

## Research Article

# Adsorption Property of Pb(II) by the Laterite-Bentonite Mixture Used as Waste Landfill Liner

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To assess the potential use of laterite-bentonite mixture as waste landfill liner, a range of batch tests were conducted to study the influence of contact time, solid to solution ratio, pH, ion strength, and temperature on Pb(II) adsorption. The experimental results showed that the uptake of Pb(II) by laterite-bentonite mixture increases with the increase of contact time and the adsorption equilibrium can be reached within 30 minutes. This process can be delineated well using a pseudo-second-order kinetics equation. Besides, with the increase of solid to solution ratio ( $s/w$ ) and pH, Pb(II) will be adsorbed more by the laterite-bentonite mixture. However, the uptake of Pb(II) will decrease when ion strength rises in the solution and this is due to the competitive adsorption and cation exchange between different cations. When conducting the batch test at 298 K and 323 K, respectively, the experiment results showed significant growth when temperature increases because the adsorption process is an endothermic reaction. This influence of temperature can be described better by the Langmuir isotherm model than that by the Freundlich isotherm model. In each experiment condition, the uptake of Pb(II) increases with the increasing of bentonite content, indicating a good improvement in the effect of bentonite on laterite used as landfill liner.

## 1. Introduction

With the economic and social development of many countries in the past few decades, industrialization and urbanization grew rapidly along with the great increase in both industrial and municipal solid waste production. In China, the overall volume of municipal solid waste (MSW) increases at a rate of 5% to 8% per year, making the effective disposal of pollution becoming an urgent environmental problem. Generally, there are three main methods for MSW disposal: composting, incineration, and landfilling. By studying the exploiting and capital cost and the treatment efficiency, the sanitary landfill method, which allows the pollutant to decompose and becomes stabilized under control, is widely accepted and used in terms of its economic advantages [1]. However, the leachate, a poisonous and harmful liquid, forms in the process due to the underground water and precipitation, and it contains many heavy metal

ions such as Zn(II), Pb(II), Cr(III), Cd(II), Ni(II), and Cu(II) [2]. If these toxic metals move out of the landfills by advection and diffusion, the surrounding environment may be contaminated and the health of living plants and animals will be jeopardized [3, 4]. An effective way to restrict the migration of toxic ions is the usage of a liner to absorb these metal ions and separate the environment from MSW [5].

To achieve this goal, the high adsorption of the material used as liners is a crucial prerequisite [6, 7]. However, there are few natural soils and rocks at the landfill that could meet this requirement. For example, laterite, a kind of soil which is distributed wildly in tropical and subtropical regions of South China, is an expected source of liner material whose mechanical property is good. However, the tectonic fissure and low adsorption capacity bring some challenges for its safe application as the landfill liner for MSW [8–10]. Therefore, a lot of additives have been studied to improve the property of natural materials such as lime, cement, fly ash, clay soils, and

shale to improve their adsorption [6, 8, 11–13]. Among them, using bentonite as additive or the main material which has high cation exchange capacity (CEC) and specific surface area (SSA) can improve the adsorption property of the liner significantly and reduce its hydraulic conductivity effectively [14, 15]. The literatures showed that the adsorption property has been influenced by contact time, solid-liquid ratio, pH, ionic strength, and temperature [16–18]. However, most of the literatures concentrate on the property of pure bentonite and natural clay [19–23]. Scarce literatures discuss the property, especially the adsorption capacity of laterite-bentonite mixture other than its hydraulic conductivity [24, 25] and shear strength [26].

In China, the laterite has been considered as the ideal material due to its small settlement, good overall performance, and low costs in many places of South China. Besides, Gaomiaozi (GMZ) bentonite from north of China is a promising additive due to its high CEC, large SSA, and low permeability. To guarantee the safe and long-term application of laterite-GMZ bentonite mixture used as MSW landfill liner, a batch test has been undertaken and effects of bentonite content, contact time, solid-liquid ratio, ionic strength, pH of solution, and temperature on the sorption of Pb(II) are discussed.

## 2. Materials and Methods

**2.1. Materials and Apparatus.** Laterite used in the present work was taken from Chenzhou City, Hunan province, China, and has been air-dried and sieved (0.5 mm sieve) for use. Some geotechnical and chemical property of this red powder are listed in Table 1 after standardized test (JTGE40-2007) [27] and XRF (X-ray fluorescence spectrometer) test. As can be seen, the laterite is composed of several minerals such as 80.2% kaolinite, 12.5% quartz, and 6.4% monticellite.

The GMZ bentonite was sampled from Gaomiaozi township in Northern China, and it had also been air-dried and sieved (0.5 mm sieve) for use. The basic properties of this light-grey powder are listed in Table 2 [28, 29]. As shown in the table, its main mineral component is montmorillonite (75.4%).

Pb(NO<sub>3</sub>)<sub>2</sub>, a white crystal, used in this experiment was bought from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and its molecular weight is 331.21. The purity of this solid is more than 99.0%, and it is a kind of dangerous chemical which can be used as strong oxidant.

In the test procedures, three apparatus were used, including a centrifuge, constant temperature incubator, and inductively coupled plasma (ICP). The type of the centrifuge is TD3(800B) whose maximum relative centrifugal force (RCF) is 1980 × *g*. The incubator (HY-2 series) was produced by Shanghai Jing Hong Laboratory Instrument Co. Ltd. (Shanghai, China). The ICP used in this study was produced by Agilent Technologies (California, America) whose type is PE8300.

**2.2. Adsorption Test.** Adsorption experiments were conducted using the batch test according to the ASTM (1993)

TABLE 1: Some geotechnical and chemical properties of laterite.

Natural dry density, $\rho$ (g·cm <sup>-3</sup> )	1.35
Natural water content, $\omega$ (%)	37.14
Natural void ratio, $e$	0.96
Specific gravity, $G_s$	2.65
Plastic limit, $\omega_p$ (%)	29.8
Liquid limit, $\omega_L$ (%)	57.0
Clay particle fraction (%)	69
Silt particle fraction (%)	31
Mineral component (%)	Kaolinite (80.2); quartz (12.5); monticellite (6.4)
Chemical component (%)	SiO <sub>2</sub> (49.96); Al <sub>2</sub> O <sub>3</sub> (28.91); Fe <sub>2</sub> O <sub>3</sub> (17.02); TiO <sub>2</sub> (1.59); K <sub>2</sub> O (1.41)

TABLE 2: Basic properties of GMZ bentonite.

Specific gravity, $G_s$	2.66
Liquid limit, $\omega_L$ (%)	276
Plastic limit, $\omega_p$ (%)	37
Total specific surface area (m <sup>2</sup> ·g <sup>-1</sup> )	570
Cation exchange capacity (cmol·kg <sup>-1</sup> )	77.30
Main exchange cations (cmol·kg <sup>-1</sup> )	Na <sup>+</sup> (43.36); 1/2 Ca <sup>2+</sup> (14.57); 1/2 Mg <sup>2+</sup> (6.17); K <sup>+</sup> (2.51)
Mineral component (%)	Montmorillonite (75.4), quartz (11.7) cristobalite (7.3); feldspar (4.3); Kaolinite (0.8); calcite (0.5)
Chemical component (%)	SiO <sub>2</sub> (67.43), Al <sub>2</sub> O <sub>3</sub> (14.20), Na <sub>2</sub> O (1.75), CaO (1.13)

standard [30] under two temperatures of 298 K and 323 K. The laterite and bentonite used in this test were mixed at the dry mass ratios of 1:0, 9:1, 8:2, and 0:1 and have been sieved with 0.5 mm mesh. Pb(II) solution (100 mg·L<sup>-1</sup>) was prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> solid in distilled water under the specific mass ratio. The experiment procedures are as follows.

Soil powder and Pb(II) solution were mixed at different solid-liquid ratios (*s/w*) in the Erlenmeyer flask which contains 200 mL solution. The Erlenmeyer flask was sealed on the top and placed in a constant temperature shaking incubator at 180 rpm for 8 hours. At a given time, the Erlenmeyer flask was pulled out and placed in a centrifuge for 10 min at 9400 rpm for solid-liquid separation. The supernatant solution was sampled by using a dropper and dripped into the testing tube of ICP. Then the ion concentration of Pb(II) of this solution was obtained, which is termed equilibrium concentrations ( $C_e$ ). To study the influence of contact time on the sorption, the concentration of Pb(II) in the supernatant is tested at regular intervals, from 5 min to 480 min. The solid-liquid ratio (*s/w*) was set as 0.5 to 200 g·L<sup>-1</sup> for the investigation of its influence on soil adsorption property. Considering the different effect of pH and ion strength of the solution, NaCl solid was added into Pb(II) solution with concentrations of 0 mol·L<sup>-1</sup>, 0.01 mol·L<sup>-1</sup>, 0.1 mol·L<sup>-1</sup>, and 1 mol·L<sup>-1</sup> and the pH of this solution was controlled from 2 to 11 in the experiment. There were 29 experiment conditions in total, and they are all listed in Table 3.

TABLE 3: Experiment conditions of Pb(II) adsorption property of soil.

Study contents	Experiment conditions						
	Bentonite content in laterite (%)	Contact time (min)	Solid-liquid ratio (g/L)	Initial solution contention (mg/L)	pH value	Ion strength (mol/L)	Temperature (K)
Kinetics adsorption test	0, 10, 20	5, 10, 20, 30, 60, 120, 240, 480	5	100	5.5	0	298
Equilibrium adsorption test	0, 10, 20	30	5	20~1000	5.5	0	298/323
Influence of $s/w$	0, 10, 20	30	0.5, 1, 2, 5, 10, 20, 40, 60, 100, 200	100	5.5	0	298
Influence of pH	0, 10, 20	30	5	100	2/5.5/7/9/11	0	298
Influence of ion strength	0, 10, 20	30	5	100	5.5	0/0.01/0.1/1	298

### 3. Results and Discussion

**3.1. Influence of Contact Time and Adsorption Kinetics.** To study the influence of contact time of Pb(II) adsorption by laterite and its mixture with bentonite, the concentration of Pb(II) was measured at different contact times between soil particles and solution from 5 to 480 minutes. The experiment results are plotted in Figure 1. As can be drawn from the figures, the adsorption rate of Pb(II) increases with the increase in contact time and the equilibrium time of four different soils decreases from 30 minutes to 5 minutes apparently. Therefore, the equilibrium contact time for other studies in this research is determined at 30 minutes. In Figure 1, the adsorption rate (%) of Pb(II) and the adsorption capacity of soil per unit mass ( $q_e$ ) are expressed in following equation:

$$\text{adsorption rate} = \frac{C_i - C_e}{C_i} \times 100\%, \quad (1)$$

$$q_e = \frac{(C_i - C_e)v}{m},$$

where  $C_i$  and  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) are the initial Pb(II) concentration and equilibrium Pb(II) concentration in the solution, respectively;  $v$  (L) is the total volume of the solution; and  $m$  (g) is the mass of adsorbent (i.e., soil particles).

Based on the experiment data, the adsorption rate of Pb(II) within 5 minutes are 10.55%, 35.11%, 55.32%, and 99.17% when bentonite content equals to 0%, 10%, 20%, to 100%, respectively. The ultimate adsorption rate of this kind heavy metal ion is 12.83%, 38.06%, 57.80%, and 100% when the bentonite content varies in the mixture. Obviously, the equilibrium adsorption rate of pure bentonite is about 8 times to pure laterite, and this can be explained by the much higher adsorption capacity of bentonite than that of laterite [31].

To analyze the influence of time on adsorption, three adsorption kinetic models are proposed to delineate the adsorption process, which are pseudo-first-order kinetics equation, pseudo-second-order kinetics equation, and intraparticle diffusion kinetics equation (i.e., W-M kinetics equation), respectively [32].

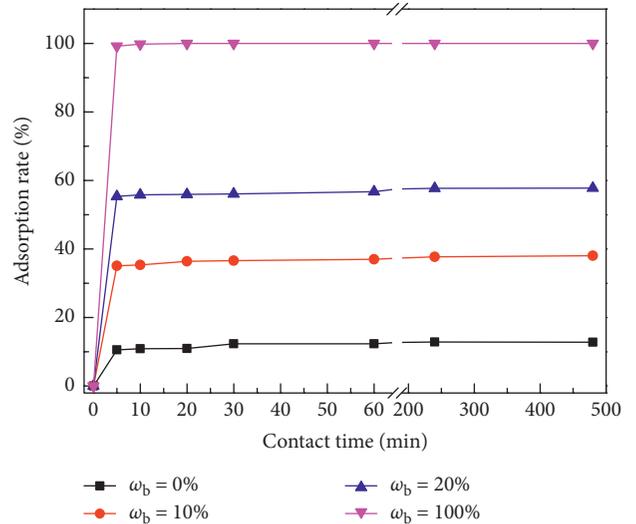


FIGURE 1: Influence of contact time on Pb(II) adsorption ( $s/w = 5 \text{ g}\cdot\text{L}^{-1}$ ;  $\text{pH} = 5.5$ ;  $C_i = 100 \text{ mg}\cdot\text{L}^{-1}$ ;  $T = 298 \text{ K}$ ;  $\omega_b$  is the mass content of bentonite in the soil mixture).

The pseudo-first-order kinetics equation and pseudo-second-order kinetics equation are based on the assumptions that the reaction rate is in direct proportion to the first and second power of reactant concentration. The equations can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (3)$$

where  $q_t$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the adsorbed quantity of Pb(II) on soil particles at time  $t$  (min) and  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the equilibrium adsorption capacity.  $k_1$  and  $k_2$  ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ) are the pseudo-first-order and pseudo-second-order rate constants of adsorption, respectively.

The intraparticle diffusion kinetics equation was proposed by Weber and Morris based on three assumptions: (1) the resistance of film only works at the initial stage of

adsorption in a short time or it is neglected; (2) the direction of diffusion is random and the concentration of adsorbate is constant; and (3) the intraparticle diffusion parameter is a constant.

$$q_t = k_i t^{1/2} + C, \quad (4)$$

where  $k_i$  ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ) is the intraparticle diffusion parameter and  $C$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is a constant.

Based on the three kinetics model, the fitting curves of the Pb(II) adsorption kinetics are plotted in Figure 2. The value of parameters in equations (2)–(4) can be calculated and are listed in Table 4. As can be drawn from the table, the values of correlation coefficient (i.e.,  $R^2$ ) for pseudo-first-order and pseudo-second-order kinetics models are greater than 0.99, indicating a good fitting effect especially for the pseudo-second-order kinetics model. Besides, similar results with the use of the pseudo-second-order kinetics model can be found in the literatures using bentonite [17, 33, 34] or laterite [21] as adsorbent. Therefore, the proposed pseudo-second-order kinetics model can delineate this process very well. However, the correlation coefficients of intraparticle diffusion kinetics equation are far from 1, suggesting an improper use of this model.

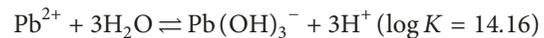
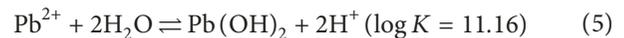
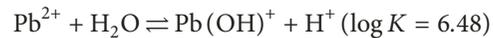
**3.2. Influence of  $s/w$ .** To study the dependence of Pb(II) adsorption on solid to solution ratio, varied  $s/w$  ( $0.5\text{--}200\text{ g}\cdot\text{L}^{-1}$ ) adsorption experiments are conducted and the results are plotted in Figure 3. It is clear that the adsorption rate of Pb(II) ions increases with the increase of  $s/w$ . Some researchers attribute this phenomenon to the greater cation availability of exchangeable sites with the increase of  $s/w$  [20,33,35]. When this value equals to  $100\text{ g}\cdot\text{L}^{-1}$ ,  $40\text{ g}\cdot\text{L}^{-1}$ ,  $20\text{ g}\cdot\text{L}^{-1}$ , and  $5\text{ g}\cdot\text{L}^{-1}$  for four laterite-bentonite mixtures whose mass content of bentonite is 0%, 10%, 20%, and 100%, respectively, the ultimate ion adsorption rate remains constant even when the solid mass into the solution is increased. Adding the soil particles into the solution does provide more adsorption sites, but the total quantities of Pb(II) cannot be adsorbed completely. This is ascribed to the decreasing concentration gradient between solution and adsorbent surface when a majority of Pb(II) ions were absorbed by the soil particles [36]. Besides, the equilibrium capacity of soil per unite mass decreases with the increase of  $s/w$ . Similar results have been found for Cd(II) on the GMZ bentonite [16] and lead on the treated laterite [37], and this can be credited to the competition of soil particles.

On the contrary, increasing content of bentonite in the soil mixture brings a higher equilibrium adsorption capacity and ultimate adsorption rate of Pb(II). These results also indicate the higher cation exchange capacity of bentonite than that of laterite, leading to important influence on adsorption characteristic by the mass content of bentonite. Parallel results have been found in copper adsorption by sand-bentonite as liners [38] and Pb(II) adsorption by mixture of kaolinite-sago waste and bentonite-sago waste [39].

**3.3. Influence of pH.** Because the existence of Pb(II) is highly dependent on the pH value, the batch test was carried out

under different pH values [2–11], and the experiment results are shown in Figure 4. Clearly, the adsorption rate of Pb(II) increases significantly with the increase of the pH value, and this trend becomes evident when bentonite content decreases. When the pH value of the solution equals to 2, the adsorption rate of Pb(II) is 0%, 4.49%, 14.08%, and 64%, respectively, for the four soil mixtures and this value aggrandize approximately to 100% when the pH of the solution is 11. The increase in the speed of ion adsorption rate is sharp when pH varies from 2 to 8, and it reduces when the pH value exceeds 8. The extent of total increase in adsorption is about 36% to 100% which indicates that pH plays a paramount role in the adsorption of Pb(II).

Similar influence of pH has been found in the literatures on Cu(II) [40], Cd(II) [20, 41], Ni(II) [41], La(III) [42], Pb(II) [41, 43], and Sr(II) [44]. The reason of the aforementioned experiment rules is ascribed to the change of hydrolysis degree of Pb(II) which depends highly on the pH of solution [45]. As is shown in equation (5) and Figure 5, the majority of Pb(II) exists as free  $\text{Pb}^{2+}$  when  $\text{pH} < 7.5$  and  $K$  is the hydrolysis equilibrium constant of Pb(II):



In this situation, the high concentration of  $\text{H}^+$  will compete for the adsorption sites on soil particles. Therefore, the adsorption rate of Pb(II) is scarce in this condition. With the rise of pH [7.5–9.5], more  $\text{Pb}(\text{OH})^+$  forms and a small part of Pb(II) has been hydrolyzed into  $\text{Pb}(\text{OH})_2$  which will enhance the adsorption of Pb(II). With the further increase of pH [9.5–11], most of Pb(II) separates out of the solution in the form of the  $\text{Pb}(\text{OH})_2$  sediment which has a strong influence on the equilibrium adsorption rate of this kind of heavy metal ion.

Besides, the surface property of soil particles will change with the increase of pH, such as surface charges of laterite and bentonite particles [37]. When the pH value of the solution is low, the high concentration of  $\text{H}^+$  leads to a positively charged surface of soil particles. The electrostatic repulsion between the surface charge and Pb(II) ions will result in a low adsorption rate of Pb(II). However, there is a specific pH value when the surface charge of soil particles equals to zero, which is named zero point charge ( $\text{pH}_{\text{zpc}}$ ). When  $\text{pH} > \text{pH}_{\text{zpc}}$ , the particle surface becomes negatively charged, leading to a high uptake of Pb(II) because of the electrostatic attraction between cations and anions.

**3.4. Influence of Ion Strength.** To find out the effect of ion strength [ $\text{Na}^+$ ] on Pb(II) adsorption, the NaCl solid was added into  $\text{Pb}(\text{NO}_3)_2$  to obtain a solution whose sodium concentration are  $0\text{ mol}\cdot\text{L}^{-1}$ ,  $0.01\text{ mol}\cdot\text{L}^{-1}$ ,  $0.1\text{ mol}\cdot\text{L}^{-1}$ , and  $1.0\text{ mol}\cdot\text{L}^{-1}$ , respectively. The experiment result is presented in Figure 6. It is obvious that the increase of ion strength plays a crucial role on the adsorption of Pb(II). The adsorption decreases sharply with the increase of NaCl concentration. For the four different soil mixtures, the

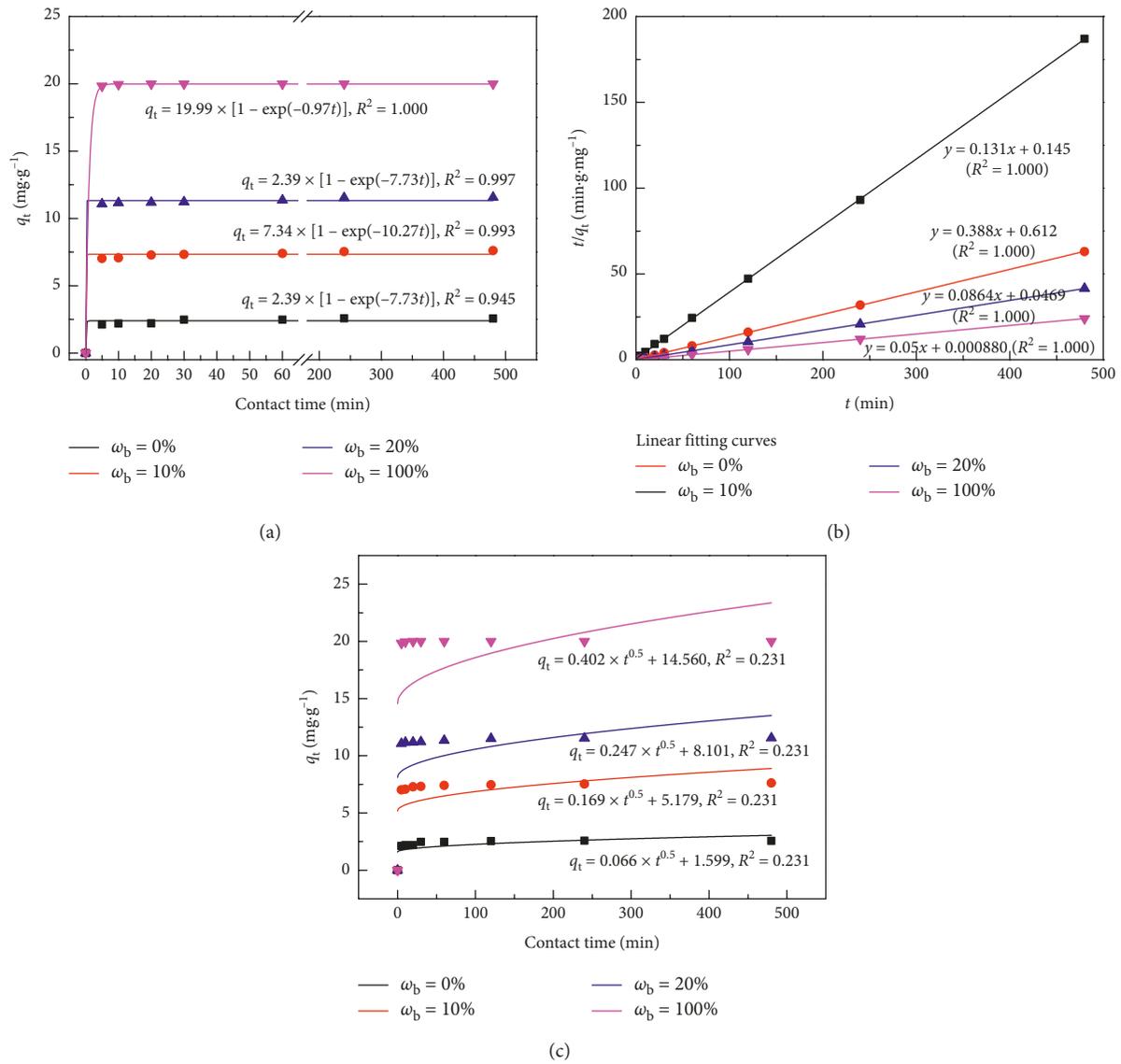


FIGURE 2: Pb(II) adsorption kinetics plots of laterite-bentonite mixtures: (a) pseudo-first order; (b) pseudo-second order; (c) intraparticle diffusion.

TABLE 4: Values of pseudo-second-order kinetics parameters.

$\omega_b$ (%)	Pseudo-first-order kinetics parameters			Pseudo-second-order kinetics parameters			Intraparticle diffusion kinetics equation			$C_i$ (mg·L <sup>-1</sup> )
	$k_1$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$q_e$ (mg·g <sup>-1</sup> )	$R^2$	$k_2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$q_e$ (mg·g <sup>-1</sup> )	$R^2$	$k_i$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$C$ (mg·g <sup>-1</sup> )	$R^2$	
0	7.73	2.39	0.945	0.21	2.53	0.99996	0.066	1.599	0.231	100
10	10.27	7.34	0.993	0.12	7.61	0.99994	0.169	5.179	0.127	100
20	23.94	11.32	0.997	0.16	11.58	0.99999	0.247	8.101	0.100	100
100	0.97	19.99	1.000	2.36	20.00	1.00000	0.402	14.560	0.064	100

adsorption rate of Pb(II) is 14.85%, 37.21%, 55.78% and 99.99%, respectively, when there is no Na<sup>+</sup>. However, the uptake extent of Pb(II) decreases to 4.63%, 4.94%, 9.51%, and 12.63% when the concentration of NaCl increases to 1.0 mol·L<sup>-1</sup>, and this decline is fast within certain range [0–0.1 mol·L<sup>-1</sup>]. This phenomenon is more apparent when

the mass content of bentonite is high which indicates that sodium ion has a greater influence on bentonite than laterite.

Similar results have been reported in the literatures, and they attribute the reason to a competitive adsorption or the cation exchange between the added cation and adsorbate [16]. When Na<sup>+</sup> is at a low concentration [0–0.1 mol·L<sup>-1</sup>], its

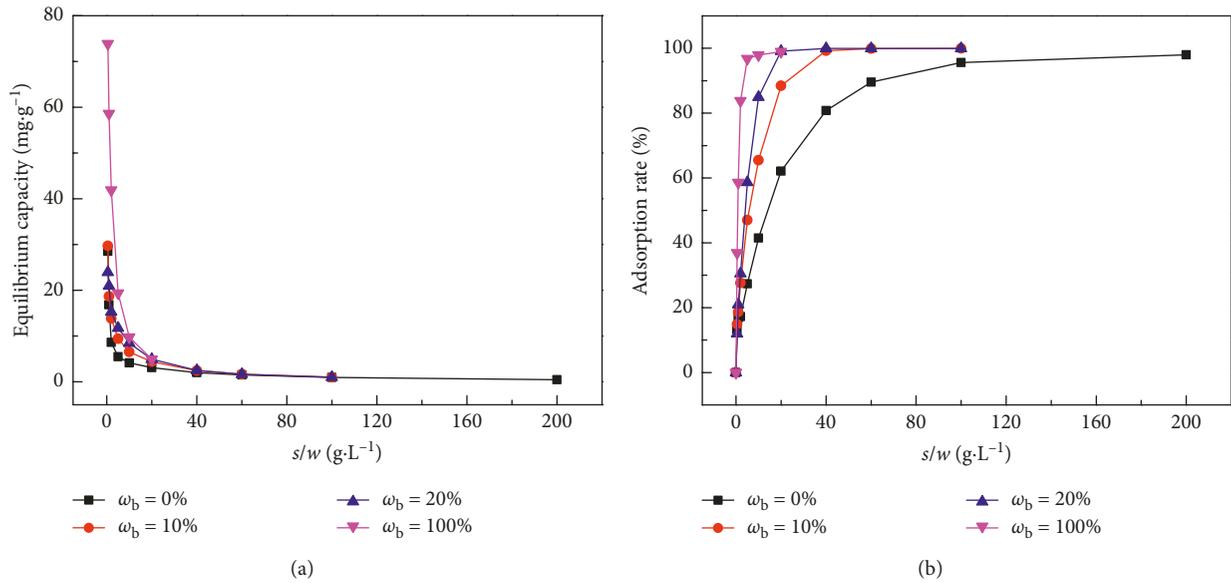


FIGURE 3: Influence of  $s/w$  on (a) equilibrium capacity of Pb(II) and (b) Pb(II) adsorption rate ( $pH = 5.5$ ;  $C_i = 100 \text{ mg}\cdot\text{L}^{-1}$ ;  $T = 298 \text{ K}$ ;  $t = 30 \text{ min}$ ),  $\omega_b$  is the mass content of bentonite in the soil mixture.

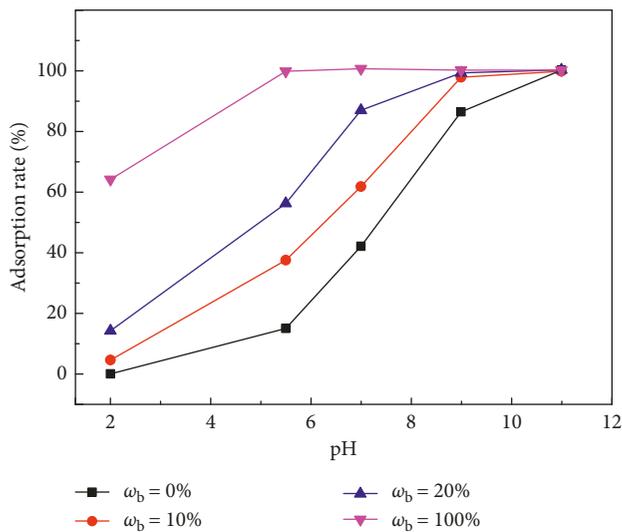


FIGURE 4: Influence of pH on Pb(II) adsorption ( $s/w = 5 \text{ g}\cdot\text{L}^{-1}$ ;  $pH = 5.5$ ;  $C_i = 100 \text{ mg}\cdot\text{L}^{-1}$ ;  $T = 298 \text{ K}$ ;  $t = 30 \text{ min}$ ).

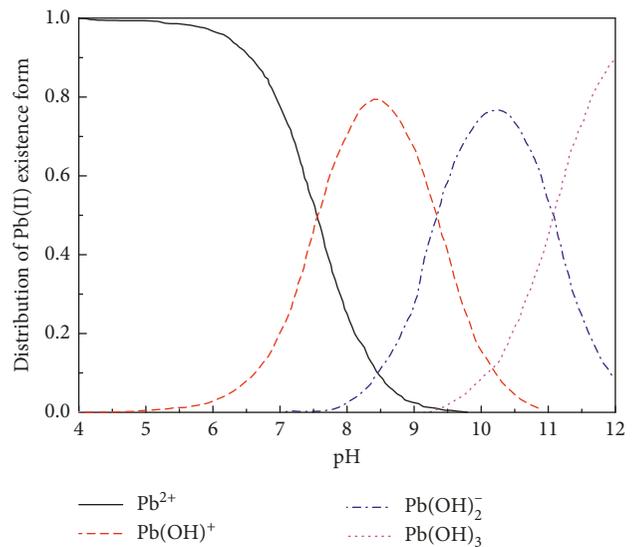


FIGURE 5: Distribution of Pb(II) existence form as a function of pH.

greater hydration power leads to a cation replacement on soil particles. The active site on laterite and bentonite particles will be occupied by  $\text{Na}^+$ . When the adsorption of  $\text{Na}^+$  saturates gradually with the increased concentration of  $\text{NaCl}$ , the decrease of Pb(II) adsorption rate slows down as shown in Figure 6 and other literatures[16].  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  have similar comparative effect on Pb(II) adsorption and the effect on these three cations can be arranged in the following order:  $\text{Mg}^{2+} > \text{Na}^+ > \text{Ca}^{2+}$  [37].

Other than cations, acid radicals also have an influence on the adsorption rate of Pb(II). The radius of  $\text{Cl}^-$  is smaller than  $\text{NO}_3^-$ , leading to a stronger complexation between  $\text{Cl}^-$  and  $\text{Pb}^{2+}$ . Therefore, the concentration of Pb(II) is lower when adding  $\text{NaCl}$  into the solution than  $\text{NaNO}_3$ . Besides,

$\text{SO}_4^{2-}$  in the solution will also reduce the uptake rate of Pb(II) due to the chelate complex compound formed between  $\text{SO}_4^{2-}$  and  $\text{Pb}^{2+}$ .

### 3.5. Influence of Temperature and Isothermal Adsorption.

It is known that the environment temperature is a crucial factor to influence the physicochemical behavior of metal ions adsorbed by materials. Therefore, the batch test of Pb(II) adsorption is carried out at  $25^\circ\text{C}$  (298 K) and  $50^\circ\text{C}$  (323 K), and the experimental results are plotted in Figure 7. Clearly, the uptake of Pb(II) is higher when the temperature is higher, suggesting that the adsorption reaction of Pb(II) is an endothermic process. When the temperature rises from

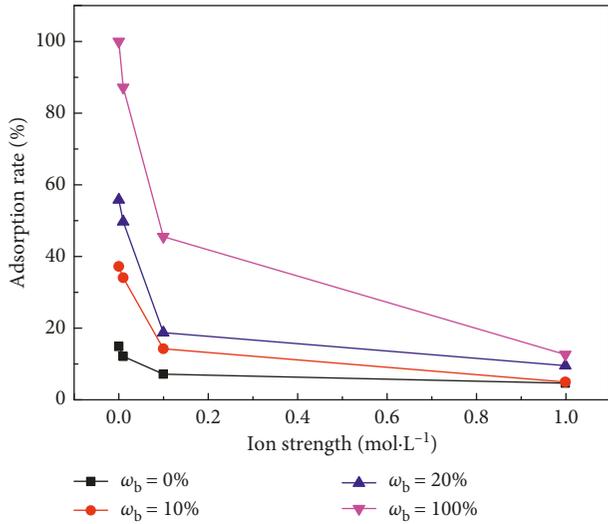


FIGURE 6: Influence of initial ion strength on Pb(II) adsorption ( $s/w = 5 \text{ g}\cdot\text{L}^{-1}$ ;  $\text{pH} = 5.5$ ;  $C_i = 100 \text{ mg}\cdot\text{L}^{-1}$ ;  $T = 298 \text{ K}$ ;  $t = 30 \text{ min}$ ).

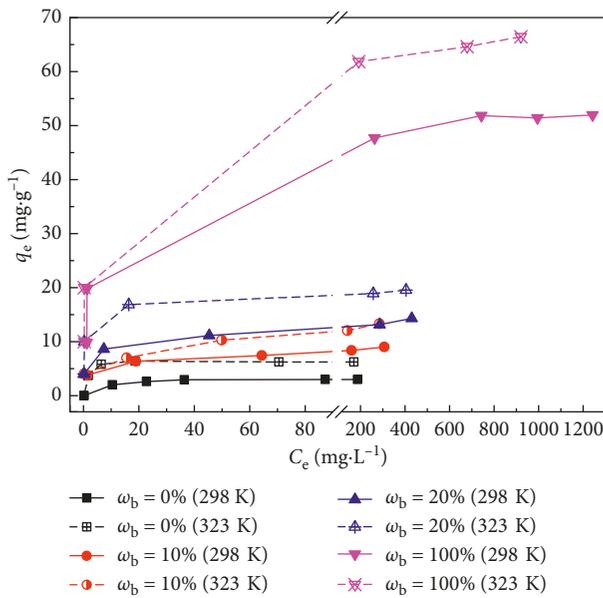


FIGURE 7: Adsorption isotherm of Pb(II) ( $s/w = 5 \text{ g}\cdot\text{L}^{-1}$ ;  $\text{pH} = 5.5$ ;  $t = 30 \text{ min}$ ).

289 K to 323 K and the equilibrium Pb(II) concentration ( $C_e$ ) varies from  $0 \text{ mg}\cdot\text{L}^{-1}$  to  $1240 \text{ mg}\cdot\text{L}^{-1}$ , the increase of adsorption capacity of soil per unit mass ( $q_e$ ) changes from  $3 \text{ mg}\cdot\text{g}^{-1}$  to as high as  $56.447 \text{ mg}\cdot\text{g}^{-1}$  for different laterite-bentonite mixtures. This influence effect is stronger for soils with more bentonite.

To simulate the adsorption isotherm of the Pb(II) adsorption on surface of soil particles, the Langmuir isothermal model and Freundlich isothermal model are adopted in this study and previous works. There are three assumptions of the Langmuir isothermal model: (1) adsorbate molecules are absorbed on the particle surface as a monolayer; (2) all the adsorption sites are the same; (3) there

is no interaction between adsorbate molecules. The Langmuir isothermal model can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b_L q_{\max}}, \quad (6)$$

where  $q_{\max}$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the maximum adsorption capacity per unit mass,  $b_L$  ( $\text{L}\cdot\text{mg}^{-1}$ ) is the Langmuir adsorption constant which relates to the change of enthalpy of reaction process, and these can be calculated through the linear relationship between  $C_e/q_e$  and  $C_e$ .

In contrast, the Freundlich isothermal model is an empirical formula for an inhomogeneous system as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (7)$$

where  $q_e$  is already defined in equation (6) and  $K_F$  ( $\text{mg}^{1-1/n}\cdot\text{L}^{1/n}\cdot\text{g}^{-1}$ ) and  $n$  are the Freundlich isotherm parameters. The experiment data of the isotherm adsorption are fitted using the Langmuir and Freundlich models, and the results are plotted in Figures 8 and 9. As can be drawn from the curves, the values of correlation coefficient ( $R^2$ ) for soils using the Langmuir model are almost more than 0.99. But this value of the Freundlich fitted curves has a great distance with 1. Therefore, the adsorption behavior of Pb(II) can be accurately described by the Langmuir isotherm model. Therefore, it can be conjectured that a majority of adsorbate molecules are absorbed on the particle surface as a monolayer which is consistent with the assumptions of the Langmuir isothermal model.

The fitted values of parameters in the Langmuir and Freundlich isotherm models are listed in Table 5. As can be drawn, with the rise of temperature, the maximum adsorption capacity per unit mass ( $q_{\max}$ ) and the value of  $K_F$  also have an apparent increment. This effect can be explained by the endothermic process of Pb(II) adsorption. In addition,  $K_F$  in the Freundlich isotherm model is a parameter which represents the degree of adsorption. Its value increases obviously with the increase of  $\omega_b$ , indicating a greater influence of bentonite on Pb(II) adsorption than that of laterite. Besides, the increase of  $q_{\max}$  in the Langmuir model also verifies this influence. To predict the maximum adsorption of the laterite-bentonite mixture, a simple equation was proposed as follows:

$$q_m = \frac{q_b - q_l}{100} \omega_b + q_l, \quad (8)$$

where  $\omega_b$  (%) is the bentonite content,  $q_b$  ( $\text{mg}\cdot\text{g}^{-1}$ ) and  $q_l$  ( $\text{mg}\cdot\text{g}^{-1}$ ) are the maximum adsorption of Pb(II) by pure laterite and bentonite, respectively, and  $q_m$  is the maximum value of Pb(II) adsorption by the laterite-bentonite mixture.

When applying equation (8) at two different temperatures, the prediction equation above can be plotted in Figure 10. As is shown in the figure, the predicted value of maximum adsorption by mixture is almost equal to the experiment results, indicating the practical application of this prediction equation.

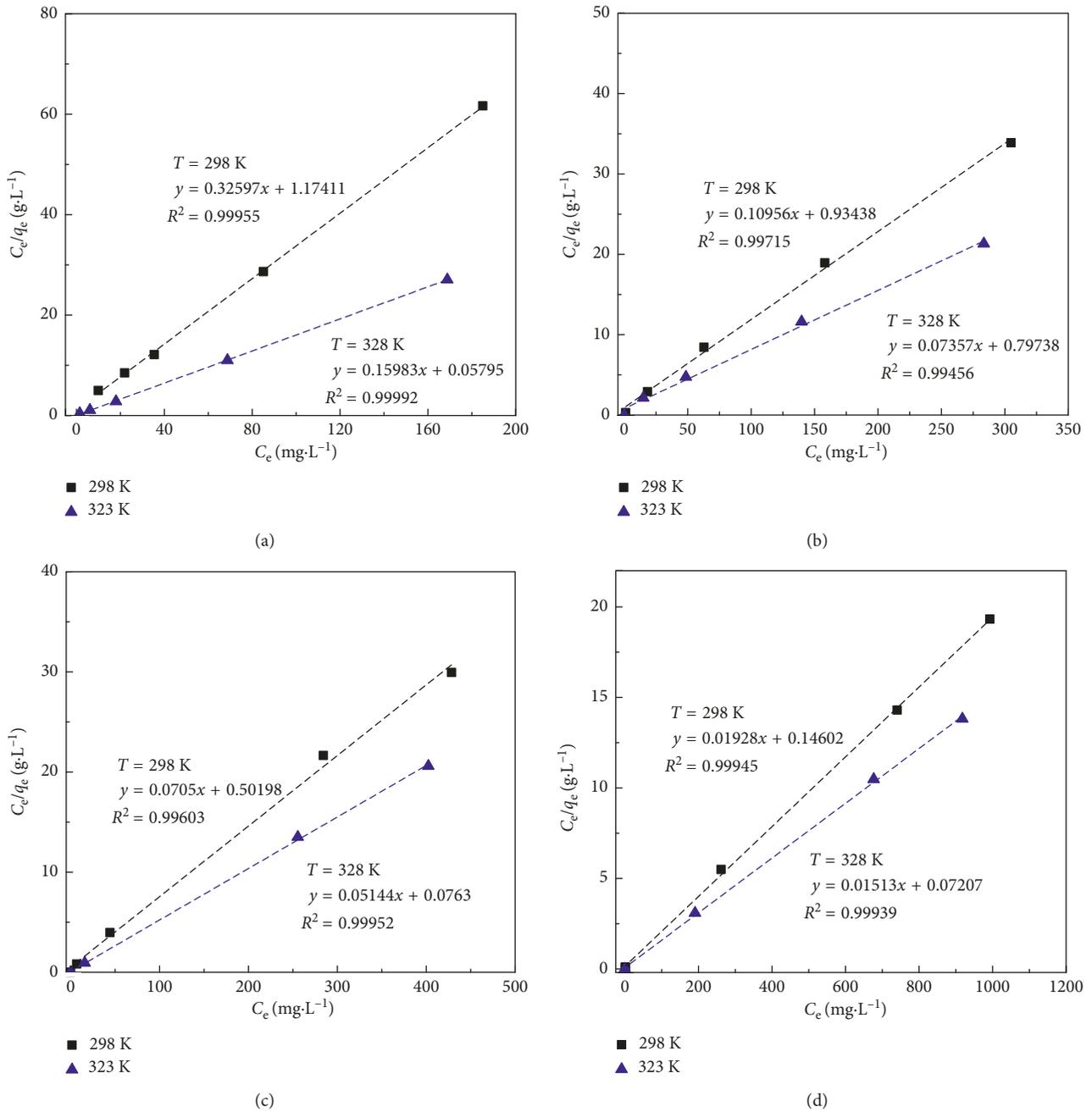


FIGURE 8: Langmuir fitting curves of Pb(II) adsorption: (a)  $\omega_b = 0\%$ ; (b)  $\omega_b = 10\%$ ; (c)  $\omega_b = 20\%$ ; (d)  $\omega_b = 100\%$ .

#### 4. Conclusion

In this study, the adsorption of Pb(II) by laterite-bentonite mixture was investigated using the batch test under different conditions, including bentonite content (0–100%), contact time (5–480 min), solid to solution ratio (0.5–200 g.L<sup>-1</sup>), pH (2–11), ion strength (0–1 mol.L<sup>-1</sup>), and temperature (328 K, 323 K). To evaluate the influence of those conditions, three adsorption kinetic models and two adsorptive isotherm models are used to analyze the experiment data and the

feasibility of different models in this research. Several important conclusions are drawn as follows:

- (1) With the increase of contact time and bentonite content, the uptake of Pb(II) will increase and reach an equilibrium concentration in the end. The higher the content of bentonite in the mixture is, the shorter the equilibrium time will be. In general, the adsorption process can reach the equilibrium within 30 minutes. The experiment data can be fitted best

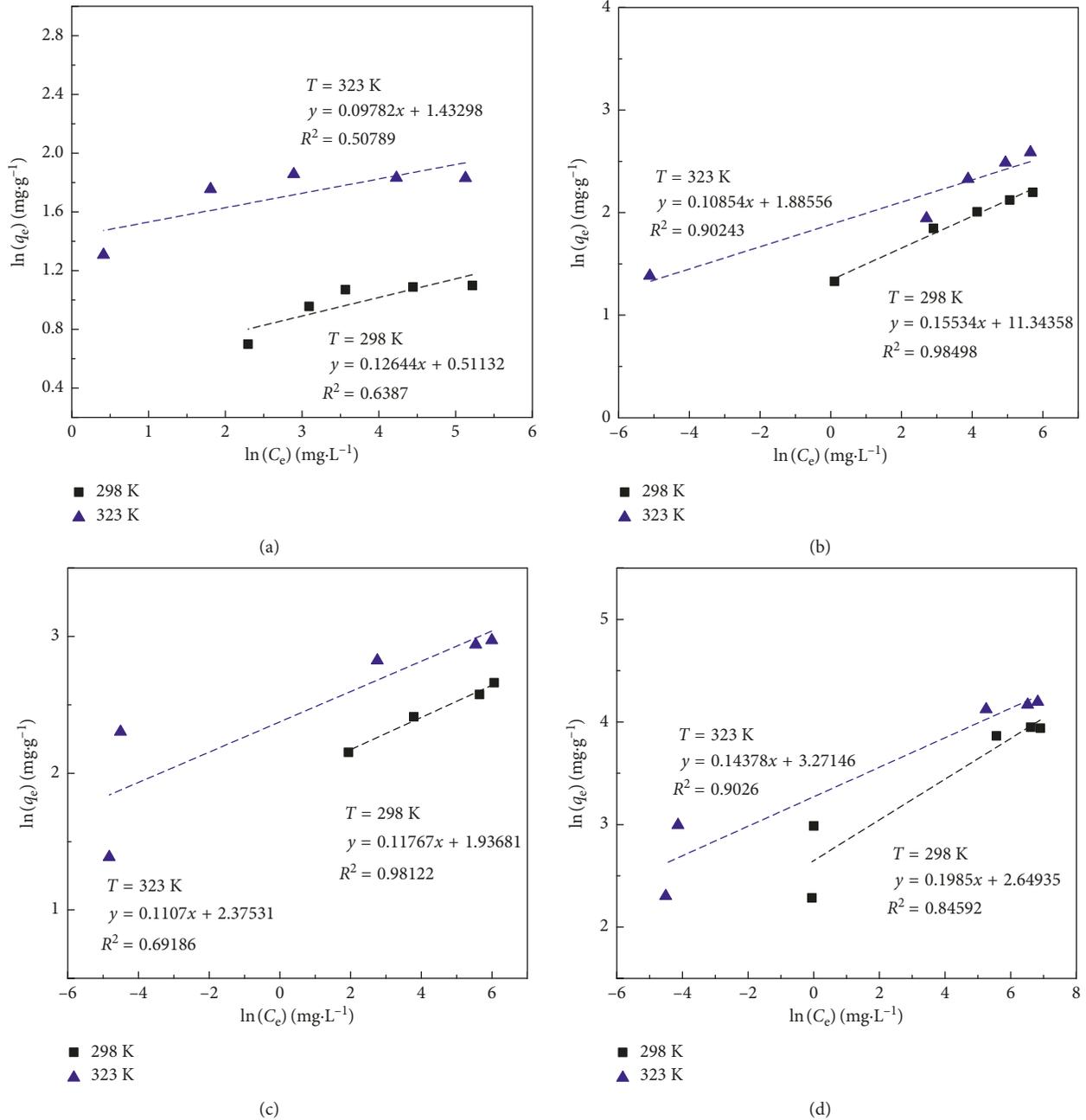


FIGURE 9: Freundlich fitting curves of Pb(II) adsorption.

TABLE 5: Parameters of the Langmuir and Freundlich isotherm models.

$\omega_b$ (%)	$T$ (K)	Langmuir adsorption model			Freundlich adsorption model		
		$q_{max}$ (mg·g <sup>-1</sup> )	$b_L$ (L·mg <sup>-1</sup> )	$R^2$	$K_F$ (mg <sup>1-1/n</sup> ·L <sup>1/n</sup> ·g <sup>-1</sup> )	1/n	$R^2$
0	298	3.07	0.28	1.000	1.67	0.13	0.639
10	298	9.13	0.12	0.997	3.83	0.16	0.985
20	298	14.18	0.14	0.996	6.94	0.12	0.981
100	298	51.87	0.13	0.999	14.14	0.20	0.903
0	323	6.26	2.76	1.000	4.19	0.10	0.508
10	323	13.59	0.09	0.990	6.59	0.11	0.902
20	323	19.44	0.67	1.000	10.75	0.11	0.692
100	323	66.09	0.21	0.999	26.35	0.14	0.846

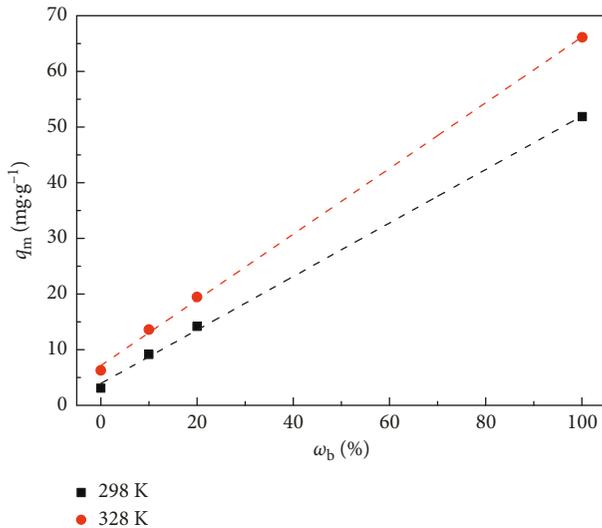


FIGURE 10: Comparison between the predicted values and experimental results of maximum Pb(II) adsorption by laterite-bentonite mixture.

with the pseudo-second-order kinetics equation among pseudo-first-order kinetics, second-order kinetics, and intraparticle diffusion kinetics equation. The Pb(II) adsorption rate of pure bentonite is about 8 times than laterite because of the much higher adsorption capacity of bentonite than laterite.

- (2) When increasing the  $s/w$ , the adsorption rate of Pb(II) ions will increase apparently because of the more adsorption sites in the  $\text{Pb}(\text{NO}_3)_2$  solution. However, the equilibrium capacity of laterite-bentonite mixture will decrease because of the decreasing concentration gradient between solution and adsorbent surface.
- (3) The uptake of Pb(II) will change significantly with the change of solution pH and  $\text{Na}^+$  concentration in the solution. When pH increases from 2 to 11 and the concentration of NaCl decreases from  $1.0 \text{ mol}\cdot\text{L}^{-1}$  to  $0 \text{ mol}\cdot\text{L}^{-1}$ , the concentration of comparative cation such as  $\text{H}^+$  and  $\text{Na}^+$  will decrease in the solution, leading to the better adsorption of Pb(II) by soil particles. This indicates that the main adsorption mechanism in this process is the cation exchange and electrostatic adsorption.
- (4) The adsorption rate of Pb(II) in higher temperature (323 K) is obviously greater than the value in lower temperature because the Pb(II) adsorption by laterite-bentonite mixture is an endothermic reaction. The Langmuir isotherm equation can delineate the adsorption result better than the Freundlich isotherm model, indicating a majority of monolayer adsorbate molecules in the Pb(II) adsorption process.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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