corresponding to the H_2O-stretching vibrations, with a shoulder near 3250 cm^{-1}, due to an overtone of the bending vibration of water observed at 1634 cm^{-1}. A sharp band at 798 cm^{-1} with inflexion near 779 cm^{-1} confirms quartz admixture in the sample. The band at 696 cm^{-1} is due to the deformation and bending modes of the Si–O bond [12]. The bands at 525 and 468 cm^{-1} are due to Al–O–Si and Si–O–Si bending vibrations, respectively. The band at 622 cm^{-1} is assigned to coupled Al–O and Si–O out-of-plane vibrations. The band corresponding to Al–Al–OH is observed at 918 cm^{-1} [13]. The bands at 2851 and 2917 cm^{-1} are due to the C–H stretching vibration [14]. The very strong absorption band at 1004 cm^{-1} is due to Si–O bending vibration [15].

The XRD pattern of the Na-bentonite is shown in Fig. 2. The peaks marked by (M) are the characteristics of the montmorillonite type. The other peaks are impurities corresponding to feldspar, quartz and Cal-Fe(Ca)CO_3.
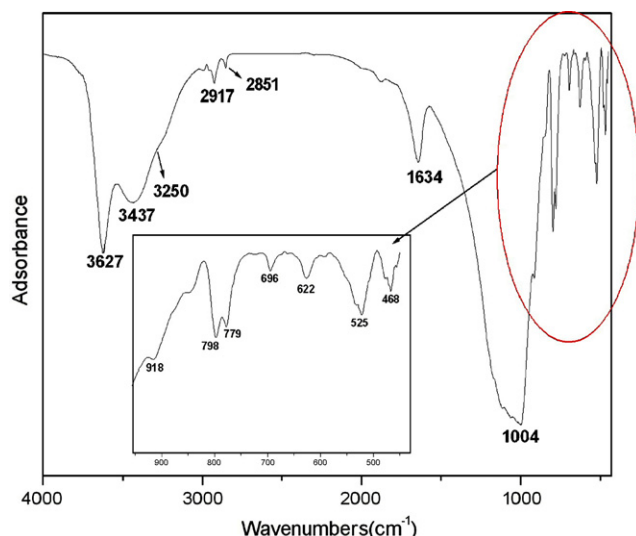

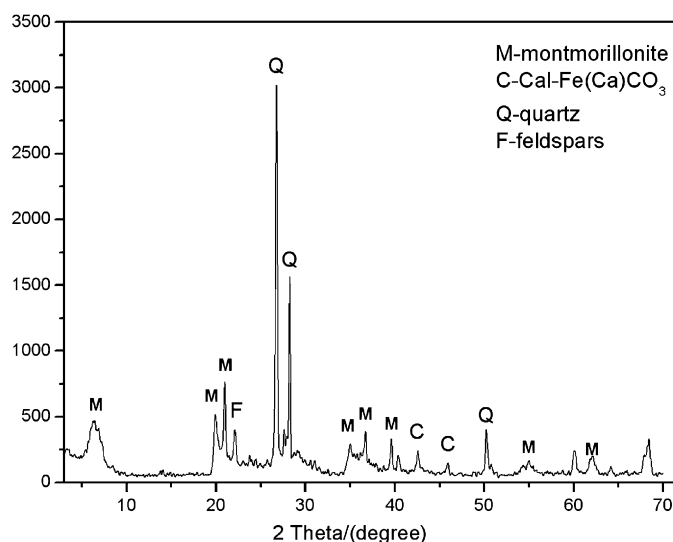**Fig. 1.** FTIR spectrum of Na-bentonite sample.

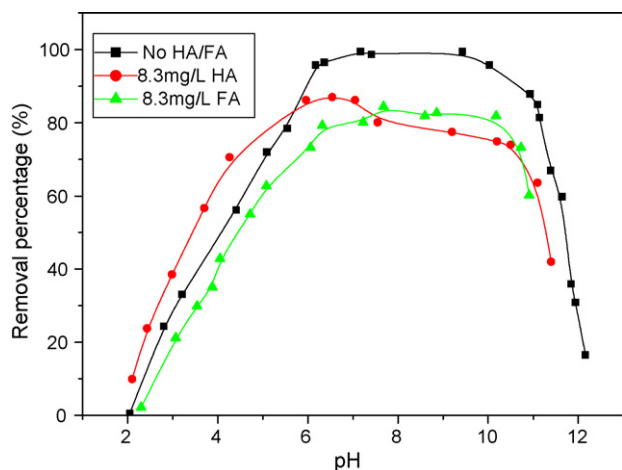**Fig. 2.** XRD pattern of Na-bentonite sample.

Fig. 3. Influence of pH on the adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA/FA, at $m/V = 0.5$ g/L, C_0(Pb(II)) = 4.83×10^{-5} mol/L, $I = 0.01$ M NaNO$_3$.

3.2. Influence of pH and HA/FA

Fig. 3 shows the pH dependent of Pb(II) adsorption on Na-bentonite in the absence and presence of HA/FA. Adsorption percentage (%) was derived from the difference of the initial concentration and the final one:

$$\text{adsorption}\,(\%) = \frac{C_0 - C_{eq}}{C_0} \times 100\% \qquad (1)$$

where C_0 (mol/L) is the initial Pb(II) concentration, C_{eq} (mol/L) is the concentration in supernatant after centrifugation. The results show that the pH of the solution plays an important role on the adsorption of Pb(II) to Na-bentonite. The removal of Pb(II) increases gradually at pH 2–6.5, maintains a high level at pH 6.5–10, and then decreases steeply at pH >10 in the absence of HA/FA. Weng [16] calculated the distribution of Pb(II) species at ionic strength of 0.01 M from the hydrolysis constants ($\log k_1 = 6.48$, $\log k_2 = 11.16$, $\log k_3 = 14.16$) and found that lead present in the forms of Pb^{2+}, Pb(OH)$^+$, Pb(OH)$_2$^{0}, Pb(OH)$_3$$^-$ at different pH values (Fig. 4). At pH <6.5, the predominant lead species is Pb^{2+} and the removal of Pb(II) is mainly accomplished by adsorption reaction. The adsorption of Pb(II) can be attributed to the ion exchange between Pb^{2+} and H$^+$/Na$^+$ on the surface ion exchange sites. In the range of pH 6.5–10, the removal of Pb(II) maintains a level and reaches maximum. At pH >6.5, lead ions will precipitate with the addition of hydroxyl.
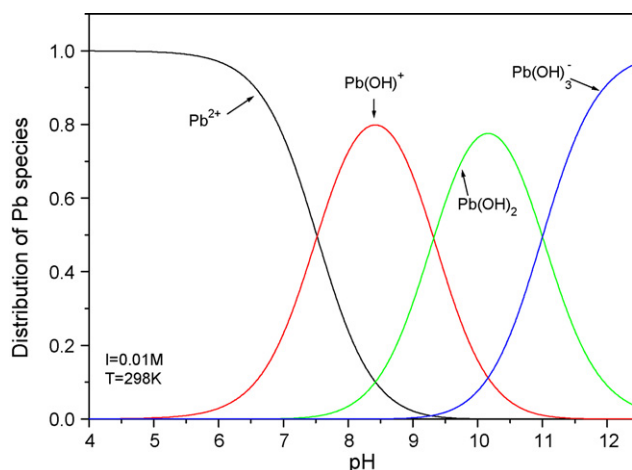

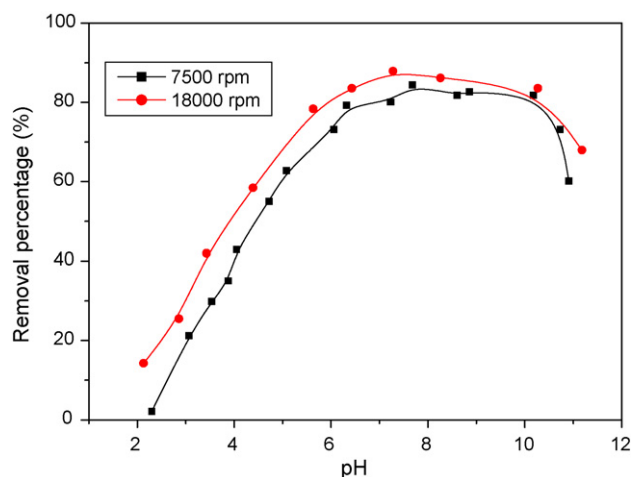**Fig. 4.** Distribution of Pb(II) species as a function of pH.

Fig. 5. Influence of centrifugal rate and pH on the adsorption of Pb(II) onto Na-bentonite in the presence of FA, at $C_{(FA)} = 8.3$ mg/L, $m/V = 0.5$ g/L, C_0(Pb(II)) = 4.83×10^{-5} mol/L, $I = 0.01$ M NaNO$_3$.

Thereby, the percentage removal of Pb(II) reaches maximum is due to precipitation reaction. The decrease of Pb(II) adsorption on Na-bentonite at pH >10 can be attributed to the formation of lead oxide ions that having a divalent anionic charge. At pH > pH$_{zpc}$, these anions get repulsed with the surface of Na-bentonite that having negatively charged and consequently decrease the adsorption efficiency.

The adsorption of Pb(II) in the presence of HA/FA as a function of pH is also shown in Fig. 3. HA obviously enhanced the adsorption of Pb(II) at pH <6, but reduced the adsorption at pH >6. A negative effect of FA on the adsorption of Pb(II) on Na-bentonite is observed at pH 2–11. HA/FA has a macromolecular structure, only a small fraction of the "adsorbed" groups are free to interact with metal ions [17]. The complexation between Pb(II) and HA/FA is more stable than the complexation between Pb(II) and Na-bentonite [18]. The free energy of the formation of HA/FA-Pb(II) is smaller than that of Na-bentonite-Pb(II). Besides, at low pH values, the negative charged HA/FA can be easily adsorbed on the positive charged Na-bentonite surface, so that the strong complexation ability of surface adsorbed HA/FA with Pb(II) should result in the adsorption of Pb(II) on Na-bentonite surface increased at pH <6. Generally, the presence of HSs enhances the adsorption of metal ions at low pH values and decreases the adsorption at high pH values [19,20]. However, in this work FA was found to decrease the Pb(II) adsorption on Na-bentonite at pH 2–11, which is an exception to the general consensus. FA generally has a lower molecular weight, and higher water soluble than HA. Therefore, the complexation of Pb(II) with FA may be difficult to be separated from the solution under 7500 rpm, leading to the negative effect of FA on the adsorption of Pb(II) on Na-bentonite. Centrifugation of the suspension was carried out under 18,000 rpm, which was used to compare with the one under 7500 rpm and the result was shown in Fig. 5. From Fig. 5, one can see that the adsorption of Pb(II) is obviously increased under 18,000 rpm, which supports our assumption. Besides, the influence of FA on the adsorption of Pb(II) on Na-bentonite depends on the complex behavior of Pb(II) with FA in solution, the complex behavior of Pb(II) with surface adsorbed FA on Na-bentonite, the complex behavior of Pb(II) with the functional groups of Na-bentonite, and cation exchange with H$^+$ or Na$^+$ at the surface of Na-bentonite. The adsorption of Pb(II) on Na-bentonite in the presence of FA is also dominated by the surface nature of Na-bentonite, the functional groups at Na-bentonite surface, the functional groups of FA, the concentration of FA, the concentration of Na-bentonite, and other cations in solution or/and on solid surfaces, pH, etc.
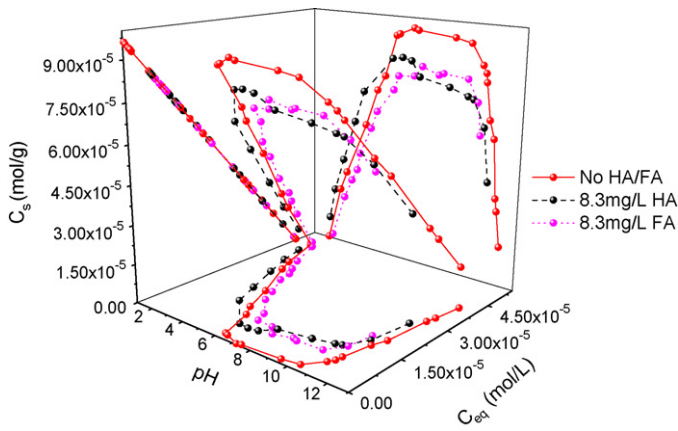
Fig. 6. 3-D plots of Pb(II) adsorption to Na-bentonite as a function of pH in the presence and absence of HA/FA, at $m/V = 0.5$ g/L, C_0(Pb(II)) $= 4.83 \times 10^{-5}$ mol/L, $I = 0.01$ M NaNO₃.

Fig. 7. Adsorption isotherms of Pb(II) onto Na-bentonite in the absence and presence of HA/FA, at $m/V = 0.5$ g/L, $I = 0.01$ M NaNO₃, pH $= 3.6 \pm 0.1$.

At pH >6, the negative charged HA/FA is easily dissolved in solution, and weakly adsorbed on Na-bentonite [1]. HA/FA forms aqueous complexation with Pb(II) in solution, and thereby diminishes the extent of Pb(II) adsorption on Na-bentonite. Abeate and Masini [21] studied the Pb(II) adsorption onto vermiculite and found that the presence of HA increased the adsorption of Pb(II) at pH 5.0 and 6.0 but decreased the adsorption at pH 7.0 as a consequence of the formation of stable complexes in solution. Tan et al. [22] found that at pH <6.5, the presence of HA enhanced Pb(II) adsorption obviously, whereas little difference on the adsorption of Pb(II) on bare and HA bound rectorite was found at pH >6.5. The results of this work are similar to the results of the references [21,22].

To illustrate the variation and relationship of pH, C_{eq}, and C_s (mol/g, the concentration of Pb(II) on Na-bentonite), the experimental data in Fig. 3 are plotted as three dimensional plots of C_s, C_{eq}, and pH (Fig. 6). On the pH–C_s plane, one can see that concentration of Pb(II) on Na-bentonite was increased in the presence of HA at pH <6, but decreased pH >6, while the presence of FA reduced the concentration of Pb(II) on Na-bentonite at pH 2–11, which is quite similar to the results shown in Fig. 3; On the pH–C_{eq} plane, the concentration of Pb(II) remained in solution was decreased in the presence of HA at pH <6, but increased at pH >6. The presence of FA increased the concentration of Pb(II) remained in solution at pH 2–11. The projection on the pH–C_{eq} plane is just the inverted image of the projection on the pH–C_s plane; On the C_{eq}–C_s plane, one can see that all the data lie in a straight line. It is well known that the initial concentration of Pb(II) in each experimental point is same. The following equation can describe the relationship of C_{eq}–C_s:

$$VC_0 = mC_s + VC_{eq} \qquad (2)$$

Eq. (2) can be rearranged as:

$$C_s = C_0 \frac{V}{m} - C_{eq} \frac{V}{m} \qquad (3)$$

where V is the volume and m is the mass of bentonite. Thereby, the experimental data of $C_{eq} - C_s$ lies in a straight line with slope $(-V/m)$ and intercept (C_0V/m). The slope and the intercept calculated from $C_{eq} - C_s$ line are -2.0 and 9.65×10^{-5}, which are quite in agreement with the values of $m/V = 0.5$ g/L and $C_0 = 4.83 \times 10^{-5}$ mol/L. The 3-D plots show the relationship of pH, C_{eq}, and C_s very clearly, i.e., all the data of $C_{eq} - C_s$ lie in a straight line with slope $-V/m$ and intercept C_0V/m at same initial concentration and same solid content.

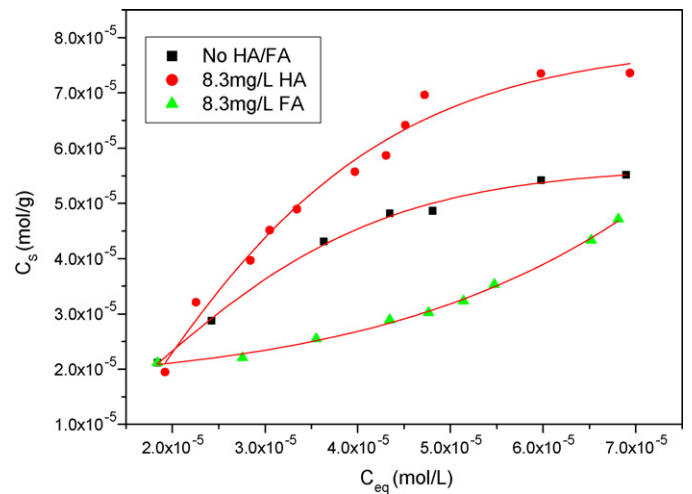### 3.3. Adsorption isotherms

Fig. 7 shows the adsorption isotherms in the absence and presence of HA/FA. It shows that the adsorption of Pb(II) on Na-bentonite increases in the presence of HA and decreases in the presence of FA. The experimental data of Pb(II) adsorption (Fig. 7) were regressively analyzed with Freundlich, Langmuir and D–R equilibrium isotherm models. The Freundlich model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface; the Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer. The D–R isotherm model is valid at low concentration ranges and can be used to describe adsorption on both homogeneous and heterogeneous surfaces. The equations of the above three types of adsorption isotherms are expressed as follows:

$$\log C_s = \log k_F + n \log C_{eq} \qquad (4)$$

$$\frac{C_{eq}}{C_s} = \frac{1}{bC_{s\,max}} + \frac{C_{eq}}{C_{s\,max}} \qquad (5)$$

$$\ln C_s = \ln C_{s\,max} - \beta \varepsilon^2 \qquad (6)$$

where C_s (mol/g) is the concentration of Pb(II) on solid phase, C_{eq} (mol/L) is the concentration in supernatant after centrifugation, k_F (mol^{1-n} L^n/g) represents the adsorption capacity when metal ion equilibrium concentration equals to 1, and n represents the degree of dependence of adsorption with equilibrium concentration; $C_{s\,max}$ (mol/g), the maximum adsorption capacity, is the amount of Pb(II) at complete monolayer coverage, and b (L/mol) is the constant that relates to the heat of adsorption; β is the activity coefficient related to mean adsorption energy (mol²/kJ²), and ε is the Polanyi potential, which is equal to:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_{eq}} \right) \qquad (7)$$

The adsorption isotherms of the three models are given in Fig. 8. The relative values calculated from the three models are listed in Table 1. The results indicate that the Langmuir model poorly describes the adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA. The Freundlich model and D–R model fit well the adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA/FA. From the data in Table 1, it can be seen that the maximum adsorption capacity of Pb(II) on Na-bentonite at a pH value of 3.6 ± 0.1 are in the following sequence: (HA + Na-bentonite) > (bare Na-bentonite) > (FA + Na-bentonite). In
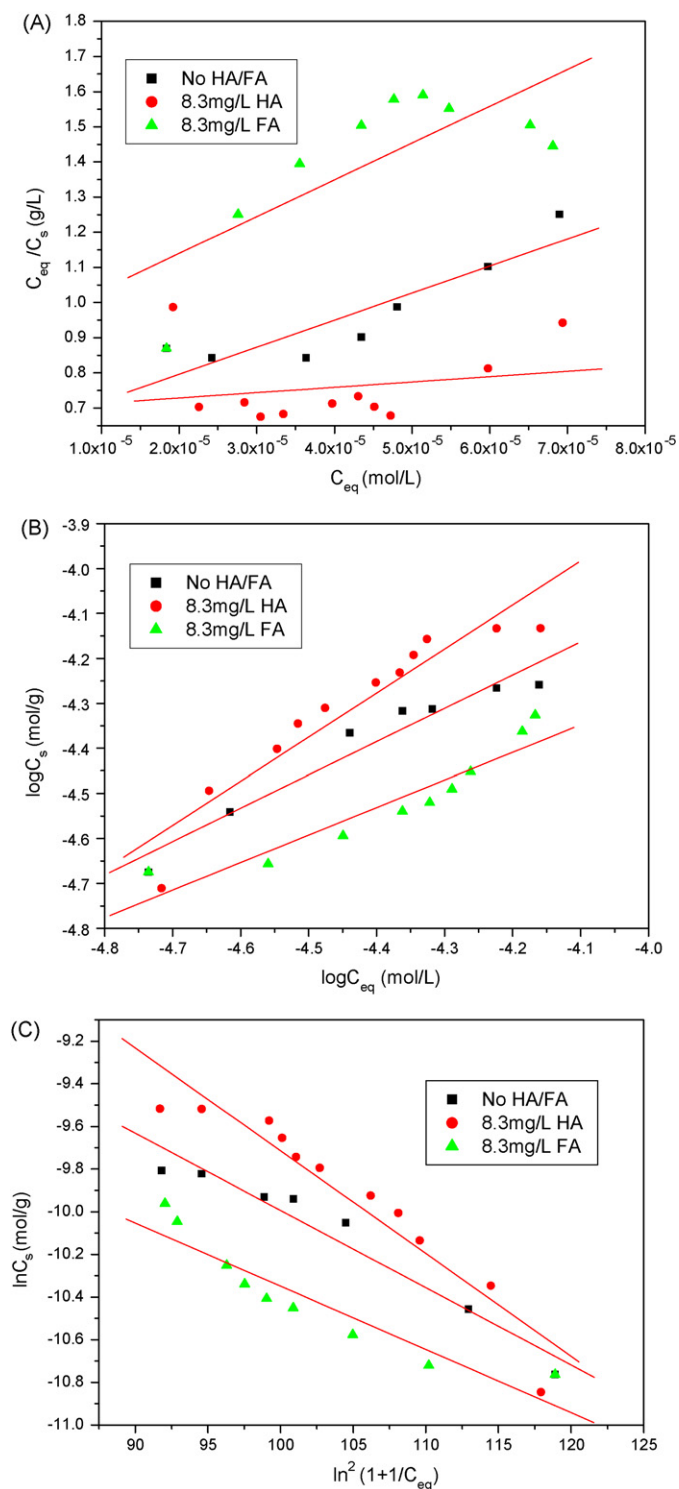
Fig. 8. Langmuir (A), Freundlich (B) and D–R (C) isotherms for Pb(II) adsorption on Na-bentonite in the absence and presence of HA/FA, at $m/V = 0.5$ g/L, $I = 0.01$ M NaNO$_3$, pH = 3.6 ± 0.1.
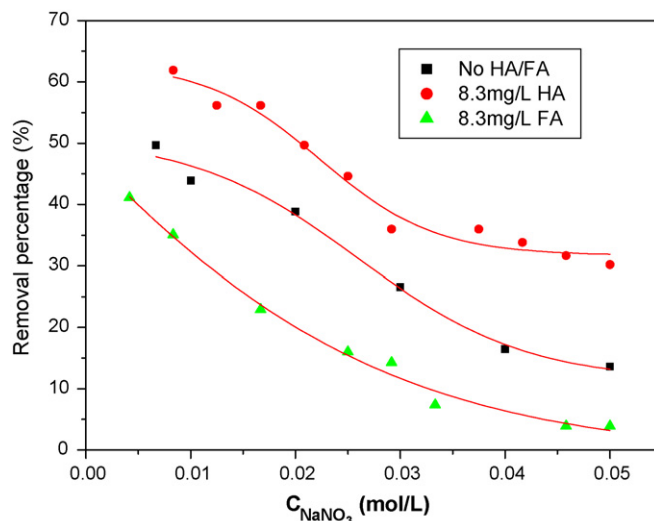

Fig. 9. Influence of ionic strength on the adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA/FA, at $m/V = 0.5$ g/L, C_0(Pb(II)) = 4.83 × 10^{-5} mol/L, pH = 3.6 ± 0.1.

the presence of HA, HA is adsorbed onto Na-bentonite, leading to the enhancement of complexation sites available on the Na-bentonite surface and therefore enhancing the saturated amount of adsorbed Pb(II). FA has a lower molecular weight and it's complexation with Pb(II) may be difficult to be separated from the solution under 7500 rpm, leading to the negative effect of FA on the adsorption of Pb(II) onto Na-bentonite.

3.4. Influence of ionic strength

Influence of ionic strength on the adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA/FA is shown in Fig. 9. The adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA/FA is obviously affected by ionic strength. The adsorption decreases steeply with increasing NaNO$_3$ concentration, which suggests that the Na$^+$ greatly affects Pb(II) adsorption. With increasing Na$^+$ concentration in solution, the competitive adsorption of Pb(II) with the Na$^+$ adsorbed on Na-bentonite surface increases and thereby the adsorption of Pb(II) on Na-bentonite decreases. Besides, the Na$^+$ in solution may influence the double layer thickness and interface potential, and thereby affect the binding of the adsorbed species. Ion exchange and outer-sphere complexes are affected by the variations of ionic strength more easily than inner-sphere complexes, since the background electrolyte ions are placed in the same plane as outer-sphere complexes. Businelli et al. [23] studied the adsorption of Pb(II) onto montmorillonite and found that increasing ionic strength from 10 to 100 mM sensibly decreased lead adsorption at the pH below the Pb hydrolysis point. Xu et al. [24] investigated the adsorption of Pb(II) onto oxidized multiwalled carbon nanotubes (MWCNTs) and found that the adsorption was independent of ionic strength.

The present results show that the adsorption of Pb(II) onto Na-bentonite in the absence and presence of HA/FA is influenced by ionic strength and pH values strongly. This suggests that the adsorp-

Table 1
The parameters for Langmuir, Freundlich and D–R isotherms in the absence and presence of HA/FA.

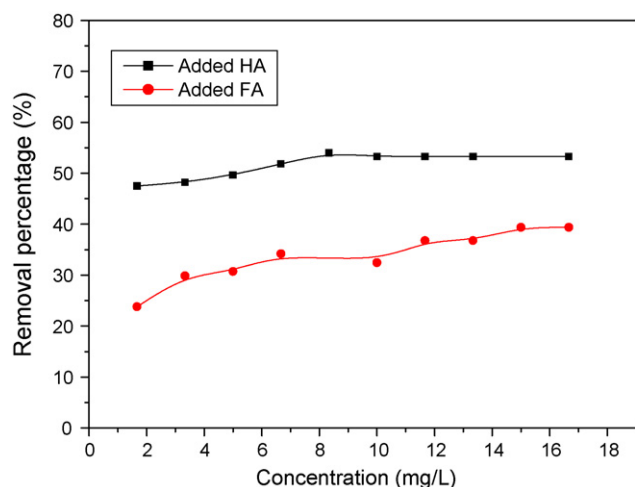|	Langmuir			Freundlich			D–R		
	$C_{s\,max}$ (mol/g)	b (L/mol)	R	K_F (mol^{1-n}L^n/g)	n	R	β (mol^2/kJ^2)	$C_{s\,max}$ (mol/g)	R
HA	6.60 × 10^{-4}	0.22 × 10^4	0.213	1.08	0.98	0.945	8.11 × 10^{-3}	7.48 × 10^{-3}	0.950
No HA/FA	1.30 × 10^{-4}	1.20 × 10^4	0.905	0.07	0.740	0.971	5.02 × 10^{-3}	1.71 × 10^{-3}	0.975
FA	9.56 × 10^{-5}	1.12 × 10^4	0.757	0.01	0.61	0.938	3.64 × 10^{-3}	0.62 × 10^{-3}	0.931

Fig. 10. Influence of HA/FA concentration on the adsorption of Pb(II) onto Na-bentonite, at $m/V = 0.5$ g/L, $C_0(Pb(II)) = 4.83 \times 10^{-5}$ mol/L, $I = 0.01$ M NaNO$_3$, pH = 3.6 ± 0.1.

Fig. 11. Influence of cations and pH on the adsorption of Pb(II) onto Na-bentonite, at $m/V = 0.5$ g/L, $C_0(Pb(II)) = 4.83 \times 10^{-5}$ mol/L.

tion of Pb(II) is mainly dominated by ion exchange and surface complexation [22]. In general, surface complexation is influenced by pH values, whereas ion exchange is mainly influenced by ionic strength.

3.5. Influence of HA/FA concentration

Fig. 10 shows the influence of HA/FA concentration on Pb(II) adsorption onto Na-bentonite. The presence of FA was found to reduce the adsorption of Pb(II) on Na-bentonite in Fig. 3, but from Fig. 10 one can see that Pb(II) adsorption increases with increasing concentration of FA. This may be interpreted that more FA macromolecule are adsorbed on Na-bentontie with increasing FA concentration, and results in more Pb(II) adsorbed on FA-bentonite hybrids. From Fig. 10 one can see that Pb(II) adsorption increases with increasing concentration of HA and maintains a level at last, which is consistent with the properties of HSs. At higher concentrations of HA, there are more functional groups of HA, such as carboxylic and phenolic groups, and these groups could form strong complexes with Pb(II). Similar experimental results were reported by Kim et al. [25]. The adsorption of Pb(II) onto Na-bentonite in the presence of HA maintains a level with increasing concentration of HA in solution, which may due to the concentration of HA reaches the saturation of the Na-bentonite surface sites. Reiller et al. [26,27] reported that the adsorption of Th(IV) on HA coated hematite decreases with increasing concentration of HA in solution, when the concentration of HA exceeds the saturation of the minerals or oxides. Therefore, the extent of these effects depends upon the relative ratio between HA and mineral phases or oxide sites. This ratio has to be smaller than a critical value in order to enhance the adsorption of Pb(II).

3.6. Influence of foreign ions

In order to investigate the influence of foreign cations and anions on the adsorption of Pb(II), the adsorption of Pb(II) on bare Na-bentonite was investigated in 0.01 M LiNO$_3$, NaNO$_3$, KNO$_3$, and NaCl solutions, respectively. Fig. 11 shows the adsorption of Pb(II) on Na-bentonite in the presence of 0.01 M LiNO$_3$, NaNO$_3$ and KNO$_3$, respectively, as a function of pH values. The adsorption of Pb(II) on Na-bentonite is obviously influenced by the cations in the suspension. One can see that the adsorption of Pb(II) on Na-bentonite under the same pH values are in the following sequence: Li$^+ \approx$ Na$^+ >$ K$^+$, indicating that the cations can alter the surface prop-

erty of Na-bentonite and thus can influence the adsorption of Pb(II) on Na-bentonite surfaces. The adsorption of Pb(II) on Na-bentonite can be considered as a competition of Pb(II) with Li$^+$ (or Na$^+$, K$^+$) at the Na-bentonite surfaces. The radius (K$^+ = 2.32$, Na$^+ = 2.76$ and Li$^+ = 3.4$ Å [28,29]) of K$^+$ is smaller than those of the other two cations and therefore the influence of K$^+$ on Pb(II) adsorption is more obvious than those of Na$^+$ and Li$^+$. The influence of monovalent alkali ions on the adsorption of bivalent Pb(II) should be weak. However, in this work the influence of Li$^+$, Na$^+$ and K$^+$ on Pb(II) adsorption is drastic. Tan et al. [30] investigated the effect of Li$^+$, Na$^+$ and K$^+$ on the adsorption of Th(IV) on TiO$_2$, respectively, and also found similar results. Before the addition of Pb(II) ions, the Na-bentonite has been pre-equilibrated with alkali ions. The adsorption of Pb(II) on Na-bentonite can be considered as the exchange of Pb(II) with alkali ions and other reactions.

Fig. 12 shows that foreign anions affect Pb(II) adsorption drastically. The adsorption of Pb(II) on Na-bentonite in NaCl solution is lower than that in NaNO$_3$ solution. This phenomenon could be attributed to two reasons: (a) Pb(II) can complex with inorganic acid radicals (e.g. Cl$^-$, NO$_3^-$) and form soluble complex species. Since the radius of Cl$^-$ is smaller than that of NO$_3^-$ [31], Pb(II) has higher affinity to Cl$^-$ and a higher tendency for complexation with Cl$^-$ compared to NO$_3^-$, leading to a stronger decrease of Pb(II) concentration. (b) In general, idiocratic adsorption of Cl$^-$
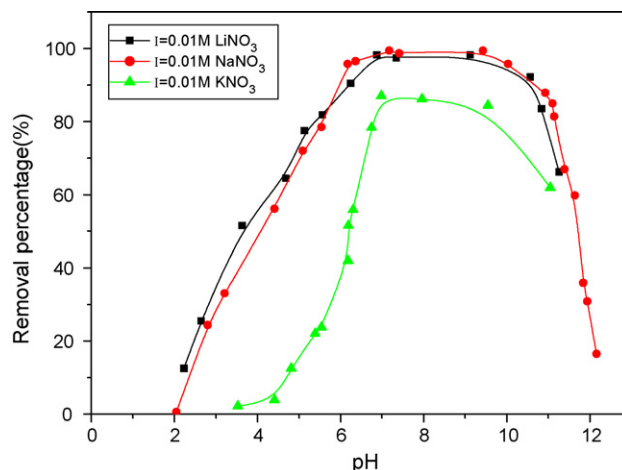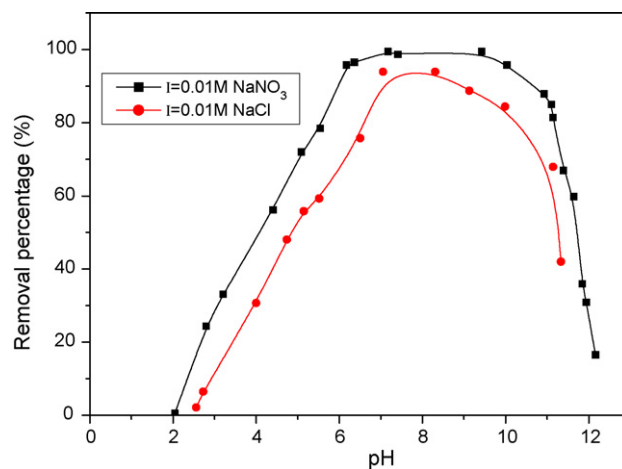

Fig. 12. Influence of anions and pH on the adsorption of Pb(II) onto Na-bentonite, at $m/V = 0.5$ g/L, $C_0(Pb(II)) = 4.83 \times 10^{-5}$ mol/L.
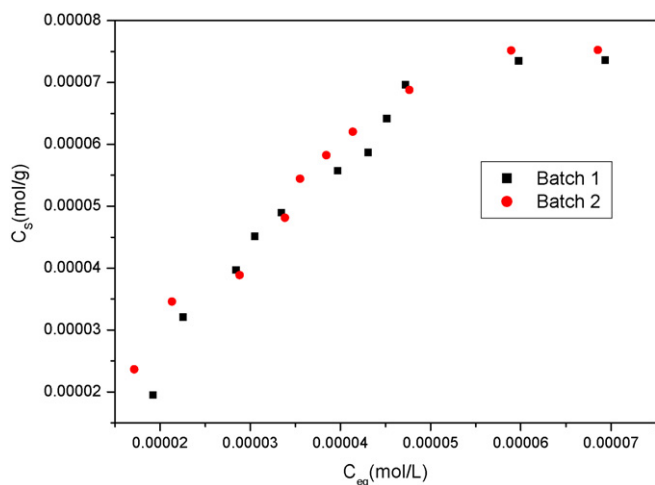
Fig. 13. Influence of addition sequences on Pb(II) adsorption onto Na-bentonite, at $C_{(HA)} = 8.3$ mg/L, $m/V = 0.5$ g/L, $I = 0.01$ M $NaNO_3$, pH = 3.6 ± 0.1.

is easier on the solid phase than NO_3^-, and Cl^- adsorption on the surface of Na-bentonite changes the surface state of Na-bentonite and decreases the availability of binding sites. The interpretations mentioned above are reasonable in principle.

3.7. Effect of addition sequences on Pb(II) adsorption in the ternary system

The question whether or not the addition sequences of metal ion and HSs to solid adsorbent suspension influence the metal ion adsorption is discussed controversially. Various authors reported the influence of addition sequences on adsorption and species of metal ions at solid surfaces [27,32]. However, other results indicated no noticeable effect of addition sequences of HS/metal ions on the adsorption of metal ions at solid surfaces [10,33,34]. Herein the adsorption of Pb(II) in the ternary Pb–HA–bentonite systems for two different addition sequences was tested and the results are shown in Fig. 13. One can see that no difference is found in Pb(II) adsorption in the ternary systems of the two addition sequences. The results are consistent with the results of references [10,33,34], but different to the results of references [27,32]. Many authors [32,35] gave the interpretation that the fraction of HSs adsorbed on solid surfaces was different to the fraction of HSs retained in solution, and thereby the adsorption of metal ions was affected by the addition sequences. However, many authors thought that HSs are homogeneous in solution and no difference in the surface adsorbed HSs and solution soluble HSs, and thereby no effect of addition sequences on metal ions' adsorption on solid surface [17,34]. This may be the plausible interpretation to the no influence of addition sequences on Pb(II) adsorption. Nevertheless, the effect of HSs on the adsorption of metal ions on solid surfaces is important. The influence of addition sequences of HS/metal ion on metal ion adsorption and species on solid surface is significant to evaluate the physicochemical behavior of metal ion in natural environment.

4. Conclusions

Based on the results achieved in this paper, the following conclusions can be obtained:

1. Adsorption of Pb(II) on Na-bentonite in the presence and absence of HA/FA is strongly dependent on pH and ionic strength, which suggests that surface complexation and ion exchange could both contribute to the adsorption of Pb(II) on Na-bentonite.

2. The presence of soil HA enhances the adsorption of Pb(II) at low pH values. But FA was shown to decrease the adsorption of Pb(II). The influence of FA on Pb(II) sorption was dominated by the separation methods.

3. The adsorption isotherms of Pb(II) onto Na-bentonite in the presence and absence of HA/FA can be described well by Freundlich and D-R isotherm models.

4. The adsorption of Pb(II) increases with increasing concentration of HA and maintains a level at high concentration of HA.

5. The adsorption of Pb(II) on Na-bentonite was influenced by the presence of foreign ions greatly.

6. The adsorption of Pb(II) onto Na-bentonite is not affected by the addition sequences.

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