



Removal of cadmium using MnO₂ loaded D301 resin

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Abstract

MnO₂ loaded weak basic anion exchange resin D301 (Anion exchange resin, macroreticular weak basic styrene) as adsorbent has been prepared and applied to the removal of cadmium. The adsorption characteristics have been investigated with respect to effect of pH, equilibrium isotherms, removal kinetic data, and interference of the coexisting ions. The results indicated that the Cd²⁺ could be efficiently removed using MnO₂ loaded D301 resin in the pH range of 3–8 from aqueous solutions with the co-existence of high concentration of alkali and alkaline-earth metals ions. The saturate adsorption capacity of the Cd²⁺ was 77.88 mg/g. The adsorption process followed the pseudo first-order kinetics. The equilibrium data obtained in this study accorded excellently with the Langmuir adsorption isotherm.

Key words: cadmium; kinetics; adsorption; loaded resin; removal

Introduction

As one of the most toxic heavy metals, cadmium has been paid more attention by environmentalists over the past years (Skubal *et al.*, 2002; Gupta *et al.*, 2003). The relationship of semen quality and reproductive endocrine function with the biomarkers of cadmium in men was also reported (Telisman *et al.*, 2000). For the removal of heavy metals from water or remediation of water resources contaminated with heavy metals, several different methods such as chemical precipitation, nano-filtration and ultra-filtration, reverse osmosis, adsorption, solvent extraction, ion exchange, etc. have been developed and used (Korngold *et al.*, 1996; Mulligan *et al.*, 2001; Ritchie and Bhattacharyya, 2002; Boddu *et al.*, 2003).

The treatment of water resources containing trace amount of heavy metals is very difficult, because their concentrations are very low (0–10 mg/L) while the co-existence of alkali and alkali-earth metals lies in much higher concentrations (Korngold *et al.*, 1996; Vilensky *et al.*, 2002).

Adsorption technology is considered as one of the most efficient and promising methods for the treatment of trace amount of heavy metal ions from large volumes of water because of its high enrichment efficiency, and the ease of phase separation (Brown *et al.*, 2001; Wang *et al.*, 2003;

Papini *et al.*, 2004; Katsumata *et al.*, 2004). Moreover, in general, the adsorption process does not require special chemicals. A number of innovative adsorbents have been prepared and reported in recent years (Zhang *et al.*, 2003; Atia *et al.*, 2005; Balaji *et al.*, 2005; Choi *et al.*, 2006; Hawari and Mulligan, 2006). Among them, oxide and hydroxide of Fe, Mn, and Al are often applied because of their high surface areas and their affinity to several heavy metals (Abdel-Samad and Watson, 1998; Mallikarjuna and Venkataraman, 2003; Bell and Saunders, 2005; Tripathy and Kanungo, 2005). However, these oxides are usually in the colloidal forms and have the drawback in obtaining the spherical beads of suitable size for practical application. In recent years, this situation has led to a growing interest in the syntheses and the application of novel adsorbents by loading an oxide on another solid. Several adsorbents, including manganese dioxide coated sand (Baipai and Chaudhury, 1999), iron(III) loaded chelating resin (Rau *et al.*, 2000), iron oxide-coated sand (Thirunavukkarasu *et al.*, 2001), Fe(III)-loaded cellulose sponge etc. (Munoz *et al.*, 2002) have been reported.

The objective of this study is to develop an efficient way for the treatment of drinking water resources contaminated with trace amount of cadmium. Considering the advantage of metal oxide or hydroxide for the adsorption and their practical application, MnO₂ loaded weak basic anion exchange resin D301 as a novel adsorbent has been prepared, characterized, and used for the removal of cadmium. The adsorption performance of the obtained MnO₂ loaded D301 resin toward Cd²⁺ was investigated and the possible

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adsorption mechanism was discussed.

1 Experimental

1.1 Materials

All chemicals were of analytical reagent grade. Stock solution of Cd(II) chloride, was prepared in double-distilled water (DDW).

The polymer resin, D301 (Shanghai Resin Co. Ltd, China), is a weakly basic, macroporous anion exchange resin, its main properties are listed in Table 1. For the experiments, the resin was pretreated with 0.05 mol/L sulfuric acid and then with 0.05 mol/L sodium hydroxide to remove impurities from its synthesis process. After extensive rinsing with DDW, the anion exchanger resin was applied for the further experiments.

Table 1 Characteristics of D301 ion exchange resin

Polymer matrix	Styrene-DVB
Functional group	di-Methyl-ammonium
Ionic form	Cl ⁻
Exchange capacity	≥1.4 mmol/ml
Operating temperature	≤100°C
Effective size	0.40–0.70 mm
Swelling	28%

1.2 Preparation of MnO₂-loaded resin

The preparation method of the absorbent MnO₂ loaded D301 resin was similar to the method proposed by Lenoble *et al.* (2004): 1 g of dry D301 resin was added to 100 ml of 0.05 mol/L KMnO₄, the mixture was shaken at 25°C for 5 h. The resulting loaded absorbent was thoroughly washed with DDW to remove excess permanganate ions and air-dried at $T \leq 40^\circ\text{C}$ before further studies.

1.3 Apparatus

A Perkin-Elmer Optima 2000DV ICP spectrometer was used for the quantitative determination of Cd²⁺ and Mn²⁺ in solution. Crystallization states of solids and the identification of the MnO₂ loaded D301 resin were detected using X-ray diffraction (XRD) analysis on a Siemens D5000 diffractometer using filtered copper $K\alpha_1$ radiation. The pH of the solution was measured using a glass electrode (Leici 3010 pH meter, Shanghai, China). An electronic temperature-controlled shaker (Yuejin THZ-82A, Shanghai, China) was used for shaking.

1.4 Point of zero charge using solid addition method

The pH of zero point of charge (pH_{zpc}) was determined according to the method proposed by Tripathy and Kanungo (2005). To a series of 125 ml polyethylene bottle that contained 40 ml of 0.01 mol/L NaNO₃, different volumes of either 0.1 mol/L HCl or 0.1 mol/L NaOH were added so as to obtain the solution with wide ranging pH 2–10. The total volume of the solution in each bottle was made up to 50 ml by 0.01 mol/L NaNO₃. After 2 h of equilibration, the pH values were measured and designated as initial pH or pH_i. A known amount of the absorbent was added in each

bottle, which was then flushed with nitrogen gas for 3–5 min and securely stoppered. After 72 h of equilibration at room temperature with intermittent shaking, the pH values of the supernatant liquid in each bottle was noted and designated as final pH or pH_f. The difference between the pH_i and the pH_f (ΔpH) was plotted against pH_i. The pH_{zpc} value for a specific adsorbent was at the pH_i value, where the curve intersects $\Delta\text{pH}=0$. At this pH, the absorbent do not induce the release of either H⁺ or OH⁻ ion in solution, the surface does not undergo or acquire any charge through acid-base dissociation.

1.5 Adsorption studies

By contacting a constant absorbent, 0.1 g of MnO₂ loaded D301 resin with a range of different concentration of the cadmium ion solutions, the resin, and the cadmium ion solutions were agitated in a series of 250 ml conical flasks with equal volumes of solution (100 ml) for a period of 24 h at room temperature. After shaking the flasks for 24 h, a solution sample was taken from the reaction mixtures after decantation. The final concentration of the unadsorbed cadmium was determined using ICP and the amount of cadmium adsorbed on the MnO₂ loaded D301 resin was calculated.

For the removal kinetic study of cadmium ions, 1.0 g of MnO₂ loaded D301 resin was added in 200 ml solution of 1 mg/L cadmium ion, the solution was agitated for a predetermined period at $25 \pm 1^\circ\text{C}$ in a shaking incubator. At appropriate time intervals, stirring was briefly interrupted while 5 ml volumes of the supernatant solution were sucked from the reactor and analyzed with ICP spectrophotometer for the concentration of residual metal ions. The metal ions uptake q (mg metal ion/g resin) was determined as follows:

$$q = (C_0 - C_t)V/m \quad (1)$$

where, C_0 and C_t are the concentrations of the initial and the final metal ions (mg/L), respectively; V is the volume of the solution (L); and m is the resin weight (g) in dry form.

2 Results and discussion

2.1 MnO₂ loaded D301 resin characterization

The Mn content in MnO₂ loaded D301 resin prepared in this study was 90 mg Mn/g D301. The MnO₂ loaded D301 resin gives the same powder X-ray diffraction pattern as MnO₂ (Fig.1), thus indicating a solid MnO₂ deposit on the D301 resin. XRD of the loaded adsorbent exhibited peaks at $d=0.241$ nm and $d=0.141$ nm for $2\theta=37.3^\circ$ and 66.7° , which are the typical synthetic birnessite phase of $\delta\text{-MnO}_2$ (Lenoble *et al.*, 2004), so the MnO₂ loaded on the D301 was also $\delta\text{-MnO}_2$.

Fig.2 illustrates the plots of pH change (ΔpH) observed before and after equilibration against pH_i for the MnO₂ loaded D301 resin. There is a distinct common point of intersection at the $\Delta\text{pH}=0$ line at pH_i 7.86, which is the pH_{zpc} of the MnO₂ loaded D301 resin. Below the pH_{zpc},

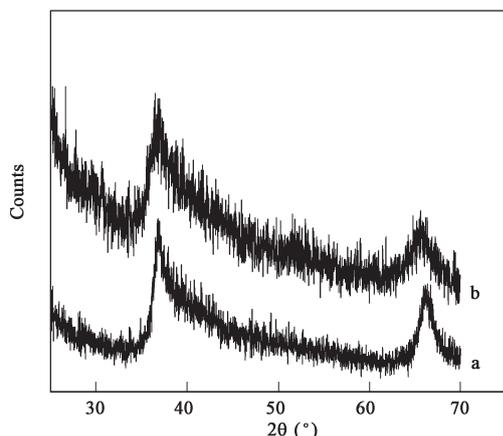


Fig. 1 XRD pattern for MnO₂ (a) and MnO₂ loaded D301 resin (b), analysis between 25° and 70°.

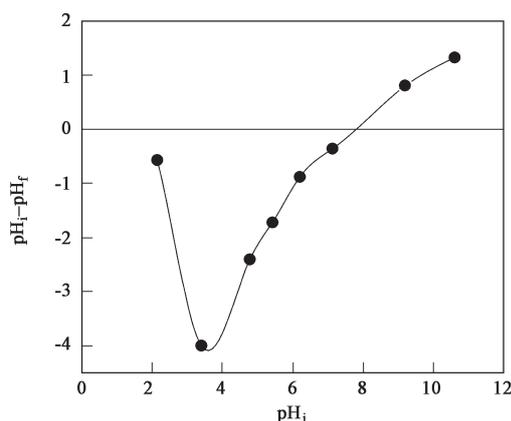


Fig. 2 pH change of the MnO₂ loaded D301 resin as a function of pHi.

the surface charge will be positive and above the pHzpc the surface charge will be negative.

2.2 Effect of pH

Uptake experiments were carried out in the pH range of 2–10 by shaking 0.1 g of MnO₂ loaded D301 resin with 100 ml cadmium ion at initial concentration of 1.0 mg/L for 24 h at 25°C. The effect of pH on the retention of trace metal ions is shown in Fig.3. As shown in the figure, the removal of cadmium from the solution was found to be nearly complete (100%) in the pH range of 3–8.

At lower pH values, both the heavy metal ions and the H⁺ ions compete for the same active sites of the adsorbent, the presence of H⁺ ions can inhibit the adsorption of cadmium ions. The obvious dissolution of Mn was found at pH < 3 in the experiments carried out by the authors of this study. While at higher pH values, the presence of OH⁻ ions may form the hydroxy complexes of heavy metals. Hence, the following experiments were carried out in the solution at a proper pH of 5.5.

2.3 Adsorption isotherms

The effect of cadmium ions concentration on their adsorption using MnO₂ loaded D301 resin is shown in Fig.4. The Langmuir model was applied to describe the adsorption equilibrium. The Langmuir isotherm is repre-

sented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (2)$$

where, C_e is the equilibrium concentration of heavy metal ions in solution (mg/L); q_e is the amount adsorbed at equilibrium concentration (mg/g); Q_0 is the maximum adsorption capacity (mg/g), and b is the Langmuir constant, which is related to the binding energy of the metal ion to the active site (L/mg). The linear plots of C_e/q_e against C_e show that the adsorption obeys the Langmuir model very well. The values of Q_0 and b were obtained from Fig.4 as 77.88 mg/g and 0.019 L/mg, respectively, which are in good agreement with the experimental results. The value of b reflects the selectivity ability of MnO₂ loaded D301 resin towards cadmium ions.

2.4 Adsorption kinetics

Fig.5 shows the adsorption of Cd²⁺ on MnO₂ loaded D301 resin as a function of time from aqueous solutions. As can be seen, the removal efficiency shows a rapid increase during the first period, then a slow increase follow-up until equilibrium state is reached. According to the experimental results, the possible removal process of the cadmium ions can be divided into two distinct steps: a relative fast step followed by a slower one. The necessary time to reach this equilibrium is about 360–420 min and

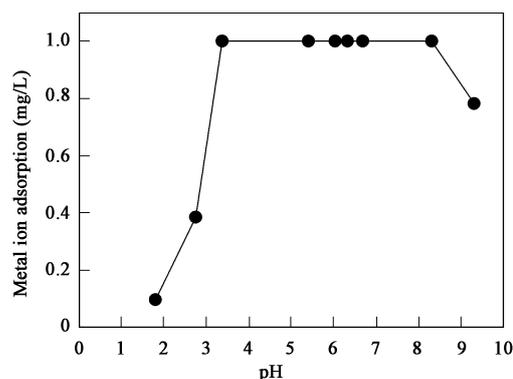


Fig. 3 Effect of pH on the adsorption of cadmium ions with the MnO₂ loaded D301 resin. Initial concentration of cadmium 1.0 mg/L; volume of solution 100 ml; and contacting time 24 h.

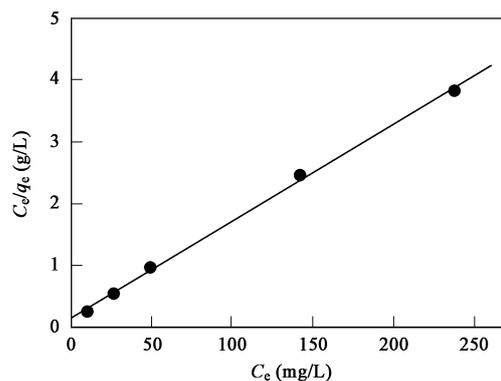


Fig. 4 Langmuir adsorption isotherm of cadmium ions using MnO₂ loaded D301 resin. Solution pH 5.5; temperature 25°C; volume of solution 100 ml; and contacting time 24 h.

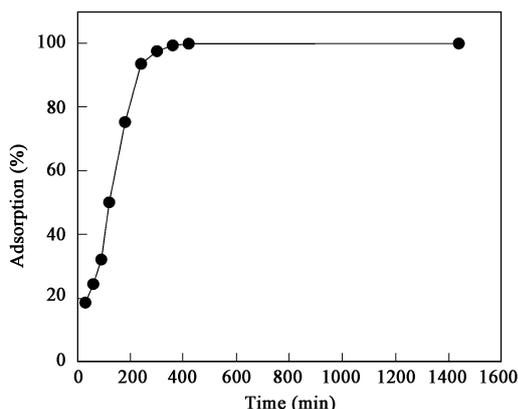


Fig. 5 The effect of the contacting time on the removal of cadmium ions using MnO₂ loaded D301 resin. Initial concentration of each heavy metal ion 1.0 mg/L; solution pH 5.5; temperature 25°C, and contacting time 1440 min.

an increase of removal time to 1440 min did not show any notable effects.

During the removal process of cadmium ions using MnO₂ loaded D301 resin, a change of the solution pH was found, from 5.40 at the beginning to 8.30 at the equilibrium. This phenomenon may be interpreted by a competition between the heavy metal ions and the H₃O⁺ for binding sites on the adsorbent surfaces. In this study, the adsorption kinetics of the heavy metals can be modeled by the pseudo-first-order Lagergren equation (Lagergren, 1898; Ho and McKay, 1999).

$$\lg (q_e - q_t)/q_e = -K_L t/2.3 \quad (3)$$

where, K_L is the Lagergren rate constant of adsorption (min^{-1}); q_e and q_t are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time t , respectively.

Linear plots of $\lg (q_e - q_t)/q_e$ vs. t are shown in Fig.6. The K_L value calculated from the slopes was found to

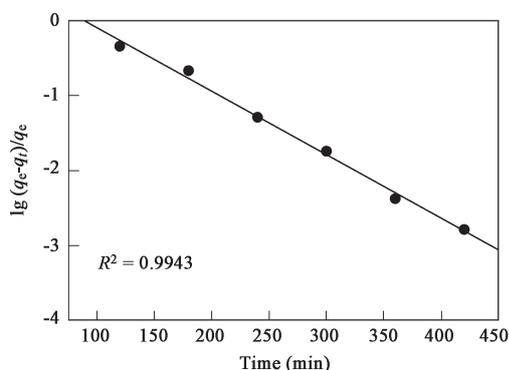


Fig. 6 The pseudo first-order Lagergren linearization of cadmium ions adsorption by MnO₂ loaded D301 resin. Initial concentration of each heavy metal ion was 1.0 mg/L; solution pH 5.5; temperature 25°C, and contacting time was 420 min.

be $1.96 \times 10^{-2} \text{ min}^{-1}$ for Cd²⁺ ($R^2=0.9943$). The results showed that the kinetics process for the adsorption of the Cd²⁺ on the MnO₂ loaded D301 resin excellently followed the characteristics of the pseudo first-order reaction.

2.5 Interference of the coexisting ions

In natural water samples, different kinds of ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻ may cause interference in the removal of heavy metals. The possible effect of coexistence of the above ions on the removal of cadmium ions with the MnO₂ loaded D301 resin was investigated. Various concentrations of the above coexistence ions were added to 100 ml of the test solution containing 1.0 mg of cadmium ions. The results are given in Table 2. It can be seen that the presence of coexistence ions such as Na⁺, K⁺, Ca²⁺, and Mg²⁺ has no significant effect on the removal of cadmium. The similar results are also observed for the coexistence anions such as Cl⁻, NO₃⁻, and SO₄²⁻, except for PO₄³⁻.

3 Mechanism discussion

Adsorbates may form different types of bonds with the mineral surface. In general, if the adsorption between the adsorbate and the surface sites is caused by relatively strong chemical bonds such as ion and covalent bonds, the adsorption is identified as “specific” adsorption. The adsorption substance formed during this process was named as “inner-sphere” type complexes. While the adsorption between the adsorbate and the surface sites results from the weaker Coulomb attraction or Van der Waals bond, the adsorption is identified as “nonspecific” adsorption. The adsorption substance formed during this process was named as “outer-sphere” type complexes (Koretsky, 2000).

Some researches have shown that Cd²⁺ and other heavy metals were strongly adsorbed as an inner sphere complex by means of surface complexation on MnO₂ (Pretorius and Linder, 2001; Xu *et al.*, 2006).

According to the previous characteristic of the surface charge, the pH_{zpc} of MnO₂ loaded D301 resin is 7.86. When $\text{pH} < 7.86$, the surface charge of the MnO₂ loaded D301 resin is positive, it is unfavorable for the removal of Cd²⁺. However, the experiments result showed that effective removal of Cd²⁺ can be carried out in the pH range of 3–8. So it could be deduced that the Cd²⁺ is specifically adsorbed on the MnO₂ loaded D301 resin through an inner-sphere complex via surface complexation rather than the electrostatic interaction.

4 Conclusions

In this study, MnO₂ loaded D301 resin was prepared and characterized. This adsorbent showed a high capacity for

Table 2 Effect of coexistence ions on the removal of cadmium ions^a

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻
Concentration of coexistence ions (mg/L)	1000	1000	200	200	1000	1000	500	100
Removal of cadmium (%)	100	100	97.3	95.6	100	100	95	83.6

^a Solution pH 5.5 at 25°C, initial concentration of cadmium ions 1.0 mg/L, and contacting time 420 min.

the removal of trace amount of cadmium with the coexistence of high concentration of alkali and alkaline-earth metal ions at the wide range of pH 3–8. The analysis results indicated that the MnO₂ particles loaded on the D301 resin was δ-MnO₂, and the prepared adsorbent had a pH_{ZPC} about 7.86. The adsorption characteristics obeyed the Langmuir adsorption isotherm, and the maximum removal capacity was 77.88 mg/g for Cd²⁺. It was also demonstrated that the adsorption process follows the pseudo first-order kinetics.

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