Impact of environmental conditions on the sorption behavior of Pb(II) in Na-bentonite suspensions

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ABSTRACT

In this study, a local bentonite from Lin'an county (Zhejiang province, China) was converted to Na-purified form and the Na-bentonite sample was characterized by using FTIR and XRD to determine its chemical constituents and micro-structure. The removal of lead from wastewaters by Na-bentonite was studied as a function of various environmental parameters such as contact time, pH, ionic strength, foreign ions, humic substances and temperature under ambient conditions. The results indicated that the sorption of Pb(II) on Na-bentonite was strongly dependent on pH and ionic strength. The Langmuir, Freundlich and D–R models were used to simulate the sorption isotherms of Pb(II) at three different temperatures of 298, 318 and 338 K. The thermodynamic parameters (ΔH°, ΔS° and ΔG°) calculated from the temperature dependent sorption isotherms indicated that the sorption process of Pb(II) on Na-bentonite was endothermic and spontaneous. At low pH, the sorption of Pb(II) was dominated by outer-sphere surface complexation and ion exchange with Na^+/H^+ on Na-bentonite surfaces, whereas inner-sphere surface complexation was the main sorption mechanism at high pH. From the experimental results, it is possible to conclude that Na-bentonite has good potentialities for cost-effective disposal of lead bearing wastewaters.

1. Introduction

Water pollution by hazardous metal ions is a worldwide problem and has aroused widespread concern of scientists and environmentalists. In recent years, the levels of toxic metal ions in surface waters have been increased due to the pollution caused by industrial and agricultural wastewater discharges. Lead, an important metal resource, is widely used in many industrial processes, such as storage battery manufacturing, printing, pigments, fossil fuels, photographic materials, and explosive manufacturing [1]. However, it is also one of the three most toxic heavy metals that are present stably in the environment with great difficulty for microbiological degradation. Its presence in drinking water above the permissible limit of $0.02 \, mg \, L^{-1}$ may directly or indirectly cause adverse health effects such as anemia, encephalopathy, diarrhea, hepatitis, nephritic syndrome the kidneys, and the dysfunction of reproductive and central nervous system [2]. The biological toxicity such as teratogenic and carcinogenic effect caused by lead has also aroused human widespread concern. For the purpose of protecting

ecosystem stability and public health, it is necessary to decrease the concentration of lead to the permissible limits before its discharge to the environment.

Retention of heavy metal ions by clay minerals is a crucial process for maintaining environmental quality in contaminated areas. Sorption, diffusion, and precipitation reactions at clay–water interfaces are closely related with the accumulation, migration, transformation and biological effectiveness of heavy metal ions in soil and water environment. Recently, the possibilities of applying multifarious clays in wastewater disposal have been studied extensively in the recent years and many mechanisms have been postulated such as ion exchange, outer-sphere/inner-sphere surface complexation, precipitation, and diffusion into particle micropores [3–8]. Most of the studies presented on this subject were restricted to the sorption of single metal solutions in the absence of other electrolyte ions. However, the metal of interest in wastewater is usually found to be in a matrix containing various electrolyte ions. The interaction between these charged particles leads to the formation of an electrostatic field with certain intensity around them, which will further modify the behavior of heavy metal ions towards the sorbent materials [9]. Therefore, to better understand the practical application of clays as potential sorbents in sewage disposal, it is of great importance to investigate the sorp-

tion behavior of heavy metal ions on clays in the presence of various coexisting electrolyte ions.

Bentonite, one of the most common of the alumino-silicate clay minerals, has been used as geochemical barriers in nuclear waste repositories and hazardous chemicals landfills owing to its outstanding physicochemical properties, i.e., large specific area, high cation exchange capacity, strong adsorptive affinity for organic and inorganic pollutants, low permeability, low cost, accessibility and ubiquitous presence in most soils. Previous studies reported that bentonite was a suitable material in the preconcentration and solidification of heavy metal ions from large volume of aqueous solutions [10–12]. Compared with raw bentonite, Na-bentonite possesses some more excellent physicochemical properties such as higher cation exchange capacity, better dispersibility and better thermostability. Hence, a local bentonite from Lin'an county (Zhejiang province, China) was converted to Na-purified form and the Na-bentonite sample was used in this study as a sorbent for the removal of Pb(II) from wastewater. The concrete objectives of this paper are: (1) to characterize the Na-bentonite sample by using Fourier transform infrared (FTIR) spectroscopy for chemical functional groups, and X-ray powder diffraction (XRD) for chemical composition and micro-structure; (2) to study the influence of different parameters on Pb(II) sorption, such as contact time, pH, ionic strength, coexisting electrolyte ions, humic substances and temperature by using batch technique; (3) to determine the thermodynamic parameters of Pb(II) sorption on Na-bentonite; and (4) to presume the sorption mechanism of Pb(II) on Na-bentonite and to estimate the possible application of Na-bentonite in wastewater disposal.

2. Experimental

2.1. Materials

The sample of raw bentonite was obtained from Lin'an county (Zhejiang, China). The main components of Lin'an bentonite are SiO_2 (68.7%), Al_2O_3 (17.2%), MgO (0.4%), Fe_2O_3 (1.6%), K_2O (0.9%), Na_2O (2.3%) and CaO (1.2%) [13]. Na-bentonite was converted from the raw bentonite. The process was as follows: The raw bentonite was treated with 1.0 M NaCl, and then washed with deionized water until it was free from chloride ion. Then the suspension was centrifuged at 5000 rpm, dried, and ground to 53 μm. The point of zero charge (pH_{pzc}) was determined to be 7.8 ± 0.1 by using potentiometric acid–base titration method at different ionic strengths, and the cation exchange capacity (CEC) was 0.91 meq g^{-1} by using ammonium acetate method. The N_2-BET specific surface was 39.5 m^2 g^{-1}.

Humic acid (HA) and fulvic acid (FA) were extracted from the soil of Hua-Jia county (Gansu province, China) near 35°N and 105°E and has been characterized in detail [14,15]. The concentrations of functional groups of HA and FA determined by fitting the potentiometric acid–base titration data using FITEQL 3.1 are given in Table 1 [15]. The weight-averaged molecular weights (MW) of dissolved HA and FA were calculated to be 2108 and 1364, respectively, by using the method of Chin et al. [16].

All chemicals used in the experiments were purchased as analytical purity and used directly without any further purification. All the reagents were prepared with high-purity deionized water from a Millipore Synthesis A10 water system (18.2 MΩ, <8 ppb total organic carbon (TOC), UV light treated, ultrafiltration membrane, 0.2 μm filtered).

2.2. Characterization

The sample of Na-bentonite was characterized using 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 XRD pattern was recorded on a MAC Science Co. M18XHF diffractometer. XRD analysis was performed with Cu Kα radiation (λ = 0.15406 nm) with a Rigaku diffractometer. The 2θ-scanning rate was 2° min^{-1}.

2.3. Experimental procedures

All the experiments were carried out by using batch technique in polyethylene centrifuge tubes under ambient conditions. The stock solutions of Na-bentonite and $NaClO_4$ were pre-equilibrated for 24 h and then lead stock solution was added to achieve the desired concentrations of different components. The pH of each test solution was adjusted to desired values by adding negligible volumes of 0.01 or 0.1 M $HClO_4$ or NaOH. After the suspensions were oscillated for 24 h, the solid and liquid phases were separated by centrifugation at 9000 rpm for 30 min. It was necessary to note that the sorption of Pb(II) on the tube wall was negligible according to the test of Pb(II) sorption in the absence of Na-bentonite.

The concentration of Pb(II) was analyzed by spectrophotometry at wavelength of 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 sorption percentage (sorption% = $(C_0 - C_{eq})/C_0 \times 100\%$) and distribution coefficient ($K_d = ((C_0 - C_{eq})/C_{eq} \cdot V/m)$) were derived from the difference of initial concentration (C_0), the final concentration (C_{eq}) in supernatant after centrifugation, the mass of Na-bentonite (m) and the volume of the suspension (V). All experimental data were the average of triplicate determinations and the relative errors were about 5%.

3. Results and discussion

3.1. FTIR and XRD characterization

Fig. 1 shows the FTIR spectrum of the Na-bentonite sample. The bands at 465 and 523 cm^{-1} are corresponded to Si–O–Si and Al–O–Si bending vibrations. The band at 626 cm^{-1} is assigned to the out-of-plane vibrations of coupled Al–O and Si–O. The band at 791 cm^{-1} confirms quartz admixture in the sample. The band at 841 cm^{-1} is assigned to the bending vibration of AlMgOH. The spectral band at 913 cm^{-1} reflects the stretching vibration of Al–O–(OH)–Al [13]. The strong band at 1038 cm^{-1} represents the Si–O–Si groups of the tetrahedral sheet. The spectral band at 1648 cm reflects the bending of H–OH bond of water molecules,
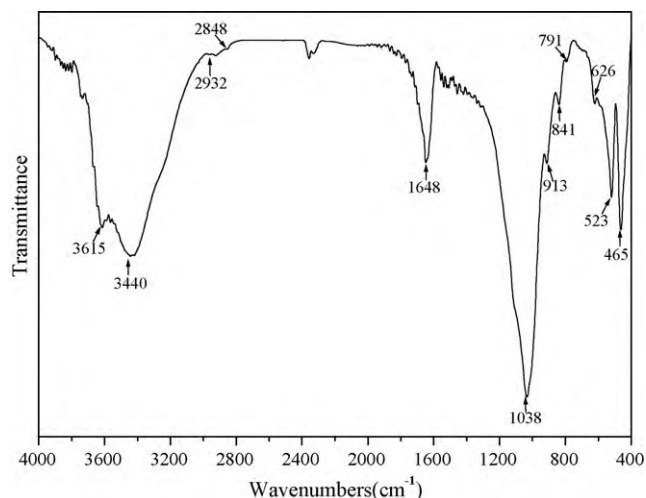
Table 1
The concentrations of functional groups of HA and FA calculated from potentiometric titration by using FITEQL 3.1 [15].

	Log K_a			C (mol g^{-1})^a			Surface sites density (mol g^{-1})	WSOS/DF
	L_1	L_2	L_3	HL_1	HL_2	HL_3		
HA	−5.04	−7.40	−9.60	2.20×10^{-3}	1.08×10^{-3}	3.18×10^{-3}	6.46×10^{-3}	2.37
FA	−5.19	−7.77	−10.53	1.83×10^{-3}	1.08×10^{-3}	2.42×10^{-2}	2.71×10^{-2}	0.10

^{a}HL_1, HL_2 and HL_3 represent the carboxyl groups (–COOH), the phenolic groups (Ar–OH) and the amine groups (–NH$_2$) of HA and FA, respectively.

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

Fig. 3. Sorption of Pb(II) on Na-bentonite as a function of contact time. $T = 298 \pm 2$ K, pH = 4.0 ± 0.1, $C_{(Pb)initial} = 7.25 \times 10^{-5}$ mol L^{-1}, $m/V = 0.5$ g L^{-1}, and $I = 0.01$ M $NaClO_4$.

which is retained in the matrix. The peaks at 2848 and 2932 cm^{-1} are assigned to the aliphatic C–H stretching vibration [17]. The broad bands at 3440 and 3615 cm^{-1} are due to H–OH vibration of the water molecules adsorbed on the solid surface and the O–H stretching vibration of the silanol (Si–OH) groups from the solid.

The XRD pattern of the Na-bentonite sample is shown in Fig. 2. The diffraction peaks of the planes at $2\theta = 5.82°$, 19.92° and 35.00° (marked by M) are the reflections indicative of 2:1 swelling clays. The other peaks are the impurities corresponded to quartz (marked by Q) and Cal-Fe(Ca)CO$_3$ (marked by C). Crystallographic parameters were evaluated by measuring (0 0 1) and (0 6 0) peaks. The Na-bentonite sample exhibits a diffraction peak of the (0 0 1) plane at $2\theta = 5.82°$, and its basal spacing is 15.1 Å. The (0 6 0) reflection at $2\theta = 61.9°$ implies the dioctahedral structure of Na-bentonite.

3.2. Time dependent sorption

Fig. 3 shows the sorption of Pb(II) on Na-bentonite as a function of contact time. One can see that sorption of Pb(II) on Na-bentonite increases rapidly at the first contact time of 3 h and then the sorption percentage maintains at an aptotic value with increasing contact time. This result symptomatizes that Pb(II) sorption on Na-bentonite surface is attributed to chemical sorption rather
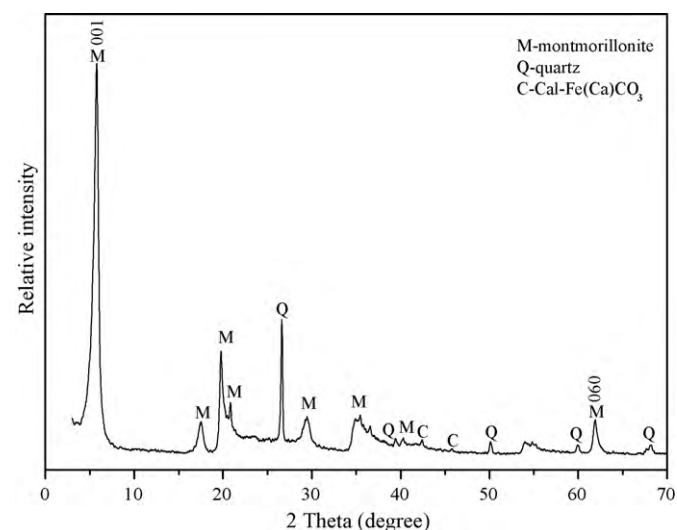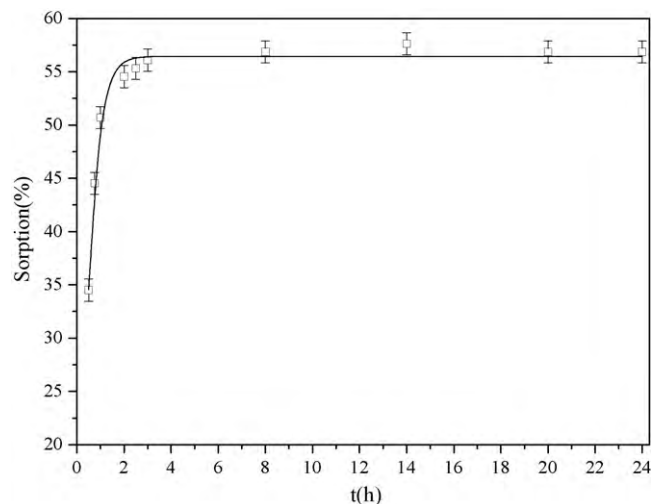
than physical sorption, and ion exchange may also contribute to the sorption of Pb(II) on Na-bentonite under the experimental condition of sorption dynamics [18,19]. The whole sorption dynamics process consists of two distinct steps: an initial fast sorption, followed by a much slow sorption. The fast Pb(II) removal rate in the beginning is attributed to the rapid diffusion of Pb(II) from the solution to the external surfaces of Na-bentonite. The subsequent slow sorption process is attributed to the longer diffusion range of Pb(II) into the inner-sphere pores of Na-bentonite or the exchange with cations in the inner surface of Na-bentonite. Such slow diffusion will lead to a slow increase in the sorption curve at later stages [20]. According to the above results, the shaking time is fixed at 24 h in the following experiments to ensure that the sorption reaction can achieve complete equilibrium. The fast sorption kinetics implies that Na-bentonite may have good potentialities for continuous water treatment systems.

3.3. Effect of pH and ionic strength

Fig. 4 shows the pH dependence of Pb(II) sorption on Na-bentonite in a series of NaClO$_4$ solutions varying from 0.001 to 0.1 M, respectively. One can see that the sorption of Pb(II) on Na-bentonite is obviously affected by pH values. The sorption curve of
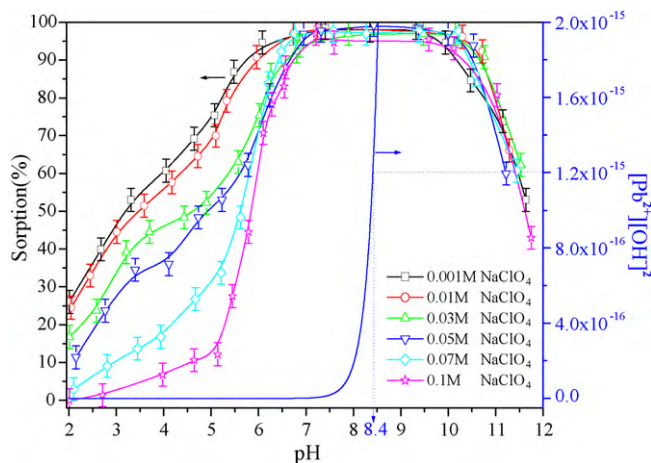

Fig. 2. XRD pattern of Na-bentonite sample.

Fig. 4. Effect of ionic strength on Pb(II) sorption to Na-bentonite as a function of pH values. $T = 298 \pm 2$ K, $C_{(Pb)initial} = 7.25 \times 10^{-5}$ mol L^{-1}, and $m/V = 0.5$ g L^{-1}.
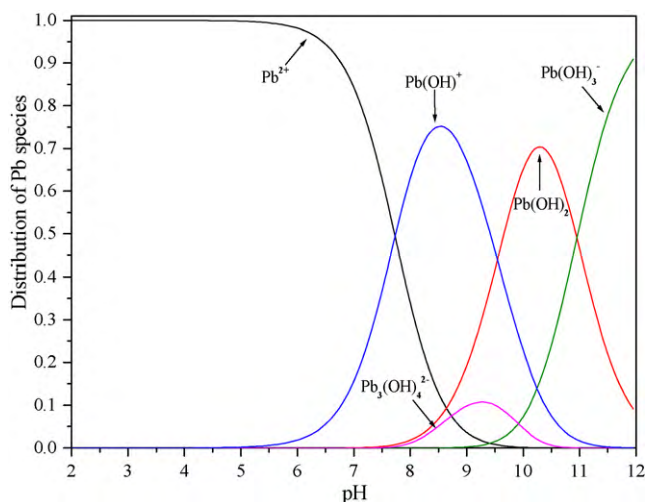
Fig. 5. Relative proportion of Pb(II) species as a function of pH.

Pb(II) on Na-bentonite can be divided into three regions. The sorption of Pb(II) in 0.01 M NaClO$_4$ solution increases gradually from 20% to 96% when pH increases from 2 to 7 (region I). In region II, from pH 7 to 10, the sorption percentage of Pb(II) on Na-bentonite maintains at the maximum value of 96%. Above pH 10, the removal of Pb(II) gradually decreases with increasing pH (region III). The results are similar to the sorption of Pb(II) on MX-80 bentonite [3], diatomite [6] and Na-rectorite [7]. The sorption edges spread over three pH units implies the formation of multifarious surface complexes and represents different sorption mechanisms [21].

The increase of Pb(II) sorption on Na-bentonite with increasing solution pH may be attributed to the surface properties of Na-bentonite in terms of surface charge and dissociation of functional groups. The surface of Na-bentonite contains a large number of binding sites and may become positively charged at low pH due to the protonation reaction on the surfaces (i.e., $SOH + H^+ \Leftrightarrow SOH_2^+$). The electrostatic repulsion occurred between metal ion and the edge groups with positive charge (SOH_2^+) on Na-bentonite surface leads to the low sorption efficiency of Pb(II). At high pH values, the surface of Na-bentonite becomes negatively charged due to the deprotonation process (i.e., $SOH \Leftrightarrow SO^- + H^+$) and electrostatic repulsion decreases with raising pH due to the reduction of positive charge density on the sorption edges, which enhances the sorption of the positively charged Pb(II) ions through electrostatic force of attraction. The characteristic of Pb(II) complex that predominates at a specific solution pH may also play an important role in the removal efficiency of Na-bentonite towards Pb(II). Fig. 5 shows the relative proportion of Pb(II) species calculated from the hydrolysis constants (Log K_1 = 6.48, Log K_2 = 11.16, Log K_3 = 14.16, $K_n = [Pb(OH)_n^{2-n}] \cdot [H^+]^n / [Pb^{2+}]$) [22]. The results demonstrate that Pb(II) present in the forms of Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2^0$, $Pb(OH)_3^-$ and $Pb_3(OH)_4^{2-}$ at various pH values. At pH < 7, the predominant Pb(II) species is Pb^{2+} and the removal of Pb(II) is mainly accomplished by sorption reaction. The sorption of Pb(II) that takes place at pH < 7 (region I) can be attributed to the ion exchange between Pb^{2+} and H^+/Na^+ on the surface ion exchange sites. In the range of pH 7–10 (region II), the removal of Pb(II) reaches maximum and maintains the same. The predominant species at pH 7–10 are $Pb(OH)^+$ and $Pb(OH)_2^0$ and thus the removal of Pb(II) is possibly accomplished by simultaneous precipitation of $Pb(OH)_2^0$ and sorption of $Pb(OH)^+$. At the pH range of 10–12 (region III), the main species are $Pb(OH)_2^0$ and $Pb(OH)_3^-$, hence, the decrease of Pb(II) sorption on Na-bentonite can be partly attributed to the competition between OH^- and $Pb(OH)_3^-$. The negative charged $Pb(OH)_3^-$ is difficult to be adsorbed on the neg-

atively charged surface of Na-bentonite at higher pH values due to electrostatic repulsion. It is necessary to make certain whether the formation of Pb(OH)$_2$(s) precipitation contributes to the sorption of Pb(II) on Na-bentonite. The precipitation curve of Pb(II) calculated from the precipitation constant of Pb(OH)$_2$(s) (1.2×10^{-15}) and the initial Pb(II) concentration (i.e., 7.25×10^{-5} mol L^{-1}) is also shown in Fig. 4. One can see that Pb(II) begins to form precipitation at pH ∼8.4 in the absence of Na-bentonite. However, more than 90% Pb(II) is adsorbed on Na-bentonite at pH 7. Thereby, it is impossible to form precipitation because of the very low concentration of Pb(II) remained in solution. Therefore, the abrupt increase of Pb(II) sorption on Na-bentonite at pH < 7 is not attributed to the formation of Pb(OH)$_2$(s). From the results, one can conclude that the best pH values of the binary system to remove Pb(II) from solution by using Na-bentonite are 7–10. However, the plausible interpretation of Pb(II) sorption on Na-bentonite as a function of pH values is still questionable, and further investigations at the molecular level by using spectroscopic techniques such as XPS and XAFS are needed to attain in-depth insight into the sorption results.

The effect of ionic strength on Pb(II) sorption on Na-bentonite as a function of pH values is also shown in Fig. 4. One can see that the sorption of Pb(II) is obviously affected by ionic strength, especially at low pH values. The sorption is strongly affected by ionic strength at pH < 7 and no effect is approximately found at pH > 7. The ionic strength can influence the double electrode layer thickness and interface potential, thereby can affect the binding of the adsorbed species. Outer-sphere surface complexes are expected to be more impressionable to ionic strength variations than inner-sphere complexes as the background electrolyte ions are placed in the same plane for outer-sphere surface complexes [23]. Based on the theory mentioned above, one can deduce that cation exchange or outer-sphere surface complexation mainly contribute to Pb(II) sorption on Na-bentonite at pH < 7, while inner-sphere surface complexation is the main sorption mechanism of Pb(II) on Na-bentonite at pH > 7 [24,25].

As can be seen from Fig. 4, the sorption of Pb(II) on Na-bentonite increases with decreasing ionic strength at pH < 7. This phenomenon could be attributed to three reasons: (1) Pb(II) ions form electrical double layer complexes with Na-bentonite, which favors the sorption when the concentration of the competing salt is decreased. This may indicate that the sorption interaction between the functional groups of Na-bentonite and Pb(II) ions is mainly an ionic interaction in nature, which is in agreement with the ion exchange mechanism; (2) the ionic strength of solution influences the activity coefficient of Pb(II) ions, which limits their transfer to Na-bentonite surfaces [26,27]; (3) ionic strength effects can impact particle aggregation by influencing electrostatic interactions. Increased ionic strength has been shown to reduce electrostatic repulsion and thereby increases particle aggregation of Na-bentonite, which reduces the amount of available binding sites and thereby decreases the sorption of Pb(II) on Na-bentonite [28].

3.4. Effect of solid content

The dependence of Pb(II) sorption on Na-bentonite at different solid content was studied at T = 298.15 K and pH = 4.0 ± 0.1. As can be seen from Fig. 6, the removal percent of Pb(II) increases rapidly with increasing Na-bentonite contents. With increasing solid contents, the number of functional groups at the Na-bentonite surfaces increases, thereby, more exchangeable surface sites are available to form complexes with Pb(II) at solid surfaces. The results also clearly indicate that the removal efficiency increases up to the optimum dosage of 72% beyond which its increase is negligible.

One can also see from Fig. 6 that the sorption capacity of Pb(II) on Na-bentonite decreases gradually with the increase of solid
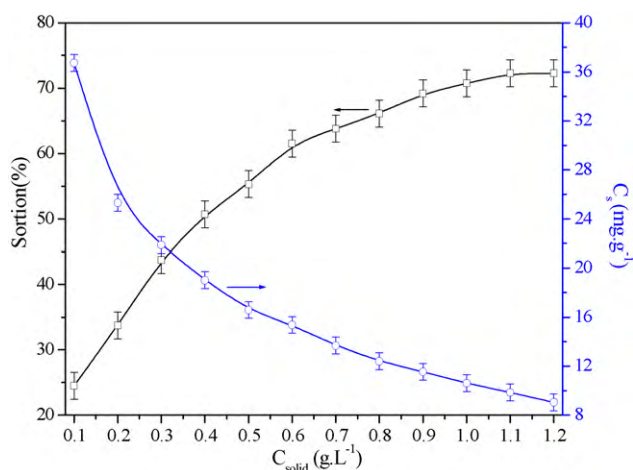
Fig. 6. Sorption of Pb(II) on Na-bentonite as a function of solid content. $T = 298 \pm 2$ K, pH = 4.0 ± 0.1, $C_{(Pb)initial} = 7.25 \times 10^{-5}$ mol L^{-1}, and $I = 0.01$ M NaClO$_4$.

content. The solid surface is composed of sites with a spectrum of binding energies. At low sorbent dose, all types of surface sites are entirely exposed for sorption and the surface reaches saturation faster, leading to a higher sorption capacity. But at higher particle concentrations the availability of higher energy sites decreases with a larger fraction of lower energy sites becoming occupied, resulting in a lower sorption capacity [29]. Besides, higher sorbent amount increases the probability of collision between solid particles and therefore creates particle aggregation, causing a decrease in the total surface area and an increase in diffusional path length, both of which contribute to the decrease in the sorption capacity of Pb(II) on Na-bentonite. Another possible interpretation is that the increase ratio of net sorption quantity of Pb(II) on Na-bentonite surface is lower than that of the solid content, correspondingly decreasing the sorption capacity of Pb(II) on Na-bentonite.

This experimental phenomenon implies that the augmentation of sorbent dosage could not unboundedly increase the contact area between metal ions and solid surface. Meanwhile, the competition between the sorbent will also reduce the sorption capacity of solid particles. Thus, for the sake of reducing pollution treatment cost in actual application, one should choose appropriate sorbent dosage according to the initial concentrations and required removal efficiency of the specific metal ion.

3.5. Effects of coexisting electrolyte ions

The metal ions of interest in wastewater are usually found to be in a matrix containing various inorganic ions. Cations in the multi-component system may compete for the binding sites of solid particles owing to the difference in their affinities on sorbent. Besides, some anions can form insoluble or soluble complexes with the metal ions, displacing with difficulty in the presence of sorbent [30]. For these reasons, it is necessary to investigate the influence of coexisting electrolyte ions on Pb(II) sorption.

Fig. 7 shows the removal of Pb(II) from aqueous solution to Na-bentonite as affected by different electrolyte ions, viz., Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, ClO$_4^-$, NO$_3^-$, Cl$^-$ and SO$_4^{2-}$, respectively. The choice of these ions has been made because of their permanent presence in natural water and industrial wastewaters. To facilitate the comparison of results, all data in the present study were obtained with perchlorate for cations and sodium salt for anions. As can be seen from Fig. 7A, the sorption of Pb(II) on Na-bentonite is strongly influences by the electrolyte cations. The competition effects of Ca^{2+} and Mg^{2+} towards Pb(II) sorption are far more important that those of Na$^+$ and K$^+$. This phenomenon can be easily interpreted
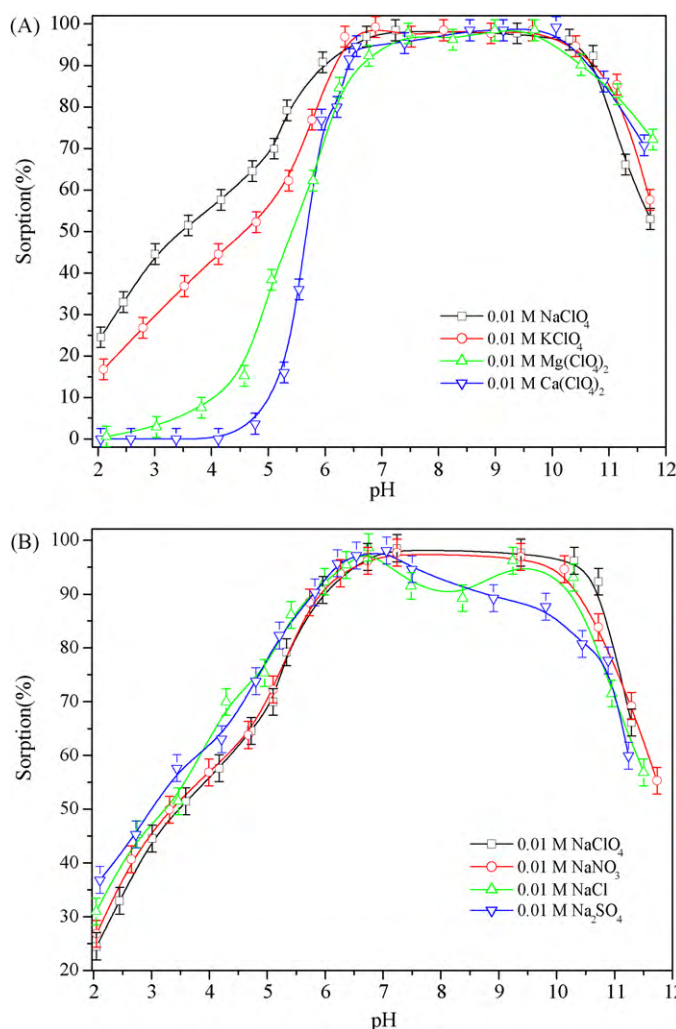

Fig. 7. Influence of foreign ions and pH on the sorption of Pb(II) on Na-bentonite. $T = 298 \pm 2$ K, $C_{(Pb)initial} = 7.25 \times 10^{-5}$ mol L^{-1}, and $m/V = 0.5$ g L^{-1}.

by the competition of different cation ions with Pb(II) for binding on the surface functional groups of Na-bentonite. The sorption ability of the four cations on Na-bentonite is Na$^+$ < K$^+$ < Mg^{2+} < Ca^{2+}, and the higher valence ion is much easily to be adsorbed by clays, thereby the influence of Ca^{2+} and Mg^{2+} on Pb(II) sorption is stronger than that of Na$^+$ and K$^+$ [3,9]. Generally, the cations may follow an order of increasing selectivity for binding to organic matter of alkali metal cations < H$^+$ < alkaline earth cations < transitional group monovalent cations (e.g., Ag$^+$) < transitional group divalent cations (e.g., Cu^{2+} and Ni^{2+}) < trivalent cations [31]. Thus, the influence of alkali metal and alkaline earth cations on the sorption of bivalent Pb(II) should be weak. However, at pH 2–7, the influence of Na$^+$, K$^+$, Mg^{2+} and Ca^{2+} on Pb(II) sorption is a little drastic. In the experiments, the concentration of the background electrolyte ions (1.00×10^{-2} mol L^{-1}) is much higher than that of Pb(II) (7.25×10^{-5} mol L^{-1}). Before the addition of Pb(II) ions, the Na-bentonite has been pre-equilibrated with background electrolyte ions. The sorption of Pb(II) on Na-bentonite is attributed to ion-exchange reaction of Pb(II) ions with the coexisting cations under the experimental conditions. Thereby, it is reasonable that the coexisting electrolyte ions can affect Pb(II) sorption.

From Fig. 7B, one can see that the sorption of Pb(II) on Na-bentonite is somewhat influenced by electrolyte anions. The presence of NO$_3^-$ shows a weak influence on Pb(II) sorption on Na-bentonite. The presence of SO$_4^{2-}$ and Cl$^-$ enhances Pb(II) sorption
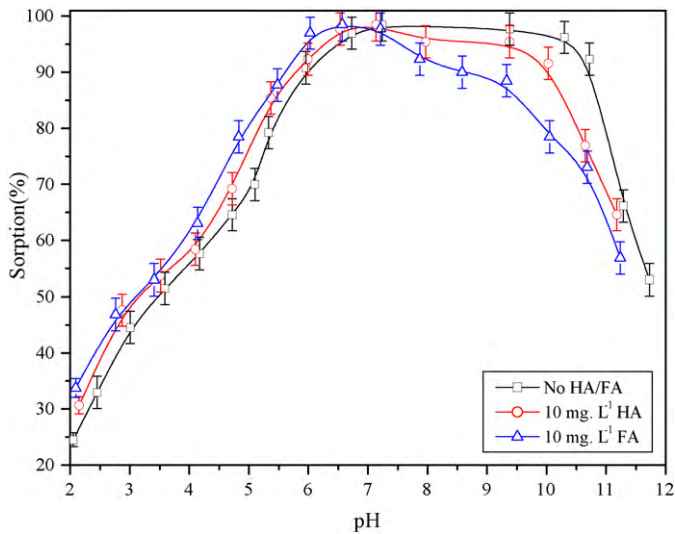
Fig. 8. Effect of pH on sorption of Pb(II) on bare and HA/FA bound Na-bentonite. $T = 298 \pm 2$ K, $C_{(Pb)initial} = 7.25 \times 10^{-5}$ mol L^{-1}, $C_{[HA/FA]} = 10$ mg L^{-1}, $m/V = 0.5$ g L^{-1}, and $I = 0.01$ M NaClO$_4$.

at pH < 7, while reduces Pb(II) sorption at pH > 7. Briefly, the sorption of metal ions on solid particles may be either enhanced or inhibited by anions through processes including ternary complex formation, site competition, formation of solution complexes, and/or alteration of surface charge. The phenomenon that Pb(II) uptake at pH < 7 is enhanced in the presence of SO$_4^{2-}$ and Cl$^-$ indicates the formation of ternary Na-bentonite–Pb–SO$_4^{2-}$ or Na-bentonite–Pb–Cl$^-$ complexes. Enhanced affinity of Pb–SO$_4^{2-}$ or Pb–Cl$^-$ complexes relative to the free Pb^{2+} ion for the Na-bentonite surface is attributable at least in part to reducing the electrostatic barrier that Pb(II) must overcome when adsorbed to the positive Na-bentonite surfaces (pH < pH$_{pzc}$ ∼ 7.8) [32]. Furthermore, the idiocratic sorption of SO$_4^{2-}$ and Cl$^-$ on Na-bentonite surface is a little easier than that of NO$_3^-$, which enhances the electronegativity of Na-bentonite surface and thereby promotes the sorption of positively charged Pb(II) ions due to electrostatic attraction. At high pH values, the SO$_4^{2-}$/Cl$^-$ are difficult to be adsorbed on the negatively charged surfaces of Na-bentonite due to electrostatic repulsion. The competition between SO$_4^{2-}$/Cl$^-$ and Na-bentonite increases the formation of stable complexes in solution, thereby competitively diminishing the extent of Pb(II) sorption on Na-bentonite.

3.6. Effects of humic substances

Humic substances (HS), with high reactivity and strong binding ability with heavy metal ions, play an important role in controlling the migration, transformation behaviors and biological effectiveness of heavy metal ions in environment. Thus, it is essential to study the effect of HS on the removal of heavy metal ions.

The pH dependence of Pb(II) sorption on Na-bentonite in the absence and presence of HA/FA is shown in Fig. 8. As is illustrated in Fig. 8, the presence of HA/FA enhances the sorption of Pb(II) on Na-bentonite at pH < 7, while a negative effect of HA/FA on Pb(II) sorption is observed at pH > 7. Yan and Bai [33] and Yang and Xing [34] determined the zeta potentials of HA and FA as a function of pH, respectively, and found that both HA and FA have negative ζ potentials at pH > 2. Therefore, at low pH values, the negatively charged HA/FA can be easily adsorbed on the positively charged surfaces of Na-bentonite due to electrostatic attraction. Actual sorption of HA/FA to Na-bentonite surface modifies both the long-range electrostatic properties of the aqueous–mineral interface as well as the concentration and molecular characteristics of

specific metal-binding sites present, which results in a more favorable electrostatic environment for Pb(II) sorption and enhances the formation of type B "ligand-bridging" ternary surface complexes where the Pb(II) ions are complexed by humic molecules that are simultaneously adsorbed on the mineral surface [35]. However, at high pH values, the negatively charged HA/FA is difficult to be adsorbed on the negatively charged surfaces of Na-bentonite due to electrostatic repulsion. The competition between the soluble HA/FA and Na-bentonite with Pb(II) increases the formation of strong HA/FA–Pb complexes in solution, thereby competitively diminishing the extent of Pb(II) sorption on HA/FA–Na-bentonite hybrids [36]. The result indicates that the complexation ability between HA/FA and Pb(II) is stronger than that between Na-bentonite and Pb(II).

From Fig. 8, one can also see that the influence of FA on the sorption of Pb(II) is a little stronger than that of HA at the whole pH range when the mass concentrations of HA and FA are the same. Although the samples of HA and FA were extracted from the same soil samples and both of them contain functional groups such as hydroxyl, carboxyl, amine and phenolic, the proportions and configurations of these functional groups and surface sites density are different. As is illustrated in Table 1, the surface sites density of FA (i.e., 2.71×10^{-2} mol g^{-1}) is higher than that of HA (i.e., 6.46×10^{-3} mol g^{-1}), which can provide more available surface sites for binding Pb(II). Furthermore, the functional groups of FA such as –OH and –COOH would be ionized as pH increased, leading to the disappearing of these hydrogen-bond donors of FA and the increase of FA solubility (i.e., the decrease of hydrophobic effects) [34]. Therefore, it is reasonable that FA has a stronger effect on Pb(II) sorption than HA at the whole pH range.

3.7. Sorption isotherms and thermodynamic studies

The sorption isotherms for Pb(II) on Na-bentonite at 298, 318 and 338 K are shown in Fig. 9. It is clear that the sorption isotherm is the highest at $T = 338$ K and is the lowest at $T = 298$ K. The result indicates that high temperature is advantageous for Pb(II) sorption on Na-bentonite. This phenomenon is attributed to a steep simultaneous decrease of real sorption of solvent or a negative temperature coefficient of the solubility of solute [37]. Three different models, viz., Langmuir, Freundlich and D–R isotherm equations
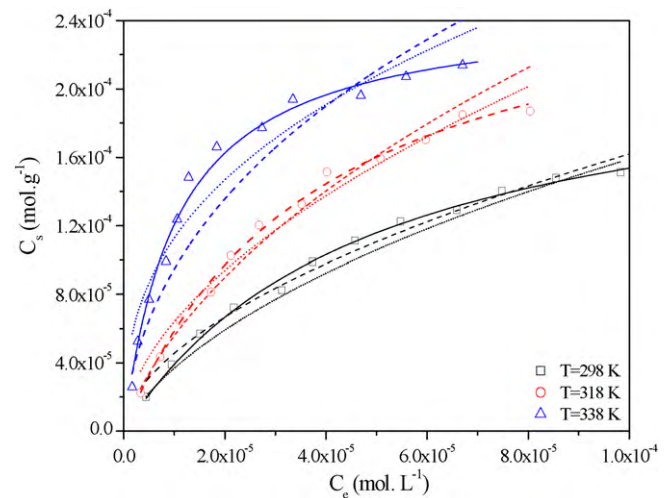
Fig. 9. Sorption isotherm and Langmuir, Freundlich, D–R models fitting for Pb(II) sorption on Na-bentonite at three different temperatures. pH = 4.0 ± 0.1, $m/V = 0.5$ g L^{-1}, $C_{(Pb)initial} = 1.45 \times 10^{-5}$–$1.74 \times 10^{-4}$ mol L^{-1}, and $I = 0.01$ M NaClO$_4$. Symbols denote experimental data, solid lines represent the model fitting of Langmuir equation, dash lines represent the model fitting of Freundlich equation and doted lines represent the model fitting of D–R equation.

are conducted to simulate the sorption isotherms and to establish the relationship between the amount of Pb(II) adsorbed on Na-bentonite and the concentration of Pb(II) remained in solution.

The Langmuir model assumes that sorption occurs in a monolayer with all sorption sites identical and energetically equivalent [38]. Its form can be described by the following equation:

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

where C_{eq} is the equilibrium concentration of metal ions remained in the solution (mol L^{-1}); C_s is the amount of metal ions adsorbed on per weight unit of solid after equilibrium (mol g^{-1}); $C_{s\,max}$, the maximum sorption capacity, is the amount of sorbate at complete monolayer coverage (mol g^{-1}), and b (L mol^{-1}) is a constant that relates to the heat of sorption. Furthermore, a dimensionless constant called separation factor (R_L, also called equilibrium parameter) is commonly used to predict whether a sorption system is favorable or unfavorable:

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where b is Langmuir constant (L mol^{-1}), and C_0 is the initial concentration of Pb(II) in solution (mol L^{-1}). The value of R_L indicates the sorption process to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [39].

The Freundlich expression is an exponential equation with the assumption that as the sorbate concentration increases so too does the concentration of sorbate on the heterogeneous sorbent surface [40]. The equation is represented by the following equation:

$$C_s = k_F C_{eq}^n \quad (3)$$

where k_F (mol^{1-n} L^n g^{-1}) represents the sorption capacity when metal ion equilibrium concentration equals to 1, and n represents the degree of dependence of sorption with equilibrium concentration.

The D–R isotherm model is more general than the Langmuir isotherm since it does not have the restriction of surface properties or constant sorption potential [41]. It has a general expression as follows:

$$C_s = C_{s\,max} \exp(-\beta\varepsilon^2) \quad (4)$$

where C_s and $C_{s\,max}$ are defined above, β is the activity coefficient related to mean sorption energy (mol^2 kJ^{-2}), and ε is the Polanyi potential, which is equal to:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_{eq}}\right) \quad (5)$$

where R is ideal gas constant (8.3145 J mol^{-1} K^{-1}), and T is the absolute temperature in Kelvin (K).

E (kJ mol^{-1}) is defined as the free energy change, which requires to transfer 1 mol of ions from solution to the solid surfaces. Its value can be calculated from the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

The magnitude of E is always used to estimate the mechanism of the sorption reaction. Sorption is dominated by chemical ion exchange if E is in the range of 8–16 kJ mol^{-1}, whereas physical forces may influence the sorption in the case of $E < 8$ kJ mol^{-1} [38,40].

The experimental data of Pb(II) sorption are regressively simulated with the Langmuir, Freundlich and D–R models and the results are given in Fig. 9. The relative values calculated from the three models are listed in Table 2. As can be seen from Fig. 9, the three isotherm equations fit the sorption isotherms of Pb(II) on Na-bentonite well, which is supported by the good correlation

Table 2
The parameters for the three isotherm models at different temperatures.

Correlation parameters	$T = 298$ K	$T = 318$ K	$T = 338$ K
Langmuir			
$C_{s\,max}$ (mol g^{-1})	2.31×10^{-4}	2.52×10^{-4}	3.10×10^{-4}
b (L mol^{-1})	2.01×10^{4}	2.50×10^{4}	8.03×10^{4}
R_L	0.223–0.775	0.187–0.734	0.067–0.462
CC (R^2)	0.995	0.996	0.991
Freundlich			
k_F (mol^{1-n} L^n g^{-1})	3.61×10^{-2}	2.57×10^{-2}	8.89×10^{-3}
n	0.550	0.539	0.379
CC (R^2)	0.985	0.974	0.922
D–R			
β (mol^2 kJ^{-2})	4.99×10^{-3}	4.30×10^{-3}	2.93×10^{-3}
$C_{s\,max}$ (mol g^{-1})	2.14×10^{-3}	2.22×10^{-3}	2.67×10^{-3}
E (kJ mol^{-1})	10.01	10.79	13.06
CC (R^2)	0.992	0.990	0.975

coefficients (all >0.90) in Table 2. Although no apparent distinction among the fitting curves of the three models can be seen from Fig. 9, it can be concluded from the R^2 values that Langmuir and D–R models simulate the experimental data better than Freundlich model (see Table 2). The fact that the sorption data of Pb(II) according with Langmuir isotherm indicates that the binding energy on the whole surface of Na-bentonite is uniform. In other words, the whole surface has identical sorption activity and therefore the adsorbed Pb(II) ions do not interact or compete with each other, and they are adsorbed by forming an almost complete monolayer coverage of the Na-bentonite particles. This phenomenon also indicates that chemosorption is the principal uptake mechanism in sorption process [42]. Moreover, Na-bentonite has a finite specific surface and sorption capacity, thus the sorption could be better described by Langmuir model rather than by Freundlich model, as an exponentially increasing sorption was assumed in the Freundlich model. At all temperatures, the value of C_s was found to be smaller than $C_{s\,max}$, which confirms that Pb(II) sorption on Na-bentonite is by a monolayer type in which the surface of Na-bentonite is not saturated. The values of $C_{s\,max}$ obtained from the Langmuir model for Pb(II) sorption on Na-bentonite are the highest at $T = 338$ K and the lowest at $T = 298$ K, which indicates that the sorption is enhanced with increasing temperature. The fact that all the R_L values for the sorption of Pb(II) on Na-bentonite at the three temperatures are in the ranges of 0.067–0.775 implies that the sorption process is favorable. The value of n calculated from the Freundlich model is from unity, indicating that a nonlinear sorption of Pb(II) takes place on Na-bentonite surfaces. The E values obtained from Eq. (6) are 10.01 ($T = 298$ K), 10.79 ($T = 318$ K) and 13.06 kJ mol^{-1} ($T = 338$ K), which are in the sorption energy range of chemical ion-exchange reaction. The sorption capacities $C_{s\,max}$ derived from the D–R model are higher than those derived from the Langmuir model. This may be attributed to the different assumptions considered in the formulation of the isotherms. The parameters calculated from the analysis of the three isotherm models concertedly manifest that sorption of Pb(II) on the surfaces of Na-bentonite is a favorable and chemisorption process.

The thermodynamic parameters ($\Delta H°$, $\Delta S°$, and $\Delta G°$) for Pb(II) sorption on Na-bentonite can be determined from the temperature dependence. Free energy change ($\Delta G°$) is calculated from the

Table 3
Values of thermodynamic parameters for Pb(II) sorption on Na-bentonite.

T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta H°$ (kJ mol^{-1})
298	−20.73	162.24	27.64
318	−23.21	162.24	28.41
338	−27.22	162.24	27.66

Table 4
Comparison of Pb(II) sorption capacities of Na-bentonite with other sorbents.

Sorbents	Solution chemistry conditions	$C_{s\,max}$ (mol g^{-1})	Reference
Oxidized MWCNTs	pH = 5.9, T = 293 K	9.92×10^{-6}	[47]
Oak bark char	pH = 5.0, T = 298 K	6.30×10^{-5}	[48]
Cicer arientinum biomass	pH = 4.0, T = 303 K	1.34×10^{-4}	[49]
Syzygium cumini L.	pH = 6.0, T = 303 K	1.57×10^{-4}	[50]
H_2O_2-oxidized activated carbon	pH = 5.0, T = 303 K	1.83×10^{-4}	[51]
Na-bentonite	pH = 4.0, T = 298 K	2.31×10^{-4}	Present study
Montmorillonite–illite type of clay	pH = 4.0, T = 300 K	2.50×10^{-4}	[52]
Modified quebracho tannin resin	pH = 5.0, T = 296 K	4.16×10^{-4}	[53]

relationship:

$$\Delta G^{\circ} = -RT \ln K^{\circ} \tag{7}$$

where K° is the sorption equilibrium constant. Values of $\ln K^{\circ}$ obtained by plotting $\ln K_d$ versus C_{eq} for sorption of Pb(II) on Na-bentonite and extrapolating C_{eq} to zero are 8.36 (T = 298 K), 8.77 (T = 318 K) and 9.68 (T = 338 K), respectively. Standard entropy change (ΔS°) is calculated using the equation:

$$\left(\frac{\partial \Delta G^{\circ}}{\partial T}\right)_P = -\Delta S^{\circ} \tag{8}$$

The average standard enthalpy change (ΔH°) is then calculated from the expression:

$$\Delta H^{\circ} = \Delta G^{\circ} + T\Delta S^{\circ} \tag{9}$$

The values obtained from Eqs. (7) to (9) are tabulated in Table 3. A positive value of the standard enthalpy change indicates that the sorption is endothermic. One possible explanation to this positive entropy is that Pb(II) is solved well in water, and the hydration sheath of Pb(II) has to be destroyed before its sorption on Na-bentonite. This dehydration process needs energy, and it is favored at high temperature [37]. The implicit assumption here is that after sorption the environment of Pb(II) ions is less aqueous than it is in solution. The removal of water from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of the enthalpy of sorption by a considerable extent. The Gibbs free energy change (ΔG°) is negative as expected for a spontaneous process under the conditions applied. The value of ΔG° becomes more negative with the increase of temperature, which indicates that the reaction is more favorable at higher temperatures. At high temperature, cations are readily desolvated and hence its sorption becomes more favorable. The positive value of entropy change (ΔS°) implies some structural changes in sorbate and sorbent during the sorption process, which leads to an increase in the disorderness of the solid–solution system [43,14]. The thermodynamic analysis derived from temperature dependent sorption isotherms suggests that the sorption process of Pb(II) on Na-bentonite is spontaneous and endothermic. However, Wong et al. [44] investigated the removal of Cu(II) and Pb(II) by tartaric acid modified rice husk from aqueous solutions and found that the sorption process was spontaneous and exothermic. The overall sorption process of Acid Blue 193 from aqueous solutions onto Na-bentonite was exothermic but it is only spontaneous at 293 K [45]. The results derived from this work and the above-mentioned references indicate that the thermodynamic parameters are related not only on the nature of sorbate, but also on the nature of solid particles [46].

3.8. Comparison of Pb(II) sorption capacity of Na-bentonite with other sorbents

In order to evaluate the potential improvements to Pb(II) removal offered by Na-bentonite over other sorbent systems, $C_{s\,max}$,

a Langmuir parameter that has been used in most of the earlier investigations for defining Pb(II) sorption capacity of different materials, was employed in the present study for comparing the efficacy of Na-bentonite with those of other sorbents reported in the literatures (see Table 4). Although a direct comparison of Na-bentonite with other sorbents is difficult due to the different experimental conditions applied, it has been found that Pb(II) sorption capacity of Na-bentonite is higher than that of oxidized MWCNTs, activated carbon and some biosorbents, comparable with montmorillonite–illite type of clay, but lower than that of modified quebracho tannin resin. However, low permeability, low cost, accessibility and ubiquitous presence in most soils make Na-bentonite an attractive sorbent for the cost-effective disposal of Pb-bearing wastewater.

4. Conclusions

In this study, a local Lin'an bentonite was converted to Na-purified form and the Na-bentonite sample was characterized by using FTIR and XRD to determine its chemical constituents and micro-structure. Batch technique was adopted to investigate the sorption of Pb(II) from aqueous solutions onto Na-bentonite as a function of various environmental factors such as contact time, pH, ionic strength, coexisting electrolyte ions, humic substances and temperature under ambient conditions. The sorption percentage of Pb(II) increases with increasing pH values at pH < 7, maintains high level at pH 7–10, and then decreases gradually at pH > 10. The sorption of Pb(II) is dependent on ionic strength at low pH values, and independent of ionic strength at high pH values. Results obtained from this study show the presences of different electrolyte ions can enhance or inhibit the sorption of Pb(II) on Na-bentonite in various degrees. The various results are attributed to the different complex abilities of these electrolyte ions with Pb(II) ions and the difference in their affinities on the binding sites of Na-bentonite. The thermodynamic analysis derived from temperature dependent sorption isotherms suggests that the sorption process of Pb(II) on Na-bentonite is spontaneous and endothermic. By integrating all the above-mentioned analysis results together, one can conclude that the sorption of Pb(II) on Na-bentonite is dominated by ion exchange or outer-sphere surface complexation at low pH values, and by inner-sphere surface complexation at high pH values. Related data show that Na-bentonite has higher Pb(II) sorption capacity than the majority of sorbents mentioned. Considering the low permeability, low cost, accessibility, ubiquitous presence in most soils and large-scale applications of Na-bentonite, one can conclude that this material has a great application potential for cost-effective disposal of Pb(II)-contaminated wastewaters.

Based on the results noted for Pb(II), Na-bentonite may also be suitable for the removal of other heavy metals and radionuclides. Hence, more investigations on the sorption property of Na-bentonite towards various environmental pollutants are ongoing in our laboratory so as to have a more thorough view of the possibility of using Na-bentonite as a high-efficiency material for wastewater disposal.

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