



Equilibrium and Kinetic Studies on Removal of Cd²⁺ Ion in Aqueous Solution by the Multiple Modified Diatomite

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ABSTRACT

The problem of metal pollution was regarded by many researchers for a long time. The wastewater containing metal ions must be treated. A composite modification technology of acid activating, sodium hydroxide and baking was applied to improve the diatomite adsorption ability, and a modified diatomite was prepared. The adsorption experiment of the metal wastewater by the modified diatomite was carried out in detail. The modified diatomite owned the high adsorption capacity of the Cd²⁺ ion. The operating parameters, such as contact time, concentration of Cd²⁺ ion and reaction temperature, had an important effect on the removal of the Cd²⁺ ion in aqueous solution. The adsorption of Cd²⁺ ions onto the modified diatomite was 9.65 mg/g. The adsorption process fits well with the Langmuir isotherm model and the pseudo-second-order kinetics model and it implied that the adsorption was mainly a physical process. The adsorption process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

INTRODUCTION

The problem of the metal pollution was regarded by many researchers for a long time. A large quantity of wastewater containing of metal ions flow into rivers without treatment (Ye et al. 2015), which leads to serious problems of the environmental pollution. Because of the characteristics of the metal wastewater like, containing high poisonous substances, long time of existence, difficult biodegradation, easy biological concentration, even a low concentration of metal wastewater can lead to the damage of ecology, environment and human health (Fernando et al. 2011, Dragana et al. 2013). Hence, the metal wastewater must be treated carefully.

The treatment methods of the metal wastewater consist of chemical sediment method, ion exchange method, electro-coagulation method, membrane separation method, plant uptake method, microorganism absorption method, and so on (Mohammad et al. 2004, Guo et al. 2011, Tica et al. 2011, Muhammad et al. 2012, Ma et al. 2016). The traditional physical and chemical methods are often time consuming, high cost, and easy to lead to pollution again. So, these methods could not be applied in practice. The bio-restore method is not a very mature method and restricted by the reaction conditions. Hence, it is also not applied in practice widely (Oladoja & Helmreich 2014, Shafeeyan et al. 2015). Compared with the traditional physical-chemical

method and bio-restore method, the adsorption method is low cost, less time consuming, difficult to lead to pollution and is simple in operation (Sabriye et al. 2012). So, the adsorption method is applied in the treatment of metal ions wastewater widely.

The selection and preparation of adsorbing material is very important in the adsorption methods. According to some literature, the diatomite is a kind of silicolite and has a big specific surface area, many micropores and surface active groups and negative charges. The diatomite has the ability of adsorption and is applied in the treatment of metal wastewater and dye wastewater (Tan et al. 2009). However, the natural diatomite contains much impurity and irregular structure, and this character restricts its application in the treatment of adsorption. In order to improve the adsorption ability of diatomite, many modification methods are applied to improve the pore structure (Ward et al. 2005). At present, the diatomite is often modified by a single method. This modification method is not able to improve the adsorption ability remarkably. Hence, it is very important that a compound modified method is applied to improve the adsorption ability of diatomite (Kaušpėdienė et al. 2010).

In this study, a composite modification technology of acid activating, sodium hydroxide and baking was applied to improve the diatomite adsorption ability and a modified diatomite was prepared. The adsorption experiment of the

metal wastewater by the modified diatomite was carried out in detail.

MATERIALS AND METHODS

Materials

Diatomite is obtained from the agent plant in Xunnan province. The density of diatomite is 0.5 g/cm^3 and the surface area is $22.5 \text{ cm}^2/\text{g}$. The chemical composition of the diatomite is SiO_2 , a little of Al_2O_3 , Fe_2O_3 , CaO , MgO and organic matter. The sample of diatomite was sieved and washed by the deionized water in order to remove the impurity. Then it was dried at 378K , cooled, ground and sieved. The obtained sample was kept for the adsorption experiments.

The metal wastewater was prepared by Cd^{2+} ions. The 2.2818 g of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ was added into the 1000 mL of the measuring flask containing the deionized water. The solid was dissolved completely by the deionized water and the solution was fixed to the capacity of 1000 mL and concentration of 1000 mg/L .

Methods

Preparation of the modified diatomite: The modified diatomite was prepared by the acid active, the sodium active and the baking technology. The 100 g of the diatomite sample was added into the 250 mL of flask containing 100 mL 10% sulphuric acid. The solution was mixed and heated for 120 min , and then cooled and centrifuged. The liquid was decanted. It was then washed many times in the $\text{pH } 6.0$

solution by the deionized water. The sample was then dried, ground and sieved and the acid activated diatomite was obtained. The 100 mL of the acid activated diatomite (1+1) was added to the 250 mL flask containing 6% NaCl , and shaken for 30 min and centrifuged. The liquid was decanted. The sample was washed three times by the deionized water, and then dried, ground and sieved. The sodium activated diatomite was obtained. The sample was baked for 120 min at 423 K . The sample was then cooled, ground and sieved. Multiple modified diatomites were prepared for the adsorption experiments.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing the modified diatomite and 100 mL of Cd^{2+} ion solution with various initial concentrations. The initial pH was adjusted with 1 mol/L HCl or 1 mol/L NaOH . The flasks were placed in a shaker at a constant temperature and 200 rpm . The samples were filtered and analysed.

Analytical methods: The concentration of Cd^{2+} ion was analysed by atomic absorption spectrophotometry (AAS). The amount of adsorbed Cd^{2+} ion q_t (mg/g) at different times was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad \dots(1)$$

Where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cd^{2+} ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All the experiments were repeated in duplicate and the data of results were the mean

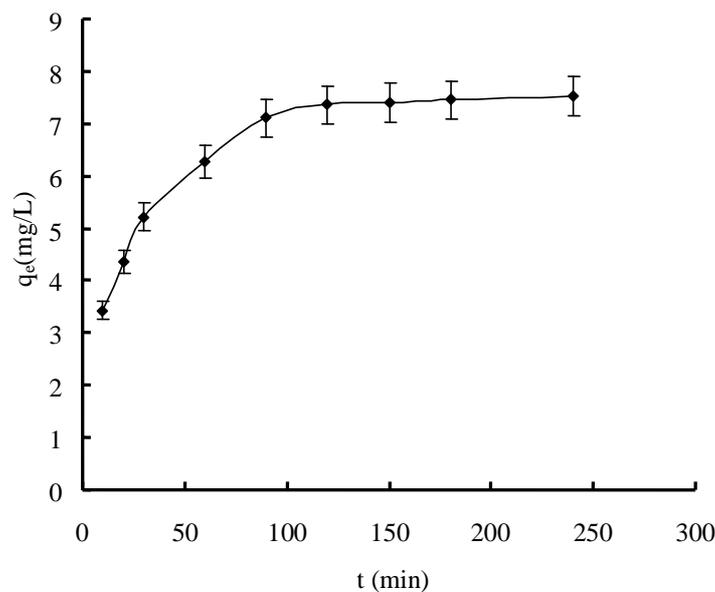


Fig. 1: The effect of contact time on the adsorption of Cd^{2+} ion in aqueous solution by the modified diatomite.

and the standard deviation (SD). The value of SD was calculated by the Excel software. All error estimates given in the text and error bars in figures are the standard deviation of means (mean±SD). All statistical significances were noted at $\alpha=0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

The effect of contact time: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5g of the modified diatomite and 100 mL of Cd²⁺ ion solution with initial concentration of 200 mg/L. The initial pH was adjusted to 5.0 with 1 mol/L HCl or 1 mol/L NaOH. The flasks were placed in a shaker at a constant temperature (318 K) and 200 rpm. The samples were filtered and analysed.

The influence of contact time on the removal of Cd²⁺ ion in aqueous solution by the modified diatomite is shown in Fig. 1.

It can be concluded that the adsorption process is very rapid at first 50 minutes. The adsorption rate of Cd²⁺ ion in aqueous solution increases sharply at a short contact time and slowed gradually as equilibrium was approached. It may be due to the availability of the initial large number of vacant surface active sites for adsorption that the adsorption rate was very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to repulsive forces between Cd²⁺ ion adsorbed on solid surface and Cd²⁺ ion from solution.

The effect of concentration of Cd²⁺ ions in aqueous solution: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5g of the modified diatomite and 100 mL of Cd²⁺ ion solutions with various initial concentrations (50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L). The initial pH was adjusted to 5.0. The flasks were placed in a shaker at a constant temperature (303 K) and 200 rpm. The samples were filtered and analysed.

The experiment results obtained are shown in Fig. 2. From Fig. 2, it can be seen that the concentration of Cd²⁺ ion in aqueous solution had an important role on the adsorption capacity of Cd²⁺ ion by the modified diatomite. When the concentration of Cd²⁺ ion in aqueous solution increased, the adsorption capacity of Cd²⁺ ion in aqueous solution also increased. This is due to the fact that with increased Cd²⁺ ion concentration, the driving force for mass transfer also increases. At low concentrations there will be unoccupied active sites on the adsorbent surface.

The effect of reaction temperature: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5g of the modified diatomite and 100 mL of Cd²⁺

ion solutions with initial concentration of 200 mg/L. The initial pH was adjusted to 5.0. The flasks were placed in a shaker at a various temperatures (303 K, 318 K and 333 K) and 200 rpm. The samples were filtered and analysed.

The effect of temperature on the removal of Cd²⁺ ion in aqueous solution by the modified diatomite is shown in Fig. 3. It was found that the adsorption rate of Cd²⁺ ion in aqueous solution decreased with increasing solution temperature from 303K to 333K. It indicated that higher temperature was not suitable for adsorption process. High temperature might lead to the breaking of existing intermolecular bonding between Cd²⁺ ion and the modified diatomite, which is an important contribution to the adsorption process.

Adsorption isotherm: For solid-liquid system, adsorption isotherm is important in the description of adsorption behaviour. To research on the mechanistic parameters associated with Cd²⁺ ion adsorption, the results obtained by the adsorption experiments were analysed by Freundlich model (Freundlich 1906) and Langmuir (Langmuir 1918) model.

The Langmuir isotherm equation is represented by the following Eq. (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \dots(2)$$

Where C_e is the equilibrium concentration of Cd²⁺ ions (mg/L), q_e is the amount of Cd²⁺ ion adsorbed (mg/g), q_m is the maximum adsorption capacity of Cd²⁺ ion (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

The Freundlich isotherm equation is described by the following Eq. (3):

$$q_e = K_F C_e^{\frac{1}{n}} \quad \dots(3)$$

Where K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity respectively.

The adsorption data were calculated by the Langmuir adsorption isotherm and Freundlich adsorption isotherm. The results are given in Table 1.

As from Table 1, the value of R² ranges from 0.9932 to 0.9976 at different temperatures, according to the Langmuir isotherm model. The value of R² ranges from 0.8849 to 0.9416 at different temperatures according to the Freundlich isotherm model. The adsorption process of the Cd²⁺ ion in aqueous solution by the modified diatomite fitted well with the Langmuir isotherm model. It also implied that the adsorption process of the Cd²⁺ ion in aqueous solution by the modified diatomite was mainly a physical process.

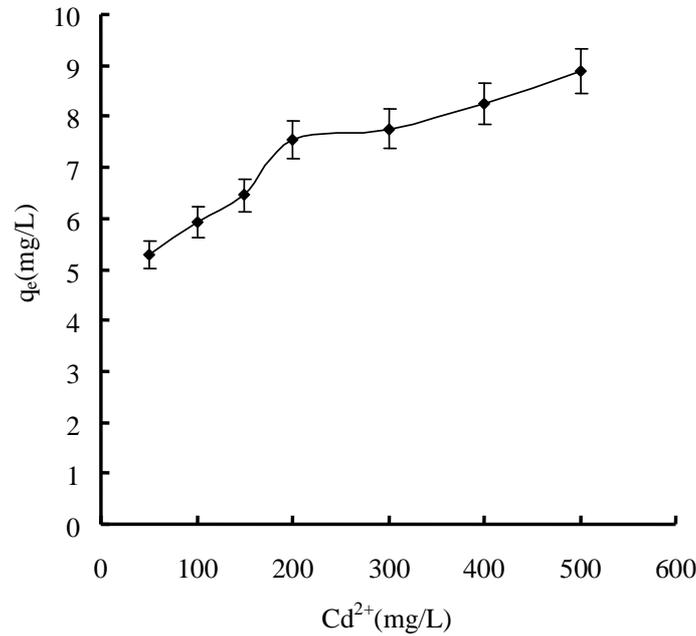


Fig. 2: The effect of concentration of Cd²⁺ ion on its adsorption in aqueous solution by the modified diatomite.

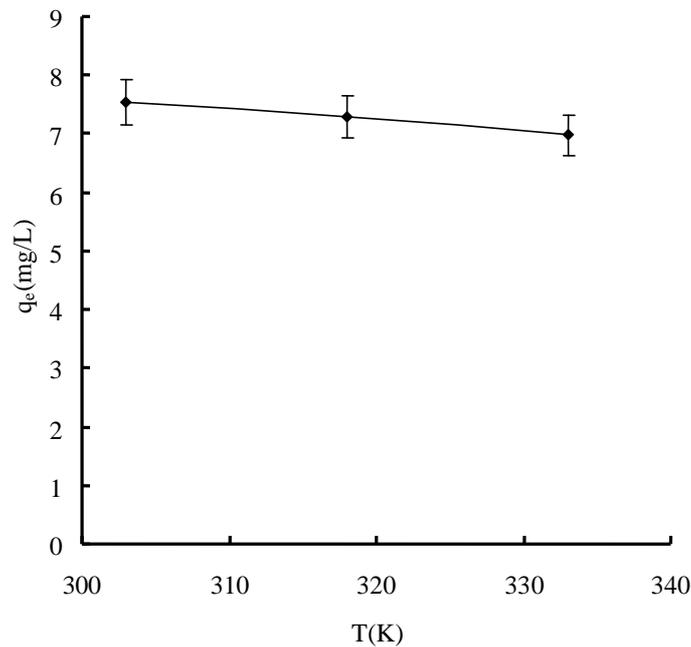


Fig. 3: The effect of reaction temperature on the adsorption of Cd²⁺ ion in aqueous solution by the modified diatomite.

Compared with the reported researches, the adsorption capacity of the modified diatomite was higher. Hence, it can be derived that, a composite modification technology is important to improve the structure of the diatomite and enhance the adsorption capacity of the Cd²⁺ ion in aqueous solution by the diatomite.

Adsorption kinetics: In order to investigate the mechanism of Cd²⁺ ion sorption, two models were used in this study.

The linear pseudo-first-order kinetic model of Lagergren is given as follows (Thinakaran et al. 2008):

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \quad \dots(4)$$

Table 1: Parameters of Langmuir isotherm model and Freundlich isotherm model for the description of Cd²⁺ ion adsorption onto the modified diatomite.

Temperature(K)	Langmuir			Freundlich		
	q _m (mg/g)	K _L	R ²	K _F	n	R ²
303	9.72	0.01	0.9976	0.43	1.73	0.8849
318	9.68	0.02	0.9932	0.82	2.26	0.9356
333	9.45	0.02	0.9938	0.49	2.17	0.9416

Table 2: Parameters of the pseudo-first-order kinetic model and the pseudo-second-order kinetic model for the description of Cd²⁺ ion adsorption onto the modified diatomite.

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
k ₁ (min)	q _e (mg/g)	R ²	k ₂ (mg/g min)	q _e (mg/g)	R ²
0.003	1.32	0.8642	0.018	9.76	0.9983

Where q_e and q_t are the amount of Cd²⁺ ion absorbed onto the adsorbent (mg/g) at equilibrium and at t respectively. k_1 is the rate constant of first-order adsorption (min⁻¹).

The pseudo-second-order kinetic model developed by Ho and McKay (Ho & McKay 1998) is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(5)$$

Where k_2 is the rate constant of second-order adsorption (g.mg⁻¹.min⁻¹).

The adsorption data were calculated by the pseudo-first-order kinetic model and the pseudo-second-order kinetic model. The results are given in Table 2.

From Table 2, it can be seen that the adsorption process fits well with the pseudo-second-order kinetics model according to the value of R². It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent (Vanessa et al. 2014).

CONCLUSIONS

Adsorption studies for the removal of Cd²⁺ ion from aqueous solutions have been carried out using the modified diatomite prepared from the natural diatomite through the composite modification technology of acid activating, sodium hydroxide and baking. The experiment result shows that the modified diatomite from natural diatomite is an effective adsorbent for the removal of Cd²⁺ ion from aqueous solution. The adsorption process fits well with the Langmuir isotherm model and the pseudo-second-order kinetics model. The

adsorption process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

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