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Adsorption removal of Pb^{2+} and Cd^{2+} on lignocellulose-*g*-acrylic acid/montmorillonite nanocomposite from aqueous solutions

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ABSTRACT

Lignocellulose-*g*-acrylic acid/montmorillonite nanocomposite materials (LNC-*g*-AA/MMT) was used as an adsorbent to remove Pb^{2+}, Cd^{2+} ions from the aqueous solutions. The effects of various experimental conditions including initial metal ions concentration, initial solution pH, contact time, and temperature were investigated. The data showed that 0.1 g of LNC-*g*-AA/MMT, 0.04 mol/L of Pb^{2+}, and 0.05 mol/L of Cd^{2+}, pH 5.5, contact time of 120 and 60 min at 30℃, a maximum adsorption capacity of Pb^{2+} (918.2 mg/g) and Cd^{2+} (482.5 mg/g) were observed. The adsorption kinetics and isotherms have been studied, which implied that all absorption processes were in good agreement with the pseudo-second-order model and the Langmuir isotherm, respectively. The desorption process was also studied. The results indicated that the desorption capacity of LNC-*g*-AA/MMT for Pb^{2+} and Cd^{2+} was 821.9 and 448.2 mg/g with 0.1 g metal ions-loaded adsorption, 0.06 and 0.04 mol/L of HNO_3 concentration, contact time 60 min, contact temperature 30℃, in which the maximum desorption percentage was 90 and 92.9%, respectively.

Keywords: Lignocelluloses; Montmorillonite; Nanocomposite; Adsorption; Pb^{2+}; Cd^{2+}

1. Introduction

With the development of modern industry, environmental pollution is getting worse, especially water pollution. Heavy metal pollution is intensified along with large-scale industrialized production. As, the most used heavy metals in various industries, lead and cadmium, can be accumulated in living tissues and transferred throughout the food chain [1], causing serious harm to the human and animals.

Many treatment technologies have been developed to remove metal ions from wastewater. These methods, include electro deposition [2], ion exchange [3], membrane separation [4], chemical precipitation as metal hydroxide [5], reverse osmosis [6], flocculation [7], and adsorption [8], have been applied. Adsorption has become an economical and effective method to remove metal ions from wastewater. There are many different types of adsorbents, such as cellulose [9], clay minerals [10], and activated carbon [11]. However, they are of high price and hard to recycle or the adsorption capacity is too low.

In recent years, natural polysaccharide/clay nanocomposite has aroused people's wide concern. It is because they have the incomparable advantages of renewable, biodegradable, and nontoxic than other

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synthetic polymers. Lignocellulose (LNC) is a kind of polymer which is nontoxic, biocompatible, biodegradable, and environmental friendly. However, the adsorption capacity of natural cellulose is relatively low and low selectivity for the adsorbate. So, diverse functionalized cellulose has been used to remove the heavy metal ions [12], and dyes [13] from wastewater because of its low cost, high surface area, and high cation exchange capacity. Montmorillonite (MMT) has been used for the removal of organic and inorganic [14, 15] materials. However, MMT has the small granular layer spacing and monomer with poor compatibility [16], which leads to the low adsorption capacity. Therefore, the development of an adsorbent, efficient, inexpensive, and environmentally friendly, is very important. With the continuous development of material science, the superior performance of nanocomposite materials has been growingly accepted. For example, mechanisms of lead adsorption on chitosan/PVA hydrogel beads were studied by Jin Li and Renbi Bai [17]. Qunwei Tang et al. had prepared the polyacrylate/polyethylene glycol interpenetrating network hydrogel, and studied the performance of adsorption for heavy metal ion. The result showed that the greatest adsorption capacity of Cd^{2+} was 33.41 mg/g in the optimal preparation condition [18]. Junpeng Zhang and Aiqin Wang [19] prepared the chitosan-*g*-poly (acrylic acid)/attapulgite/sodium humate composite hydrogels, used to adsorb Pb^{2+}. Results displayed that the maximum adsorption capacity of Pb^{2+} was about 800 mg/g when used 0.1 g of CTS-*g*-PAA/APT/SH, 4000 mg/L of Pb^{2+} concentration at initial pH 5.5. Moreover, 0.05 mol of HCl is the best choice for desorption of Pb^{2+} and the desorption percentage was 77.47%. Rui Han [20] studied the adsorption property of Cd^{2+} by carboxymethyl chitosan and two types of carboxymethyl chitosan/modified pineapple peel fiber (CMC/MPPF) compounds. The results showed that the optimum pH values of carboxymethyl chitosan and two types of CMC/MPPF compounds for Cd^{2+} removal exhibited at 7, 7, and 5.5, respectively, and the maximum adsorption capacity is 93.80, 95.69, and 92.73 mg/g, respectively.

So far, as far as we know, there is no literature focusing on the adsorption removal of metal ions on LNC-*g*-AA/MMT nanocomposite. Therefore, in our study we prepared the LNC-*g*-AA/MMT by *in situ* intercalative polymerization, that is, the graft copolymerization of acrylic acid （AA） onto LNC chitin intercalated into MMT interlayer, and the adsorption behaviors of Pb^{2+} and Cd^{2+} on LNC-*g*-AA/MMT nanocomposite were researched.

2. Experimental

2.1. Materials

LNC was purchased from BeiJing HuaDuo Biological Technology Co., China. MMT was supplied by ChiFeng of Inner Mongolia Mineral Co., China. Lead nitrate ($Pb(NO_3)_2$, analytical grade) was purchased from TianJin FengChuan Chemical Reagent Technology Co., China. Cadmium nitrate ($Cd(NO_3)_2$, analytical grade) was purchased from TianJin GuangFu JingXi chemical research institute. Other agents used were of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of LNC-g-AA/MMT nanocomposite

A 7.0 g of AA was adjusted to 50% of neutralization degree with 20% NaOH mixed with distilled water, in which 0.024 g of ammonium peroxydisulfate (APS) and 0.006 g of N,N′-methylenebisacrylamide (MBA) were dissolved and 1.6 g MMT was added into a 50 mL of beaker. A 1.0 g of LNC, 0.2 g of dispersant, and 20 mL of distilled water were added to a reactor, and then was stirred for 15 min under nitrogen. Then, the mixture, kept in the beaker, was added to the reactor and stirred continuously for 3 h at 70℃. The product was dried under vacuum oven (DZF-6210). All samples after adsorption were grounded and sieved to 200 mesh sizes.

2.3. Adsorption experiments

All batch adsorption experiments were performed on a thermostated shaker (SHA-C) with a shaking of 120 rpm. A stock solution of different concentrations of the Pb^{2+} and Cd^{2+} was prepared separately by dissolving $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in distilled water. The effect of the initial metal ions concentrations on Pb^{2+} and Cd^{2+} removal was carried out by agitating 50 mL metal ions solutions of different concentrations at pH 5.5 by adding 0.1 g adsorbent at 30℃ for 120 min and 60 min, respectively. The influence of pH on Pb^{2+} (0.04 mol/L) and Cd^{2+} (0.05 mol/L) removal was studied by adjusting metal ions solutions to different pH values (3.5–6.5 and 3.5–6) with amount of CH_3COOH–CH_3COONa and $C_6H_{12}N_4$–HCl solution using a pH meter (PB-10) with 0.1 g adsorbent at 30℃ for 120 and 60 min, respectively. The effect of contact time on metal ions removal was studied in the 50 mL metal ions solutions (0.04 mol/L, pH 5.5 and 0.05 mol/L, pH 5.5) by adding 0.1 g adsorbent at 30℃ for predetermined intervals of time. The effect of temperature on metal ions removal was carried out in 50 mL metal ions solutions (0.04 mol/L, pH 5.5, 120 min and 0.05 mol/L, pH 5.5, 60 min) by adding 0.1 g adsorbent.

The samples were withdrawn when reaching adsorption equilibrium, and then the mixture was rapidly centrifuged by centrifugation (H-2050R) at 6,000 rpm for 5 min. The residual metal ions concentration was measured using a microburet by complexometric titration with EDTA [21]. The adsorption capacity of metal ions was calculated through the following Eq. (1):

$$Q_e = (n_o - n_e) \times M/m \tag{1}$$

where Q_e is the amount of adsorption metal ions (mg/g) at equilibrium, n_0 is the initial moles of metal ions in solution (mol/L), n_e is the equilibrium concentration of metal ions in solution (mol/L), M is the molecular weight of metal ions (g/mol), m is the mass of adsorbent used (g).

2.4. Desorption experiments

For batch desorption study, the adsorbent utilized for the adsorption of Pb^{2+} (0.04 mol/L) and Cd^{2+} (0.05 mol/L) were separated from the metal ions solution by centrifugation. The experiments were performed on a SHA-C with shaking at 120 rpm. A 0.1 g metal ions-loaded adsorbent was used for all desorption experiments. The effect of initial concentrations of HNO_3 was carried out at 30℃ for 60 min. The effect of contact time was studied in 50 mL of HNO_3 solutions (0.06 mol/L for Pb^{2+}, 0.04 mol/L for Cd^{2+}) at 30℃ for predetermined intervals of time. The effect of temperature was carried out in 50 mL of HNO_3 solutions (0.06 mol/L for Pb^{2+}, 0.04 mol/L for Cd^{2+}) for 60 min.

The samples were withdrawn when reaching desorption equilibrium, and then the mixture was rapidly centrifuged by centrifugation (H-2050R) at 6,000 rpm for 5 min. The absorbencies of solution were measured using a microburet by complexometric titration with EDTA. The desorption capacity of metal ions was calculated through the following Eq. (2):

$$Q = n \times M/m \tag{2}$$

where Q is the amount of desorption metal ions (mg/g) at equilibrium, n is the equilibrium concentration of metal ions in solution (mol/L), M is the molecular weight of metal ions (g/mol), m is the mass of adsorbent used (g).

3. Results and discussion

3.1. Adsorption isotherm

The influence of initial concentration on adsorption capacity of metal ions for the composite is shown in Fig. 1. It can be seen that the adsorption capacity of the composite increased from 668.2 to 918.2 mg/g for Pb^{2+} and 382.5 to 482.7 mg/g for Cd^{2+} as the initial metal ions concentration increases from 0.01 to 0.04 mol/L for Pb^{2+} and 0.01 to 0.05 mol/L for Cd^{2+}, and then tended to balance or decrease slightly with further increase in initial metal ions concentration. This result may be attributed to the fact that with the increase in the initial concentration of the metal ions, the mass transfer driving force of ions has increased, thereby reducing the resistance of adsorption, meanwhile increasing the contact area between adsorbent and adsorbate, leading to increase in adsorption capacity for metal ions [22]. When the metal ions concentration is higher than a certain value, the concentration of cations increases in the solution, which increases the competition between cations for adsorption sites, so the adsorption capacity decrease [23].

Adsorption isotherms are important for the description how molecules of adsorption interact with adsorbent surface. Two well-known models, the Langmuir [24] and Freundlich [25] isotherms were selected to explicate metal ions-adsorbent interaction in this study. The Langmuir and the Freundlich models, which are given as Eqs. (3) and (4), respectively:

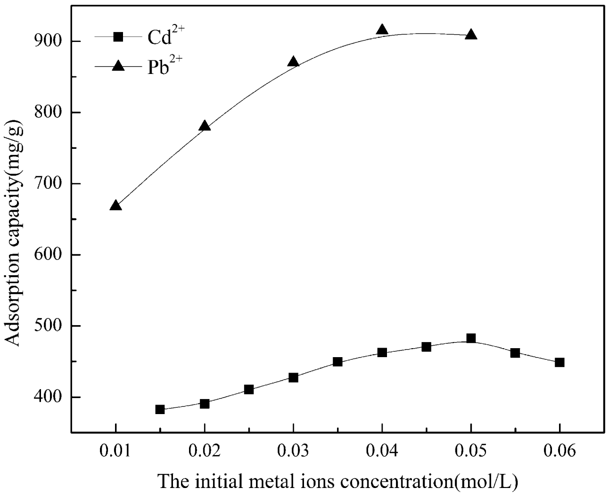

Fig. 1. Effect of the metal ions concentration on adsorption capacity of LNC-*g*-AA/MMT for Pb^{2+}, Cd^{2+}. Adsorption experiments-sample, 0.1 g/50 mL; pH 5.5; temperature, 30℃; equilibrium time, 120 and 60 min.

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad (3)$$

$$q_e = k_f c_e^{1/n} \quad (4)$$

where q_m (mg/g) and b (L/mg) are Langmuir isotherm coefficients. The value of q_m represents the maximum adsorption capacity. k_f (mg/g) and n are Freundlich constants. Two adsorption isotherms were constructed by plotting the C_e/q vs. C_e, log q vs. log C_e, respectively.

The Langmuir plot and Freundlich plot of LNC-*g*-AA/MMT adsorption metal ions are shown in Figs. 2 and 3, respectively. The parameters of Langmuir and Freundlich models are shown in Table 1. It can be seen that the correlation coefficients (R^2) of Langmuir and Freundlich models are 0.9982, 0.9654 for Pb^{2+} and 0.9904, 0.5926 for Cd^{2+}, respectively. In addition, the q_m value for adsorption of Pb^{2+} and Cd^{2+} by LNC-*g*-AA/MMT nanocomposite were 1,000 and 500 mg/g, which are the same as the experiment data 918.2 and 482.5 mg/g for LNC-*g*-AA/MMT on Pb^{2+} and Cd^{2+}, respectively. Hence, the adsorption of metal ions on LNC-*g*-AA/MMT is in good agreement with Langmuir isotherm. This means the surface of LNC-*g*-AA/MMT was covered by the monolayer of metal ions.

3.2. Effect of pH value on adsorption

Fig. 4 shows the relationship between pH value of the original solution and adsorption capacity of LNC-*g*-AA/MMT. As seen from Fig. 4, it is observed that the adsorption capacity of metal ions increase with increasing the pH value of the solution and then decrease with further increase in pH value. In addition, the better adsorption of LNC-*g*-AA/MMT for Pb^{2+} and Cd^{2+} appear at the pH of 5.5. This result may be attributed to the following reasons. At lower pH, there is a large number of H^+ ions in the solution. They compete for the adsorption sites with metal ions [26], which results in a low adsorption capacity. At higher pH, the competing phenomena becomes weaker, and the –COOH groups dissociate to form –COO$^-$, increasing the number of fixed ionized groups of polymer networks, leading to a high adsorption capacity. The pH value over 5.5, the adsorption capacity decreases lightly due to the precipitate of metal ions [27]. In addition, high pH values affect the activity of adsorption sites on the surface of the adsorbent. Throughout this study, pH value was controlled to 5.5.

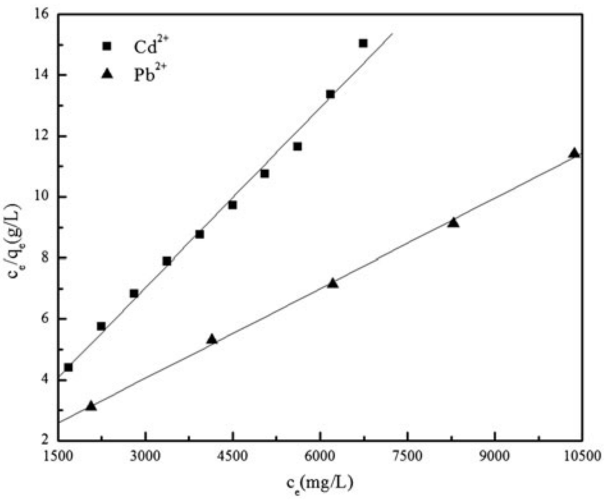

Fig. 2. Langmuir plot.

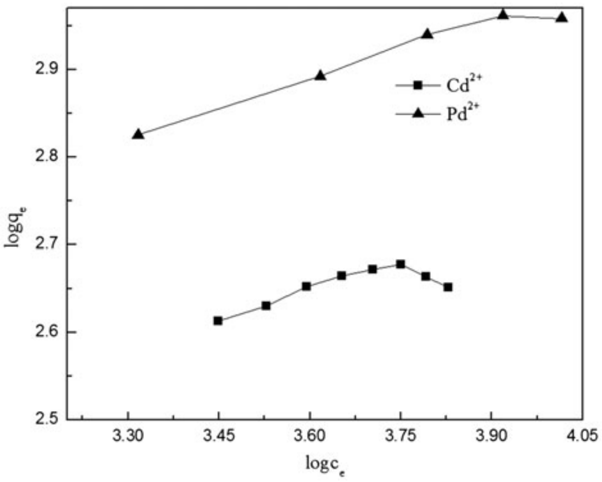

Fig. 3. Freundlich plot.

3.3. Adsorption kinetics

Contact time is an important parameter of adsorption, which can reflect the adsorption kinetics of an adsorbent. Fig. 5 shows the effect of contact time on the adsorption capacity of metal ions by the composite. It can be seen that the adsorption capacity of the composite increased rapidly in the initial stages of contact time and gradually increased with prolonging the contact time until equilibrium. It is clear that the adsorption equilibrium of the composite was reached at 120 min for Pb^{2+} and 60 min for Cd^{2+}. So, adsorption time of 120 min for Pb^{2+} and 60 min for Cd^{2+} was chosen to make sure that the adsorption equilibrium was reached.

Table 1
The parameters of Langmuir and Freundlich models

	Langmuir			Freundlich		
Metal ions	q_m(mg/g)	b	R^2	n	K_F	R^2
Pb^{2+}	1,000	0.0009	0.9982	4.8757	141.2	0.9654
Cd^{2+}	500	0.0018	0.9904	7.8678	154.2	0.5926

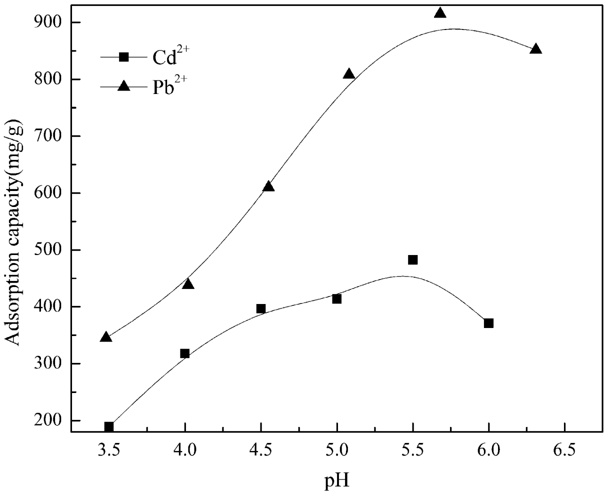

Fig. 4. Effect of the pH values on adsorption capacity of LNC-*g*-AA/MMT for Pb^{2+}, Cd^{2+}. Adsorption experiments-sample, the metal ions concentration: 0.04 mol/L for Pb^{2+} and 0.05 mol/L for Cd^{2+}; 0.1 g/50 mL; pH range: 3.5–6.5; temperature: 30°C; equilibrium time: 120 min for Pb^{2+} and 60 min for Cd^{2+}.

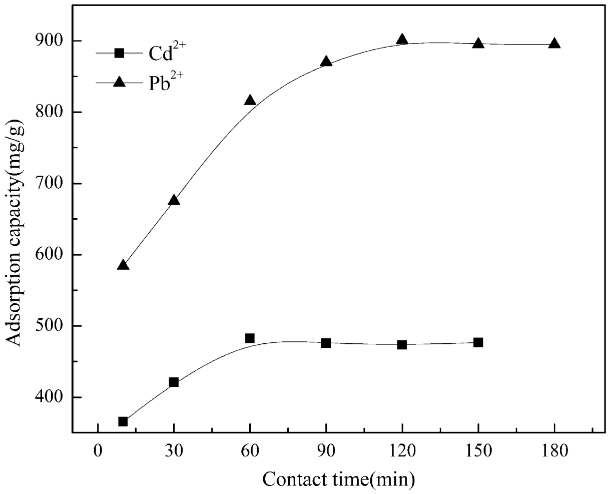

Fig. 5. Effect of the contact time on adsorption capacity of LNC-*g*-AA/MMT for Pb^{2+}, Cd^{2+}. Adsorption experiments-sample, the metal ions concentration: 0.04 mol/L for Pb^{2+} and 0.05 mol/L for Cd^{2+}; 0.1 g/50 mL; pH 5.5; temperature: 30°C.

Studying the kinetics of the adsorption process is mainly used to describe the adsorption rate of adsorbent. The dynamics model is used to fit the data, and further to explore the mechanism of adsorption. So, pseudo-first-order and pseudo-second-order models were used to investigate the adsorption processes of metal ions on LNC-*g*-AA/MMT.

The pseudo-first-order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites.

The pseudo-first-order formula [28] is given as follows, Eq. (5):

$$\frac{dq_e}{dt} = k_1(q_e - q_t) \tag{5}$$

After integration with the initial condition $q_t = 0$ at $t = 0$, Eq. (6) can be obtained:

$$\log\,(q_e - q_t) = \log\,q_e - \frac{k_1 t}{2.303} \tag{6}$$

The pseudo-second-order model is based on adsorption equilibrium and it assumes that the rate-controlling step is chemisorptions and adsorption follows a second-order mechanism, whereby the rate of sorption is proportional to the square of the number of unoccupied sites.

The pseudo-second-order model [29] can be defined as Eq. (7):

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

When the initial condition is $q_t = 0$ at $t = 0$, Eq. (8) can be given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e and q_t are the amounts of adsorption metal ions (mg/g) at equilibrium and at time t (min), k_1

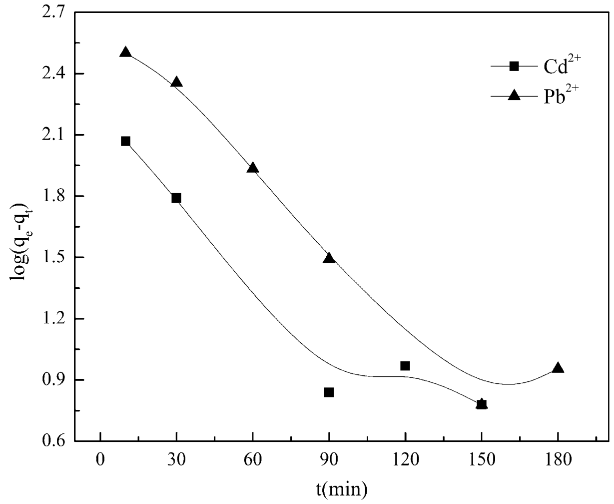

Fig. 6. Pseudo-first-order model.

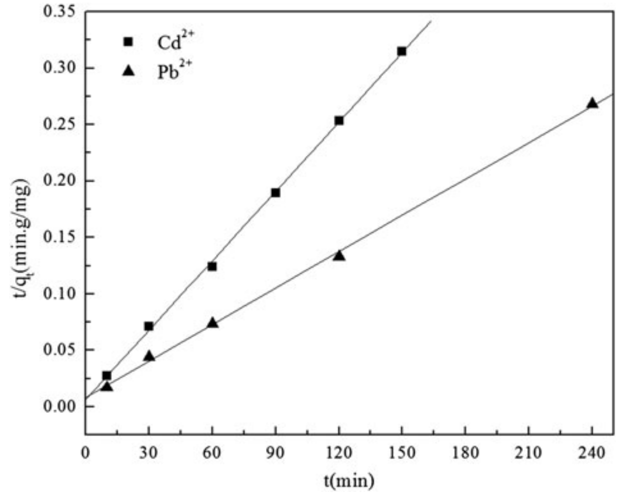

Fig. 7. Pseudo-second-order model.

(min^{-1}), and k_2 ($g/mg\ min^1$) are the adsorption rate constant of pseudo-first-order, pseudo-second-order adsorption rate, respectively. The linear plots of log (q_e–q_t) vs. t, and (t/qt) vs. t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

The pseudo-first-order model and pseudo-second-order model of LNC-*g*-AA/MMT adsorption of metal ions are shown in Figs. 6 and 7, respectively. The parameters of pseudo-first-order and pseudo-second-order kinetic models are shown in Table 2. It can be seen that the correlation coefficient (R^2) of the pseudo-first-order model is 0.9415 for Pb^{2+} and 0.8827 for Cd^{2+}. For the pseudo-second-order model, the correlation coefficient (R^2) is 0.9990 for Pb^{2+} and 0.9993 for Cd^{2+}. In addition, the calculated q_e values of the pseudo-first-order and the pseudo-second-order models for the adsorption of metal ions by LNC-*g*-AA/MMT were 368.7 and 909.1 mg/g for Pb^{2+}, 111.4 and 487.8 mg/g for Cd^{2+}, respectively. Obviously, the calculated q_e value agree with the experimental data (918.2, 482.5 mg/g) in the case of the pseudo-second-order model. Therefore, the adsorption of metal ions on LNC-*g*-AA/MMT followed the pseudo-second-order rather than the pseudo-first-order model.

3.4. Effect of temperature on adsorption

The relationship between the temperature and the adsorption capacity of metal ions on the composite is shown in Fig. 8. It is found that the adsorption capacity of the composite increased with increasing the temperature, and then decreased with further increase in temperature. Because increasing temperature may produce a swelling effect [30] on LNC-*g*-AA/MMT, making the surface porosity to increase and then helping the metal ions to diffuse to the composite, which lead to the increase in adsorption capacity. The metal ions have higher velocity and activation energy with increasing temperature, it is easier for ions to escape from the restrictions of adsorption sites [18], resulting in a decrease in adsorption capacity. Besides, the adsorption is an exothermic process, the adsorption capacity decrease when the temperature increases [31].

3.5. Effect of the initial HNO_3 concentration on desorption

Fig. 9 shows the effect of HNO_3 concentration on desorption. It can be seen that desorption capacity increases with increasing the concentration of HNO_3 and then decreases slightly with further increase in the concentration of HNO_3. In addition, the better

Table 2
The parameters of pseudo-first-order and pseudo-second-order kinetic models parameter

	Pseudo-first-order model			Pseudo-second-order model		
Metal ions	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
Pb^{2+}	0.0237	368.7	0.9415	0.0001	909.1	0.9990
Cd^{2+}	0.0219	111.4	0.8827	0.0007	487.8	0.9993

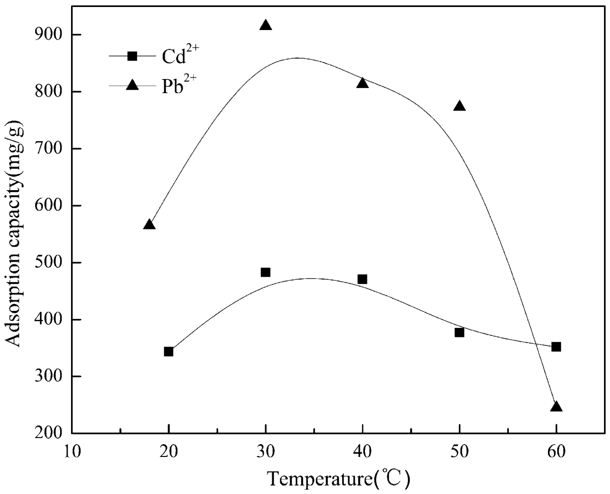

Fig. 8. Effect of the contact temperature on adsorption capacity of LNC-*g*-AA/MMT for Pb^{2+}, Cd^{2+}. Adsorption experiments-sample, the metal ions concentration: 0.04 mol/L for Pb^{2+} and 0.05 mol/L for Cd^{2+}; 0.1 g/50 mL; pH 5.5; contact time: 120 min for Pb^{2+} and 60 min for Cd^{2+}.

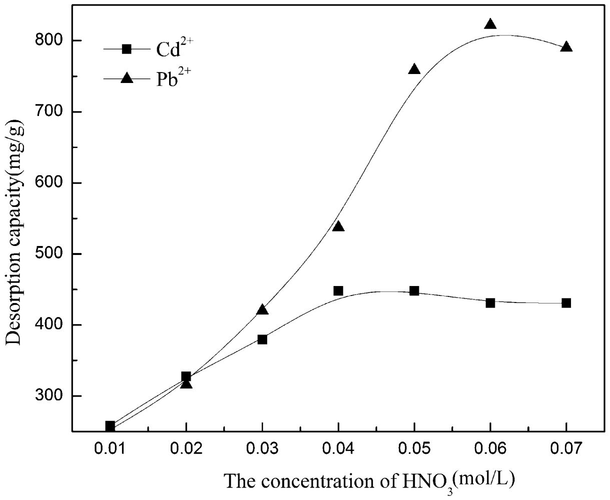

Fig. 9. Effect of the concentration of HNO_3 on desorption capacity of metal ions from metal ions-loaded LNC-*g*-AA/MMT. Desorption experiments-metal ions concentrations: 918.2 mg/g of Pb^{2+} and 482.5 mg/g of Cd^{2+} for LNC-*g*-AA/MMT; sample dose: 0.1 g/50 mL; contact time: 60 min; temperature: 30℃.

desorption of LNC-*g*-AA/MMT for Pb^{2+} and Cd^{2+} appear at the concentration of HNO_3 of 0.06 and 0.04 mol/L, respectively. This result may be due to the following reasons. HNO_3 solution of higher concentration solution contain much of H^+, which can compete for adsorption sites with metal ions, and then metal ions lose the opportunity to combine with them, resulting in desorbing of metal ions into the solution. So, desorption capacity increases. In addition, this process occurred due to adsorption during desorption, while adsorption is difficult to re-desorb, so desorption decreases.

3.6. Effect of contact time on desorption

Fig. 10 show the effect of contact time on desorption. It can be seen that desorption capacity increases sharply with increasing contact time and then decrease slightly or tend to equilibrium with further increase in contact time. It is clear that desorption equilibrium of the composite was reached at 60 min. This may be attributed to the fact that there is a large concentration difference between aqueous and solid phase in the beginning of desorption, leading to a larger release. However, the concentration of metal ions increases in solution with further increase in contact time, resulting in a phenomenon of adsorption [32]. So, desorption increases and then tend to equilibrium or decrease slightly.

3.7. Effect of contact temperature on desorption

Fig. 11 shows the effect of contact temperature on desorption. It can be seen that desorption capacity increases sharply with increasing contact temperature

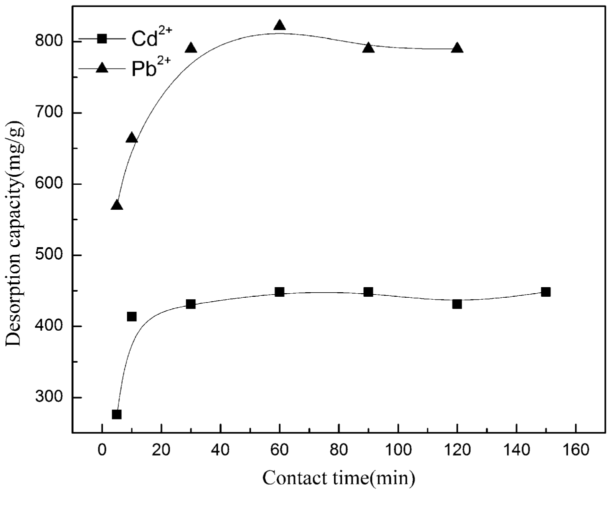

Fig. 10. Effect of contact time on desorption capacity of metal ions from metal ions-loaded LNC-*g*-AA/MMT. Desorption experiments-metal ions concentrations: 918.2 mg/g of Pb^{2+} and 482.5 mg/g of Cd^{2+} for LNC-g-AA/MMT; sample dose: 0.1 g/50 mL; concentration of HNO_3: 0.06 mol/L for Pb^{2+} and 0.04 mol/L for Cd^{2+}; temperature: 30℃.

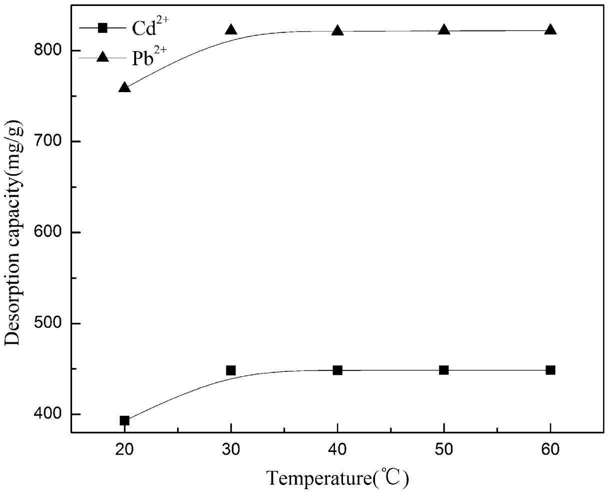

Fig. 11. Effect of contact temperature on desorption capacity of metal ions from metal ions-loaded LNC-*g*-AA/MMT. Desorption experiments-metal ions concentrations: 918.2 mg/g of Pb^{2+} and 482.5 mg/g of Cd^{2+} for LNC-*g*-AA/MMT; sample dose: 0.1 g/50 mL; concentration of HNO_3: 0.06 mol/L for Pb^{2+} and 0.04 mol/L for Cd^{2+}; contact time: 60 min.

then increases slightly and at last tend to equilibrium with further increase in contact temperature. It is clear that desorption capacity of the composite was very small after 30℃. So, we choose 30℃ as the desorption temperature from an economic point of view. This may be attributed to the fact that as the temperature rises, the thermal motion of the metal ions increases, providing energy for the metal ions to get rid of the adsorbent [33] to provide.

4. Conclusions

Adsorption test of metal ions on the LNC-*g*-AA/MMT nanocomposite were carried out and the results showed that Pb^{2+}, Cd^{2+} adsorption process are dependent on initial metal ions concentration, initial solution pH, contact time, and temperature. The maximum adsorption capacity was 918.2 and 482.5 mg/g on the LNC-*g*-AA/MMT for Pb^{2+} and Cd^{2+}, respectively. The absorption processes are in good agreement with the pseudo-second-order model and the Langmuir isotherm, respectively. In desorption studies, the results indicated that LNC-*g*-AA/MMT have high desorption capacity of Pb^{2+} (821.9 mg/g) and Cd^{2+} (448.2 mg/g), the maximum desorption percentage was 90 and 92.9%, respectively. This indicates that LNC-*g*-AA/MMT provided the potential for regeneration and reuse after metal ions adsorption. Therefore, LNC-*g*-AA/MMT can be used as an effective adsorbent for the removal of Pb^{2+}, Cd^{2+} from wastewater.

Acknowledgments

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