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Adsorption behavior and mechanism of cadmium on strong-acid cation exchange resin

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Abstract: The adsorption behavior of Cd^{2+} on 001×7 strong-acid cation exchange resin was studied with the static adsorption method. The adsorption process was analyzed from thermodynamics and kinetics aspects. The influences of experimental parameters such as pH, temperature, initial concentration and adsorption rate were investigated. The experimental results show that in the studied concentration range, 001×7 resin has a good sorption ability for Cd^{2+} , and the equilibrium adsorption data fit to Freundlich isotherms. The adsorption is an exothermic process which runs spontaneously. Kinetic analysis shows that the adsorption rate is mainly governed by liquid film diffusion. The best adsorption condition is pH 4–5. The saturated resin can be regenerated by 3 mol/L nitric acid, and the desorption efficiency is over 98%. The maximal static saturated adsorption capacity is 355 mg/g (wet resin) at 293 K. The adsorption mechanism of Cd^{2+} on 001×7 resin was discussed based on IR spectra.

Key words: cadmium; strong-acid cation exchange resin; adsorption; thermodynamics; kinetics

1 Introduction

Both cadmium and soluble cadmium salts are poisonous and deleterious to human beings and animals. The half life of cadmium lasts 20–40 years in body[1] and can harm body's immune system and reproductive system[2]. As environmental pollution, shortage of resources and other issues are becoming increasingly serious now, effectively and economically disposing wastewater containing cadmium has become an important research topic.

The regular methods of treatment on wastewater containing cadmium are chemical precipitation[3–4], biological adsorption[5–7], ferrite method[8], membrane separation[9], resin adsorption[10–12] and so on. The resin adsorption seems to be the most suitable method for the recovery of precious metals in the case of low concentration due to low cost and high efficiency. In recent years, the studies of macroporous resin adsorption cadmium are active. CHEN et al[13] prepared a new chelating resin (PASP) by anchoring sodium aspartate to crosslinked poly. The adsorption of Cd²⁺ tended toward

equilibrium at 60 min and the equilibrium adsorption capacity was 1.28 mmol/g in non-competitive conditions. ZHU et al[14] prepared a new adsorbent by loading MnO₂ on weak basic anion exchange resin D301. This absorbent showed a high capacity for the removal of trace amount of cadmium with the coexistence of high concentration of alkali and alkaline-earth metal ions at the wide pH range of 3–8, and the maximum removal capacity was 77.88 mg/g for Cd²⁺. MO et al[15] investigated the sorption of Cd²⁺ with iminodiacetic acid D401 resin. The results showed D401 had a good sorption ability for Cd²⁺ and the statically saturated sorption capacity of resin was 363 mg/g. The reports of study for adsorption of cadmium on gel-strong acid cation exchange resin are few.

In this work, the adsorption behavior of cadmium on 001×7 strong-acid cation exchange resin (—SO₃H as the function group) was studied. The influences of pH value, temperature, initial concentration and contact time on the adsorption of Cd²⁺ were investigated by using 001×7 resin as adsorbent. The adsorption process was analyzed from the thermodynamic and kinetic aspects, and the adsorption mechanism was discussed by using

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infrared spectroscopy.

2 Experimental

2.1 Instruments and materials

Instruments included: AA320 CRT atomic absorption spectrometer (Shanghai Analysis Instrument Factory, China), MB-154S FTIR spectrometer (Bomem Company, Canada), pHS-3B exact pH meter (Shanghai Precision & Scientific Instrument Co., Ltd, China), SHA-B constant temperature shaking machine (Changzhou Guohua Appliance Co., Ltd, China).

The used materials were 001×7 strong-acid cation exchange resin (provided by the Chemical Plant of Nankai University, China); cadmium nitrate (provided by the Nanjing Chemical Reagent Company, China); and the other reagents used were of AR grade.

2.2 Experimental methods

2.2.1 Resin pretreatment

The resin was dipped in double volumes of deionized water, then in 3% hydrochloric acid, deionized water, 3% sodium hydroxide, deionized water, 3% hydrochloric acid for 24 h, respectively. At last the resin was washed by deionized water repeatedly before using. 2.2.2 Effect of pH on adsorption

0.1 g wet resin was added to relevant 250 mL conical flasks, then 100 mL aqueous solution with initial Cd^{2+} content $\rho_0=300$ mg/L was added. The flask was shaken in a shaker with the speed of 132 r/min at 293 K for 24 h to ensure that the adsorption reached equilibrium. Q_e (mg/g) is calculated by the following equation:

$$Q_{\rm e} = V(\rho_0 - \rho_{\rm e})/m \tag{1}$$

where V is the volume of solution, L; ρ_e is the equilibrium content of Cd²⁺, mg/L; *m* is the mass of resin, g.

2.2.3 Static equilibrium adsorption experiment

The static adsorption test of Cd²⁺ on 001×7 resin at different temperatures (293, 308 and 323 K) was conducted. 0.1 g wet resin was added to relevant 250 mL conical flasks, then 100 mL aqueous solution of Cd²⁺ was added. The initial content ρ_0 of the solution was 300, 350, 400, 450 and 500 mg/L respectively. The flasks were shaken with the speed of 132 r/min at different temperatures for 24 h to ensure the adsorption process reaching equilibrium. The equilibrium adsorption capacity Q_e (mg/g) is calculated by Eq.(1).

2.2.4 Kinetics experiment

0.1 g wet resin was added to relevant 250 mL conical flasks, then 100 mL of the same initial content aqueous solution of Cd^{2+} was added. The flasks were shaken with the speed of 132 r/min at 293 K and the

samples were taken at different intervals until the adsorption reached equilibrium. The instantaneous adsorption capacity Q_t (mg/g) is calculated by the following equation:

$$Q_t = V(\rho_0 - \rho_t)/m \tag{2}$$

where ρ_0 is the initial concentration of Cd²⁺, mg/L; ρ_t is the instantaneous content of Cd²⁺ at time *t*, mg/L; *V* is the volume of solution, L; *m* is the mass of resin, g.

2.2.5 Desorption experiment

The saturated resin was washed by deionized water for 3 times after being separated from solution, then the desorbent was added to a 250 mL conical flask and the flask was shaken with the speed of 132 r/min at 298 K for 24 h to ensure the desorption process reaching equilibrium.

2.3 Mensuration condition

The mensuration conditions of Cd^{2+} concentration with AA320 CRT atomic absorption spectrometry were: analytical line 228.8 nm, lamp electricity 5 mA, air flux 0.4 m³/h, ethane flux 0.05 m³/h, and bandpass width 0.4 nm.

3 Results and discussion

3.1 Effect of pH on adsorption

The effect of pH on adsorption is shown in Fig.1.



Fig.1 Effect of pH on adsorption

As shown in Fig.1, the adsorption capacity decreases with the decrease of solution pH value under pH<4. This is because that with the decrease of solution pH value or increase of H⁺ concentration, the dissociation degree of exchange group and exchange capacity between H⁺ and Cd²⁺ will decrease, so the adsorption capacity will decrease. When pH>4, the free concentration of Cd²⁺ in solution will decrease because of hydrolyzation, and the adsorption capacity will reduce too. So the optimal pH is between 4–5.

3.2 Adsorption isotherm

The adsorption isotherm indicates the relationship between equilibrium adsorption capacity and equilibrium concentration at constant temperature. The adsorption isotherms of Cd^{2+} on 001×7 resin are shown in Fig.2.



Fig.2 Equilibrium adsorption isotherms of Cd^{2+} on 001×7 resin

It is seen from Fig.2 that the equilibrium adsorption capacity will decrease with the increment of temperature, and higher temperature is unfavorable to the adsorption process, indicating adsorption is an exothermic process. The equilibrium adsorption capacity increases with the increment of equilibrium concentration.

The adsorption isotherms are analyzed by Freundlich isothermal equation[16]. The predigestion equation is as follows:

$$\ln Q_{\rm e} = \ln K_{\rm F} + \frac{1}{n} \ln \rho_{\rm e} \tag{3}$$

where Q_e is the equilibrium adsorption capacity, mg/g; ρ_e is the equilibrium concentration, mg/L; K_F and n are the constants of Freundlich isothermal equation. The fitting results are listed in Table 1.

Table 1 shows all the correlation coefficients exceed 0.98, indicating that the adsorption can be described by the Freundlich isothermal equation.

3.3 Adsorption thermodynamics

Table 2 Thermodynamics parameters of adsorption

3.3.1 Adsorption enthalpy ΔH

Table 1 Correlated parameters of Freundlich isotherm

	-			
T/K	Fitting equation	$K_{ m F}$	n	R^2
293	$\ln Q_{\rm e} = 1.686 \ln \rho_{\rm e} - 3.977$	0.019	0.593	0.981 7
308	$\ln Q_{\rm e} = 1.358 \ln \rho_{\rm e} - 2.428$	0.088	0.736	0.985 6
323	$\ln Q_{\rm e} = 1.212 \ln \rho_{\rm e} - 1.759$	0.172	0.825	0.983 4

The isosteric enthalpy can be calculated at given adsorption capacity with the following equation[17]:

$$\ln \rho_{\rm e} = \frac{\Delta H}{RT} - \ln K_0 \tag{4}$$

where *R* is the gas constant, ρ_e is the equilibrium concentration under given adsorption capacity, *T* is the absolute temperature, and K_0 is a constant. ΔH is obtained from the slope of line plotted by $\ln \rho_e$ vs 1/T. 3.3.2 Adsorption free energy ΔG

When the adsorption data fit well to Freundlich isothermal equation, ΔG can be obtained by [17]

$$\Delta G = -nRT \tag{5}$$

3.3.3 Adsorption entropy ΔS ΔS is obtained by [17]

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{6}$$

At 293, 308 and 323 K, the adsorption thermodynamics parameters of Cd^{2+} on 001×7 resin are shown in Table 2.

It is seen from Table 2 that ΔH is negative, indicating the adsorption is an exothermic process, and higher temperature makes against the adsorption progression. And the results show that the adsorption free energy is negative, indicating the adsorption is with better impetus, and the process runs spontaneously. ΔS values are all negative, showing the adsorption process is impelled by enthalpy[18].

3.4 Adsorption kinetics

The Boyd liquid film diffusion[19] and the intraparticle diffusion[20] equations were used to fit the adsorption kinetics data. The liquid film diffusion equation is

$$-\ln(1-F) = k_1 t \tag{7}$$

Intraparticle diffusion equation is

Qe/	$\Delta H/$ (kJ·mol ⁻¹)	$\Delta G/(\text{kJ}\cdot\text{mol}^{-1})$		$\Delta S/(J \cdot mol^{-1} \cdot K^{-1})$			
$(mg \cdot g^{-1})$		293 K	308 K	323 K	293 K	308 K	323 K
130	-5.70				-14.54	-12.40	-10.77
150	-7.07	-1.44	-1.88	-2.22	-19.22	-16.85	-15.02
180	-8.14				-22.87	-20.32	-18.33

(8)

$$Q_t = k_2 t^{0.5}$$

where $F = Q_t/Q_e$ is the adsorption percent at time *t*, k_1 and k_2 are the rate constants of liquid film diffusion and intraparticle diffusion, respectively, Q_t is the instantaneous adsorption capacity at time *t*, mg/g, and Q_e is the equilibrium adsorption capacity, mg/g. The fitting results are shown in Fig.3 and Fig.4.







Fig.4 Correlation of intraparticle diffusion

The results show that the linear relationship between $-\ln(1-F)$ and t is better (the correlative coefficient is larger than 0.99), and the linear relationship between Q_t and $t^{0.5}$ is bad. This indicates the adsorption rate is mainly governed by liquid film diffusion.

3.5 Saturated adsorption capacity

The results show that equilibrium adsorption capacity increases with the increment of initial concentration, but the equilibrium adsorption capacity does not increase anymore when the initial concentration reaches a certain value. The saturated adsorption capacity is 355 mg/g (wet resin) at 293 K.

3.6 Static desorption and repeated use capability

The saturated resin is regenerated by 3 mol/L nitric acid at 298 K, and the desorption efficiency can reach 98%. This indicates that the resin is easily desorbed and can be used in enrichment of cadmium.

The adsorption capacity reduces from 355 mg/g to 341 mg/g when the resin is repeatedly used for 5 times. It is seen that the resin still has good capability after being used several times.

3.7 Adsorption mechanism

Fig.5 shows the IR spectra of blank and Cd^{2+} loaded 001×7 resin. It is found that the absorption peak of the bond S—OH shifts from 1 007 cm⁻¹ to 1 003 cm⁻¹ and the absorption peak of the bond S—O shifts from 1 038 cm⁻¹ to 1 032 cm⁻¹.



Fig.5 IR spectra of blank and Cd^{2+} loaded 001×7 resin

4 Conclusions

1) Under the studied conditions, the adsorption is an exothermic process which runs spontaneously and the equilibrium adsorption data fit Freundlich isotherm. Liquid film diffusion is the main control step of the adsorption.

2) The maximal static saturated adsorption capacity is 355 mg/g (wet resin) at 293 K, and the desorption efficiency can reach 98% with 3 mol/L nitric acid at 298 K.

3) 001×7 resin is easily desorbed, with good adsorption capacity and repeated use capability, which can be used in wastewater treatment and enrichment of cadmium.

References

- CUI Yu-jing, HUANG Yi-zong, ZHU Yong-guan. Adverse health effects of cadmium and related factors [J]. Journal of Hygiene Research, 2006, 35(5): 656–659. (in Chinese)
- [2] AN Hong-min, ZHENG Wei, GAO Yang. Research progress in cadmium toxicity [J]. Journal of Environment and Health, 2007,

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24(9): 739-742. (in Chinese)

- [3] MA Yan-fei, WANG Jiu-si, SONG Guang-shun, ZHANG Shu-ying. Study on the treatment of cadmium in wastewater with magnesium hydroxide [J]. Journal of Lanzhou Jiaotong University, 2003, 22(4): 120–122. (in Chinese)
- [4] ZHANG Yu-mei. Study on the treatment of cadmium containing wastewater [J]. Environmental Engineering, 1995, 13(1): 15–21. (in Chinese)
- [5] LODEIRO P, BARRIADA J L, HERRERO R, SASTRE DE VICENTE M E. The marine macroalga cystoseira baccata as biosorbent for cadmium (II) and lead (II) removal: Kinetic and equilibrium studies [J]. Environmental Pollution, 2006, 142(2): 264–273.
- [6] FENG D, ALDRICH C. Adsorption of heavy metals by biomaterials derived from the marine alga *Ecklonia maxima* [J]. Hydrometallurgy, 2004, 73(1/2): 1–10.
- [7] HASHIM M A, CHU K H. Biosorption of cadmium by brown, green, and red seaweeds [J]. Chemical Engineering Journal, 2004, 97(2/3): 249–255.
- [8] ZHANG Jian-ru, YE Jin-wu, XU Li-hong. Progress of the research on the treatment of cadmium-contained wastewater [J]. Guangdong Chemical Industry, 2007, 34(2): 28–30. (in Chinese)
- [9] WANG Yan, WANG Yu-jun, LUO Guang-sheng, DAI You-yuan. A treatment of Cd²⁺ solution with hollow fiber membrane extraction process [J]. Chemical Engineering (China), 2002, 30(5): 62–65. (in Chinese)
- [10] BEDOUI K, BEKRI-ABBES I, SRASRA E. Removal of cadmium (II) from aqueous solution using pure smectite and Lewatite S 100: The effect of time and metal concentration [J]. Desalination, 2008, 223(1/3): 269–273.
- WU Xiang-mei, XIONG Chun-hua. Adsorption mechanism of Cd on amino methylene phosphonic acid resin [J]. Nonferrous Metals, 2003, 55(4): 61–64. (in Chinese)
- [12] XIONG Chun-hua, WU Xiang-mei. Studies on the sorption behavior

and mechanism of macroporous phosphonic acid resin for cadmium (II) [J]. Acta Scientiae Circumstantiae, 2000, 20(5): 627–630. (in Chinese)

- [13] CHEN C Y, LIN M S, HSU K R. Recovery of Cu(II) and Cd(II) by a chelating resin containing aspartate groups [J]. Journal of Hazardous Materials, 2008, 152(3): 986–993.
- [14] ZHU Zhi-liang, MA Hong-mei, ZHANG Rong-hua, GE Yuan-xin, ZHAO Jian-fu. Removal of cadmium using MnO₂ loaded D301 resin [J]. Journal of Environmental Sciences, 2007, 19(6): 652–656.
- [15] MO Jian-jun, XIONG Chun-hua. Sorption behavior and mechanism of iminodiacetic acid resin for cadmium [J]. The Chinese Journal of Nonferrous Metals, 2006, 16(5): 924–928. (in Chinese)
- [16] TRACI P, GAIL M B, MARIT J, FRANK D. Investigating the effect of carbon shape on virus adsorption [J]. Environ Sci Technol, 2000, 34(13): 2779–2783.
- [17] LI Ai-min, ZHANG Quan-xing, LIU Fu-qiang, FEI Zheng-hao, WANG Xue-jiang, CHEN Jin-long. Thermodynamic study of adsorption of phenolic compounds on a phenol hydroxyl modified polystyrene [J]. Ion Exchange and Adsorption, 2001, 17(6): 515–525. (in Chinese)
- [18] WANG Mu-jun, SUN Yue, ZHOU Wei, FEI Zheng-hao, ZHANG Quan-xing, REN Huai-xing. Study on thermodynamic properties for adsorption of *o*-phthalic acid from aqueous solution by macroreticular resin [J]. Ion Exchange and Adsorption, 2004, 20(6): 533–540. (in Chinese)
- [19] MA Hong-mei, ZHU Zhi-liang, ZHANG Rong-hua, LIN Jian-wei, ZHAO Jian-fu. Kinetics of adsorption of copper from water by weak base epoxy anion-exchange resin [J]. Ion Exchange and Adsorption, 2006, 22(6): 519–526. (in Chinese)
- [20] WANG Xue-jiang, ZHANG Quan-xing, LI Ai-min, CHEN Jin-long. Adsorption of salicylic acid from aqueous solution by NDA-100 macroreticular resin [J]. Acta Scientiae Circumstantiae, 2002, 22(5): 658–660. (in Chinese)

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