



Simultaneous adsorption of lead and cadmium on MnO₂-loaded resin

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Abstract

MnO₂-loaded D301 weak basic anion exchange resin has been used as adsorbent to simultaneously remove lead and cadmium ions from aqueous solution. The effects of adsorbent dosage, solution pH and the coexistent ions on the adsorption were investigated. Experimental results showed that with the adsorbent dosage more than 0.6 g/L, both Pb²⁺ and Cd²⁺ were simultaneously removed at pH range 5–6. Except for HPO₄²⁻, the high concentration coexistent ions such as Na⁺, K⁺, Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻, showed no significant effect on the removal efficiency of both Pb²⁺ and Cd²⁺ under the experimental conditions. The coexistence of Mg²⁺, Ca²⁺ caused the reduction of Cd²⁺ removal, but not for Pb²⁺. The adsorption equilibrium for Pb²⁺ and Cd²⁺ could be excellently described by the Langmuir isotherm model with $R^2 > 0.99$. The maximum adsorption capacity was calculated as 80.64 mg/g for Pb²⁺ and 21.45 mg/g for Cd²⁺. The adsorption processes followed the pseudo first-order kinetics model. MnO₂-loaded D301 resin has been shown to have a potential to be used as an effective adsorbent for simultaneous removal of lead and cadmium ions from aqueous solution.

Key words: MnO₂-loaded resin; adsorption; cadmium; lead; simultaneous removal

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Introduction

There is an increasing public concern regarding the contamination in natural water caused by heavy metals. Heavy metal pollution such as lead, cadmium can be toxic and carcinogenic even at low concentration, and usually pose a serious threat to the environment and public health (Liu et al., 2008). Various treatment techniques and processes, including chemical precipitation (Perret et al., 2000; González-Muñoz et al., 2006), ion exchange (Inglezakis et al., 2002; Mier et al., 2001), filtration (Bouranenea et al., 2008; Ritchie and Bhattacharyya, 2002) have been used to remove the heavy metals from contaminated water. Actually, the concentration of heavy metals is very low in natural water (Vilensky et al., 2002). Thus, these methods are not widely used because of their high cost. Under this condition, adsorption is one of the most popular methods and is currently considered as an effective, efficient, and economic method for water purification (Qu, 2008). A variety of solid adsorbents such as activated carbon (Patnukao et al., 2008; Imamoglu and Tekir, 2008), metal oxides (Hu et al., 2008; Feng et al., 2007), minerals (Chaari et al., 2008; Bhattacharyya and Sen Gupta, 2007), peat (Kalmykova et al., 2008; Sutcu, 2007), chelating resins (Dinu and Dragan, 2008; Lin and Juang, 2007) have been used for the removal of heavy metal ions. In recent years, considerable attention has been paid to the investigation of different types of

low-cost adsorbents especially using metal-oxide modified adsorbents, such as manganese oxide-coated bentonite (Eren et al., 2009), iron oxide-coated sand (Boujelben et al., 2009) and manganese oxide-coated zeolite (Han et al., 2006).

In our previous work (Zhu et al., 2007), D301 resin was functionalized with potassium permanganate (KMnO₄) to develop an adsorbent with a high adsorptive capacity and selectivity for cadmium. The purpose of this study was to use this MnO₂-loaded D301 weak basic anion exchange resin (R-MnO₂) as adsorbent for the simultaneous removal of Pb²⁺ and Cd²⁺ from aqueous solution. The effect of adsorbent dosage, pH and presence of coexistent ions on the adsorption of Pb²⁺ and Cd²⁺ was investigated. The adsorption isotherms and kinetics were also discussed.

1 Materials and methods

1.1 Materials

All chemicals used were analytic grade, commercially available and used without further purification. Solutions of KMnO₄ and Pb(NO₃)₂ were prepared using distilled water, and pH was adjusted by HCl or NaOH. D301 resin was purchased from Shanghai Resin Company, China. Its main physical and chemical properties are listed in Table 1. Before surface modification, the resin was pretreated with 0.05 mol/L sulfuric acid and then with 0.05 mol/L sodium hydroxide. After washing with distilled water for several times, the D301 resin was used for the further experiments.

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Table 1 Characteristics of D301 ion exchange resin

Polymer matrix	Styrene-DVB
Functional group	-N(CH ₃) ₂
Ionic form	Cl ⁻
Exchange capacity (mmol/mL)	≥ 1.4
Operating temperature (°C)	≤ 100
Effective size (mm)	0.40–0.70
Swelling (%)	28

1.2 Preparation of MnO₂-loaded resin

The method for preparation of MnO₂-loaded D301 resin (R-MnO₂) was described in our previous work (Zhu et al., 2007), according to the method proposed by Lenoble et al. (2004). The mixture of 1 g dry D301 resin and 100 mL of 0.05 mol/L KMnO₄ solution was shaken at 25°C for 5 hr. Then, after rinsed with distilled water, the loaded adsorbent was air-dried at temperature ≤ 40°C before using.

1.3 Apparatus

An inductively coupled plasma optical emission spectrometer (Optima 2100DV, Perkin-Elmer, USA) was used for the determination of Pb²⁺ and Cd²⁺ ions in solution.

1.4 Adsorption studies

Adsorption isotherm studies were conducted by mixing 0.1 g R-MnO₂ with 100 mL solutions of varying initial Pb²⁺ and Cd²⁺ concentrations from 10 to 50 mg/L in 250-mL conical flasks. Solutions of 0.1 mol/L HCl or 0.01 mol/L NaOH were used for pH adjustment. After shaking at 150 r/min and at 25°C for 24 hr, a solution sample was taken out from the adsorption system and analyzed for the concentration of metal ions.

Adsorption kinetic experiments were carried out by batch adsorption method at 25°C on a shaker at 150 r/min, using 250 mL conical flasks containing 100 mL solution with 10 mg/L Pb²⁺, 10 mg/L Cd²⁺ and 0.1 g R-MnO₂. Samples were withdrawn at intervals of 1, 2, 3, ..., 8 and 24 hr for metal ions determination.

The adsorption capacity can be calculated according to the following Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

The removal efficiency of heavy metal ions was calculated by the difference of heavy metal concentrations in aqueous solution using Eq. (2):

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where, q_e (mg/g) is the amount of metal ions adsorbed onto the unit amount of the adsorbent, C_0 (mg/L) is the initial heavy metal concentration, C_e (mg/L) is the final or equilibrium heavy metal concentration, V (L) is the volume of the solution, and m (g) is the loaded resin weight in dry form.

2 Results and discussion

2.1 Characterization of R-MnO₂

The characteristics of the MnO₂-loaded D301 resin was presented in our previous work (Zhu et al., 2007). The Mn content in R-MnO₂ was 90 mg Mn/g D301. Its XRD pattern (Zhu et al., 2007) indicated two characteristic peaks at $d = 0.241$ and 0.141 nm for 2θ 37.3° and 66.7°, respectively, which were the typical synthetic phase of δ -MnO₂. The pH point of zero charge (pH_{pzc}) for the R-MnO₂ was 7.86.

2.2 Effect of adsorbent dosage

As shown in Fig. 1, when the adsorbent dosage was less than 0.01 g, Pb²⁺ showed a stronger affinity to R-MnO₂ than Cd²⁺. The further increase of the adsorbent dosage increased the removal efficiency both for Pb²⁺ and Cd²⁺. When the adsorbent dosage increased to 0.06 g, the adsorbent can simultaneously remove Pb²⁺ and Cd²⁺ with high efficiency of 98% and 99%, respectively. Considering the removal efficiency and relative less adsorbent dosage, 0.1 g adsorbent in 100 mL solution was selected for following studies.

2.3 Effect of pH

Batch equilibrium experiments were performed in pH range 2–8 to determine the effect of pH on the removal efficiency of Pb²⁺ and Cd²⁺ with R-MnO₂ (Fig. 2). For Cd²⁺, when pH was lower than 4, the removal efficiency dropped steeply. Since the surface of R-MnO₂ contained a large number of active sites, and may become positively charged at very low pH, which increased the competition between H⁺ and the metal ions for available adsorption sites. However, as solution pH increased further, this competition became weaker and the removal efficiency of Cd²⁺ increased obviously. When pH was higher than 5, the removal efficiency reached up to 90%. This R-MnO₂ adsorbent showed a high efficiency for Pb²⁺ removal in the pH range 2–8. As well known, the solution pH could affect the precipitation reaction of the heavy metals. Precipitation

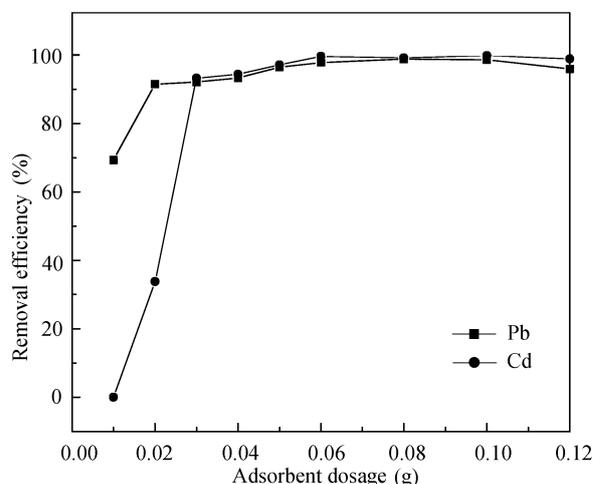


Fig. 1 Effect of adsorbent dosage of R-MnO₂ on the removal of Pb²⁺ and Cd²⁺. Initial Pb²⁺ or Cd²⁺ concentration: 10 mg/L; pH: 5–6; temperature: 25°C; adsorption time: 24 hr.

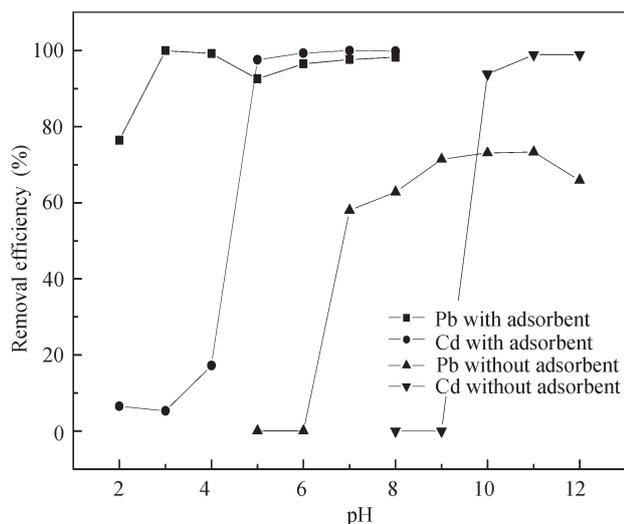


Fig. 2 Effect of solution pH on the removal of Pb²⁺ and Cd²⁺ by R-MnO₂. Adsorbent: 1 g/L; initial Pb²⁺ or Cd²⁺ concentration: 10 mg/L; pH: 2–12; temperature: 25°C; adsorption time: 24 hr.

reaction may contribute to the removal of Pb²⁺ and Cd²⁺ at high pH ($K_{sp-Pb(OH)_2} = 1.2 \times 10^{-15}$; $K_{sp-Cd(OH)_2} = 2.5 \times 10^{-14}$). The pH of the solution should be lower than the critical pH of hydroxide precipitation (6.69 for Pb²⁺ and 9.03 for Cd²⁺) when considering the adsorption efficiency. According to the removal efficiency and the effect of precipitation, the most feasible pH range was selected as 5–6.

2.4 Effect of coexistent ions

The natural water often contains different kinds of cations and anions which may affect the adsorption of heavy metals. The presence of the common ions coexisting with heavy metals invariably implies competition for available adsorptive sites. Although some adsorption sites can only adsorb certain solutes and not all solutes compete for exactly the same sites, the presence of other solutes will reduce the adsorption of any target solute to some degree (Hu et al., 2005).

To explore the competitive effects of various coexisting ions (such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻,

Table 2 Effect of coexisting ions on the adsorption of Pb²⁺ and Cd²⁺ by R-MnO₂

Ions	Ions concentration (mg/L)	Removal of Pb ²⁺ (%)	Removal of Cd ²⁺ (%)
Na ⁺	1000	100	96
K ⁺	1000	99.3	98.6
Ca ²⁺	200	98.3	56.6
Mg ²⁺	200	98.9	51.46
Cl ⁻	1000	99	99.1
NO ₃ ⁻	1000	98.7	99.6
SO ₄ ²⁻	500	98.3	99.6
HCO ₃ ⁻	200	98.7	100
HPO ₄ ²⁻	100	88.07	79.2

Adsorbent: 1 g/L; initial Pb²⁺ or Cd²⁺ concentration: 10 mg/L; pH: 5; temperature: 25°C; adsorption time: 24 hr.

HCO₃⁻ and HPO₄²⁻) on the removal of Pb²⁺ and Cd²⁺, 100 mL of 10 mg/L Pb²⁺ and 10 mg/L Cd²⁺ solutions containing each coexisting ion and 0.1 g R-MnO₂ were shaken at pH 5. The results are summarized in Table 2. Except for HPO₄²⁻, other ions have no significant effect on the removal of Pb²⁺ under the experimental conditions. But for Cd²⁺, besides HPO₄²⁻, the presence of Mg²⁺ and Ca²⁺ also caused the obvious decreasing of removal efficiency.

2.5 Adsorption isotherms

The Langmuir model assumes that the uptake of metal ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions (Zhai et al., 2004). The model can be described by following Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where, C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the adsorption amount at equilibrium, Q_0 is the maximum adsorption amount and b is the Langmuir constants related to adsorption capacity and energy of adsorption. Figure 3a presents the Langmuir isotherm of Pb²⁺ adsorption. It is found that the Langmuir isotherm equation gives a good fit for the adsorption of Pb²⁺ ($R^2 > 0.991$) with the maximum adsorption capacity Q_0 80.64 mg/g.

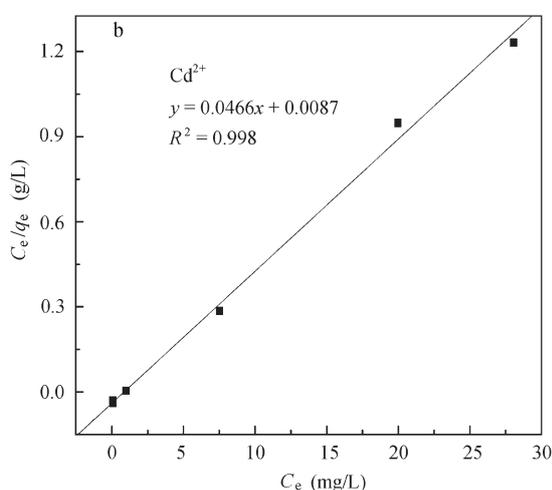
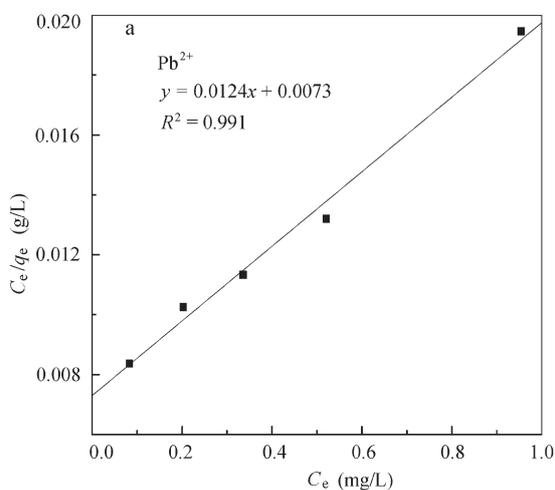


Fig. 3 Langmuir adsorption isotherms for Pb²⁺ (a) and Cd²⁺ (b) adsorption by R-MnO₂. Adsorbent: 1 g/L; Pb²⁺ and Cd²⁺ concentration: 10–50 mg/L; pH: 5; temperature: 25°C; adsorption time: 24 hr.

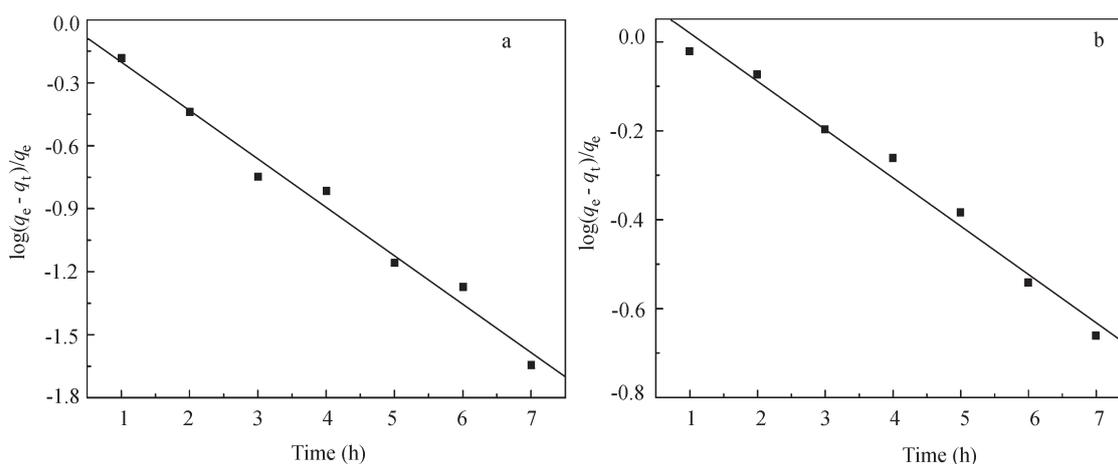


Fig. 4 Lagergren linearization of Pb²⁺ (a) and Cd²⁺ (b) ions adsorption by R-MnO₂. Adsorbent: 1 g/L; initial Pb²⁺ or Cd²⁺ concentration: 10 mg/L; pH: 5; temperature: 25°C; adsorption time: 7 hr.

The Langmuir adsorption isotherm for Cd²⁺ ions is shown in Fig. 3b. The linear plot of C_e/q_e against C_e showed that the adsorption obeys the Langmuir model very well ($R^2 > 0.998$). The Q_0 of Cd²⁺ was calculated as 21.45 mg/g, which was less than the value 77.81 mg/g of single cadmium ion adsorption system (Zhu et al., 2007). Experimental results indicated the competition between the coexistent heavy metals for that the adsorption sites, and that the adsorption capacity of Cd²⁺ may be reduced by the coexistence of Pb²⁺ ions.

2.6 Adsorption kinetics

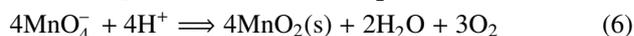
To examine the controlling mechanism of the adsorption process, kinetic models are often used to test the experimental data. In this study, the adsorption kinetics of the heavy metals was analyzed according to the pseudo first-order Lagergren equation (Lagergren et al., 1898) (Eq. (5)).

$$\log(q_e - q_t) = -\frac{K_1 t}{2.303} + \log q_e \quad (4)$$

where, K_1 (min⁻¹) is the Lagergren rate constant of adsorption; q_e (mg/g) and q_t (mg/g) are the quantities of metal ions adsorbed at equilibrium and at time t , respectively. Figure 4 shows the adsorption kinetics of Pb²⁺ and Cd²⁺. The good linear correlation for both metal ions indicated that the adsorption conformed to the pseudo first-order Lagergren mechanism, and the possible adsorption controlling step was chemical adsorption. The K_1 value calculated from the slopes was 8.75×10^{-2} min⁻¹ for Pb²⁺ and 4.14×10^{-2} min⁻¹ for Cd²⁺. The result showed that pseudo first-order rate constant for Pb²⁺ was higher than that for Cd²⁺. When Pb²⁺ and Cd²⁺ existed simultaneously in the same aqueous solution, the sorption of Pb²⁺ was preferential to that of Cd²⁺ by this loaded adsorbent R-MnO₂. This phenomenon may be related to the differences in the electronegativity and ionic radius of the atoms, because both the electronegativity and ionic radius of Pb²⁺ are higher than that of Cd²⁺ (Balasubramanian et al., 2009).

3 Mechanism discussion

D301 resin is one of weak basic anion exchange resins. After reacting with KMnO₄ in aqueous solution, MnO₂ was formed on the surface of resin. Its XRD data (Zhu et al., 2007) indicated that the loaded MnO₂ was the typical synthetic phase of δ -MnO₂. The major characteristic reactions that may take place at the solid-solution interface of the system can be expressed by the following Eqs. (5) and (6).



Compared with Fe or Al oxides, manganese oxides have a higher affinity for many heavy metals (Fan and Anderson, 2005), which could be strongly adsorbed as an inner sphere complex by means of surface complexation on MnO₂ (Xu et al., 2006). The pHzpc of the MnO₂-loaded D301 resin was determined as 7.86. In pH range 5–6, the surface of the loaded adsorbent had a net positive charge, which was unfavorable for the adsorption. From the result, it was conformed that a surface complexation mechanism may be involved in the sorption of heavy metals for R-MnO₂ rather than electrostatic interaction.

4 Conclusions

This work confirmed the potential use of MnO₂-loaded resin (R-MnO₂) as a good adsorbent for simultaneous removal of Pb²⁺ and Cd²⁺ from aqueous solution. When the adsorbent dosage was more than 0.6 g/L, and pH was varied between 5 and 6, the R-MnO₂ was quite efficient for the removal of Pb²⁺ and Cd²⁺. Under the experimental conditions, the presence of coexistent ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, has no significant effect on the removal of Pb²⁺. But for Cd²⁺, HPO₄²⁻, Mg²⁺ and Ca²⁺ caused the obvious decrease in the removal efficiency. The adsorption behaviour of both

Pb²⁺ and Cd²⁺ followed the Langmuir adsorption isotherm with a maximum adsorption capacity of 80.64 mg/g and 21.45 mg/g, respectively. The adsorption process obeyed the pseudo first-order kinetics model. The experimental data demonstrated that the presence of Pb²⁺ resulted in a decrease in Cd²⁺ removal efficiency by R-MnO₂, mainly due to the competition ion of metal ions for adsorption sites. The adsorption of Pb²⁺ was preferential to that of Cd²⁺. Surface complexation mechanism may play an important role in the adsorption of Pb²⁺ and Cd²⁺ on R-MnO₂.

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