Removal of Cadmium(II) from Wastewater Using Novel Cadmium Ion-Imprinted Polymers

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Supporting Information

ABSTRACT: Cadmium ion-imprinted polymers (Cd-IIP) were synthesized by precipitation polymerization using a complex of dithizone and cadmium as a template. The saturation adsorption capacity of the Cd-IIP is two times that of the nonimprinted polymers (Cd-NIP). Homogeneous binding sites are confirmed by the Langmuir isotherm. The adsorption kinetics fit a pseudo-second-order model well; and the adsorption equilibrium time is only approximately 20 min. The effect of coexisting ions on the Cd(II)-IIP and NIP were investigated by competing with Pb(II), Zn(II), Co(II), and Cu(II), and the ratio of relative selectivity coefficients was greater than 1.68. Thermodynamic parameters indicated that Cd(II) adsorption over IIP and NIP was a spontaneous and exothermic process. The enthalpy changes in different temperatures and adsorption energy are lower than -20.0 and 8 kJ/mol; respectively. These indicate that the adsorption process may be dominated by physisorption. The Cd-IIP was used for five cycles with a small decrease in adsorption capacity, which validated a significant potential of Cd-IIP in wastewater treatment.

1. INTRODUCTION

The presence of cadmium in the natural environment is related to both natural (cadmium coexists in earth with zinc in copper mines) and anthropogenic discharge sources. The metal has various applications in electroplating, nickel–cadmium batteries, alloys, pigments, phosphors, pesticide, and many other branches of industry.¹ Because of these circumstances, cadmium can be easily transferred into animals and human beings by smoke in the air, water, and food and subsequently accumulated in the body.² Long-term exposure to cadmium has been demonstrated to have detrimental influence on the heart, lungs, bones, and especially, the kidneys.¹ Because cadmium effortlessly passes through the food chain system of the earth and is transferred into human beings, the World Health Organization (WHO) has recommended a maximum permissible limit ($5 \mu\text{g L}^{-1}$) for cadmium in normal blood.³ In addition, along with increased industrialization, cadmium pollution has become increasingly serious. Consequently, the development of high-efficiency methods for the removal of cadmium from wastewater samples is a pressing task.⁴

At present, reliable treatment technologies have been developed for wastewater containing cadmium, including

chemical precipitation, the ferrite method, ion exchange method, electrocoagulation, membrane separation, and adsorption.⁵ Chemical precipitation is a low-cost treatment but not environmentally sound.⁶ Stephanie et al.⁷ added sodium decanoate as a precipitant to selective precipitation of cadmium, but a mass of waste residue was left behind. Khaled⁸ designed a new electrocoagulation reactor for the removal of cadmium from phosphate industrial wastewater from phosphate production; however, the large energy consumption and high operational cost limit its widespread application. Comparatively, membrane filtration and ion-exchange resin are efficient processing methods for both inorganics and organics in wastewater. Wong et al.⁹ recommended that cadmium ions be removed by ion-exchange resin until its maximum sorption capacity has reached 2.2 mmol/g . Mehdi et al.¹⁰ reported porous anionic exchange membranes for the removal of cadmium from wastewater; and Kamal et al.¹¹ separated cadmium from wastewater by a liquid membrane-based

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Figure 1. Synthesis route of Cd-IIP.

method, resulting in about a 79 % recovery of cadmium. Nevertheless, this method has no special selectivity and poor performance in reuse. In addition, the membrane is easily fouled. Biosorption has become a popular technology for removing metal from wastewater because of its excellent adsorption performance but lacks a detailed mechanism for the adsorption sites. *Eichhornia crassipes*, *Pinus halepensis* sawdust, and *Triticum aestivum* were used for the adsorption of cadmium ion with a removal rate as high as 73.75 %; meanwhile, Abdulazi used activated carbon produced from rubber tires to evaluate the adsorption of cadmium.^{12–15} All of these methods failed to provide a detailed mechanism of adsorption and required a single adsorption environment. As a consequence, a novel material for complex matrices that satisfies the requirements of an environmentally friendly and economically efficient separation technique is essential and needs much more attention. Moreover, a detailed adsorption mechanism can contribute to the future industrial application of such a method.

One of the most widely used and effective pretreatment techniques for metal separation is adsorption by ion-imprinted polymers that have a strong preference for a specific target and produce no secondary pollution; this technique is rapid and effective, safe, and easy to regenerate.¹⁶ Guo et al.¹⁷ functionalized –SH onto a magnetic ion-imprinted polymer by surface imprinting for selective removal of Pb(II) from aqueous samples, and Luo et al.¹⁸ used a crown ether as a functional monomer by inverse emulsion polymerization for the selective removal of Pb(II), both of which methods have shown excellent selectivity and adsorption performance. Many researchers have made great progress in the preparation of cadmium imprinted polymers. Chen et al.¹⁹ through modification of thiourea onto magnetic ion-imprinted

chitosan/TiO₂ reported a much higher adsorption capacity, 180 mg/g, but the method required 120 min to reach saturation adsorption; Lü et al.²⁰ imprinting a carboxymethyl chitosan-silica hybrid reported 20.7 mg/g adsorption capacity in 30 min; Li et al.²¹ applied a polysaccharide-incorporated sol–gel to prepare a silica-supported organic–inorganic hybrid sorbent, for which the adsorption capacity reach 33.4 mg/g; Guo et al.²² reported the adsorption of cadmium(II) ion in silica gel imprinted sorbents with an adsorption capacity of 30.8 mg/g which reached saturation adsorption in 30 min; Candan et al.²³ using ion-imprinted beads reported cadmium adsorption of 5.48 mg/g. In this study, we got an adsorption capacity of 44.6 mg/g in 20 min. Dithizone was used to chelate nickel ion to form a complex to be used as a template molecule. Together with functional monomers, methylacrylic acid (MAA) was applied to an ion-imprinted polymer to prepare nickel ion selective membranes through bulk polymerization, and time-permeation curves of ions through the Ni(II) imprinted membrane required 48 h.^{24,25} Herein, dithizone was applied to Cd(II) complexes, and the complex thus obtained was used as a template molecule together with functional monomer methylacrylic acid (MAA) resulting in homogeneous binding sites on the Cd-IIP by precipitation polymerization. However, there is still a big challenge to a prepare a novel cadmium ion imprinted polymer. We used solvent (ethyl acetate) to dissolve the coordination compound. The cross-linking agent ethylene glycol dimethacrylate (EGDMA) and 2,2-azobis(isobutyronitrile) (AIBN) as a initiator were added to obtain the Cd-IIP, and the adsorption equilibrium time is only approximately 20 min. The adsorption environment was studied using batches of adsorption experiments to confirm the adsorption mechanism of Cd-IIP. These experiments

Figure 2. SEM photographs of Cd-IIP (a) and NIP (b) and EDX spectra of the free (a) and loaded (b) Cd(II) onto Cd-IIP.

include measured pH, isotherms at different temperatures, kinetics at different initial concentrations, thermodynamics, adsorption energy, selectivity, recycling, and the mechanism of this adsorbent toward Cd(II).

2. EXPERIMENTAL SECTION

2.1. Reagents and Apparatus. Details for chemical reagents and instruments for characterization are described in the [Supporting Information, text S1](#).

2.2. Synthesis of Cadmium Ion-Imprinted Polymer. The Cd-IIP was prepared by a precipitation polymerization technique that is shown in [Figure 1](#).

The Cd–dithizone complex was primarily synthesized to serve as a template molecule; afterward, Cd-IIP and NIP were synthesized by the precipitation polymerization method ([Supporting Information, text S2](#)).

2.3. Batch Adsorption Experiments. Batch sorption experiments were carried out to test the adsorption property and mechanism of the cadmium ion imprinted.

The effect of pH on the cadmium adsorption process was studied over the pH range 1.0–7.0 (pH510, Kesheng, Shenzhen); and the initial cadmium concentration was fixed at 200 mg/L. The aqueous solutions of cadmium were adjusted to the desired pH levels using 0.1 M HCl or 0.1 M NaOH. Next, 25 mg of Cd-IIP were added to a conical flask that contained 50 mL of the above-mentioned solution and the conical flasks were shaken on an incubator shaker (Jingqi, IS-RDD3, USA) at 25 °C and 120 rpm. After 4 h, the samples were taken from the flasks. Finally, the cadmium concentrations (C_e) were measured by atomic absorption spectrometry (AAS). The Cd(II) uptake at equilibrium was calculated from [eq 1](#):

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

where Q represents the adsorption capacity (mg/g); C_0 and C_e are the initial and equilibrium concentrations of cadmium ions (mg/L), respectively; m is the mass of polymers (g); and V is the volume of the metal ion solution (L).

Batch adsorption experiments of isothermal adsorption, kinetics adsorption, and regeneration studies have detailed description in the [Supporting Information, text S3](#).

Competitive sorption of Zn(II), Cu(II), Co(II), Pb(II) in the presence of Cd(II) was investigated for both cadmium ion-imprinted or nonimprinted polymer. The initial concentrations of Cd(II)/Zn(II), Cd(II)/Cu(II), Cd(II)/Co(II) and Cd(II)/Pb(II) in the binary aqueous solutions (pH = 6.0 ± 0.1) were 200 mg/L. The distribution ratio (K_D , mL/g), the selectivity factor of Cd(II) with respect to other ions ($\alpha_{Cd/M}$), and the relative selectivity factor (β) were calculated using the following equations:

$$K_D = \frac{q_e}{C_e} \quad (2)$$

$$\alpha = \frac{K_{D1}}{K_{D2}} \quad (3)$$

$$\beta = \frac{\alpha_1}{\alpha_2} \quad (4)$$

where q_e represents the adsorption capacity and C_e is the equilibrium concentration of Cd(II); K_{D1} and K_{D2} represent the distribution coefficient of Cd(II) and D_2 ($D_2 = \text{Zn(II), Pb(II), Co(II), or Cu(II)}$); α is the selectivity coefficient; β is the relative selectivity coefficient; and α_1 and α_2 are the selectivity coefficients of Cd(II)-IIP and NIP, respectively.

3. RESULTS AND DISCUSSION

3.1. Morphology Study. The scanning electron microscopy (SEM) images of the Cd-IIP and NIP are shown in [Figure 2a,b](#). We can recognize that both of Cd-IIP and NIP particles were packing in disorder. There is no obvious difference between Cd-IIP and NIP for the little variation on the surface area of Cd-IIP and NIP, they are 107.04 m²/g and 110.99 m²/g, respectively.

The energy dispersive X-ray (EDX) analysis spectrum was employed to evaluate the elements on the surface of the Cd-IIP. It is possible for the spectrum to change following metal uptake. Comparing the EDX spectra before ([Figure 2c](#)) and

after (Figure 2d) adsorption onto the Cd-IIP, there is an obvious cadmium peak in the EDX spectrum after adsorption, which indicates that cadmium was adsorbed on the Cd-IIP. Moreover, the ratio of the atom numbers of S to Cd is 2.1 conforming to the complexation mechanism of dithizone with cadmium ions with molar ratio of 2. The actual value being little greater than theoretical value may be attributed to the maximum adsorption capacity not reached.

3.2. The Influence of pH. It is well-known that the pH of a solution is the most important variables affecting the amount of adsorption of heavy metal ions. It not only has an impact on the protonation of the functional groups on the sorbents but also the solution chemistry properties of the heavy metal ions (such as hydrolysis, complexation, and redox reaction).²⁶ Precipitation of cadmium hydroxide occurs, when the solution is estimated to be $\text{pH} > 8.2$ for $\text{Cd}(\text{OH})_2$ at the highest initial metal concentration of 5 mmol/L of $\text{Cd}(\text{II})$.²⁷ Consequently, the effect of pH on $\text{Cd}(\text{II})$ adsorption by Cd-IIP and NIP were studied at different pH values ranging from 1 to 7, as shown in Figure 3. It was evident that the efficiency of the $\text{Cd}(\text{II})$

Figure 3. Effect of the pH of solution on equilibrium sorption capacity of $\text{Cd}(\text{II})$.

adsorption relied on the pH value of the aqueous solution. The amount of $\text{Cd}(\text{II})$ adsorbed onto the Cd-IIP was approximately 2.3 times that of the Cd-NIP, and the $\text{Cd}(\text{II})$ uptake performance was found to increase sharply with an increase in pH from 1 to 6, and later decrease slightly at pH of 7. When the pH is below pH 3.0, the adsorption capacity of $\text{Cd}(\text{II})$ is low due to the protonation for the $\text{Cd}(\text{II})$ –dithizone complex; when the pH is higher than pH 3.0, a high adsorption capacity of $\text{Cd}(\text{II})$ is obtained as a result of deprotonation of the $\text{Cd}(\text{II})$ –dithizone complex. It can be deduced from these results that the solution pH should be adjusted at pH 6 to obtain the optimal adsorption efficiency, and the material can readily adsorb $\text{Cd}(\text{II})$ from solution in a range of pH 3–7.

3.3. Adsorption Isotherm. Figure 4 and Figure S1 show the adsorption isotherms of Cd-IIP and NIP toward $\text{Cd}(\text{II})$ ions at 298 K, 308 K, and 318 K, respectively, and the detailed data of equilibrium concentration, adsorption capacity, and standard deviation for each temperature are shown in Table S1. It could be observed that the equilibrium adsorption capacity (q_e) of Cd-IIP and NIP for $\text{Cd}(\text{II})$ steadily increased as the initial concentration of $\text{Cd}(\text{II})$ increased from 40 to 200 mg/L, and finally reached the maximum equilibrium adsorption capacity at 250 mg/L and 300 mg/L, while the amount of $\text{Cd}(\text{II})$ adsorbed onto Cd-IIP was approximately 2.3 times of the Cd-NIP at different temperatures. At a constant ion

Figure 4. Adsorption isotherms for Cd-IIP adsorption at different temperatures, insert is the fitting plots of Langmuir model for adsorption isotherm.

concentration, the $\text{Cd}(\text{II})$ uptake dose slightly decreased as the temperature increased. This finding indicated that the adsorption of $\text{Cd}(\text{II})$ was an exothermic process.

Adsorption isotherm experiments have contributed to an understanding of the adsorption property of the cadmium ion-imprinted polymer. Langmuir, Freundlich, and Dubinin–Raduskevich (D–R) isotherms were generally employed to analyze the sorption data in the study. These isotherm modes help the comprehensive understanding of the relationship between the adsorbate and that adsorbed on the sorbent while the two phases were reaching the equilibrium state.²⁸

The Langmuir model is a theoretical equation for which it is supposed that the binding sites on the outer surface of adsorbent are homogeneous and the adsorbate is adsorbed at well-defined sites, leading to monolayer coverage of the adsorbate surface. These sites are also presumed to be energetically identical and distant from each other as well, so that the adsorbed molecules have reactions with those adsorbed on adjacent sites.²⁹ The Langmuir equation could be expressed in the illustrated as

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (5)$$

where q_e (mg/g) and C_e (mg/L) are the equilibrium metal ion adsorption amount and concentration in the solution, respectively. The quantity q_m (mg/g) is the maximum adsorption capacity of metal ions on the ion-imprinted polymer, b (L/mg) is a constant of the Langmuir model.

The essential feature of the Langmuir isotherm is R_L , which is a dimensionless equilibrium parameter that can be predicted. It can be defined as

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where b is the Langmuir isotherm constant and C_0 (mg/L) is the initial concentration of $\text{Cd}(\text{II})$. The value of R_L at different temperatures in the Cd-IIP and NIP studies was calculated and shown in Figure S2a,b. When the value of R_L is between 0 and 1, this suggests favorable adsorption for all the initial concentrations and temperatures studied. Otherwise, a value of $R_L > 1$ indicated unfavorable adsorption.

The Freundlich equation is an empirical expression which is employed to describe a multilayer adsorption on the heterogeneous system. The Freundlich equation can be expressed as

Table 1. Freundlich, Langmuir, and D–R Model Constants of Cd(II) Adsorption on the Cd-IIP at Different Temperatures

T	Freundlich isotherm parameters			Langmuir isotherm parameters			Dunin–Radushkevich parameters		
K	n	K_F	R^2	q_m	b	R^2	K_{DR}	E	R^2
298	1.895	2.483	0.953	63.0	0.009	0.988	0.0206	4.92	0.977
308	1.798	1.789	0.931	56.3	0.007	0.987	0.0212	4.85	0.971
318	1.682	1.186	0.969	49.3	0.006	0.986	0.0215	4.81	0.969

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (7)$$

where K_F ((mg/g)(L/mg)^{1/n}) and 1/n are the Freundlich constants and relate to adsorption capacity and adsorption intensity. If the value of 1/n is in the range of 0 to 1, the adsorption process is feasible and favorable.

The fitting results and constant parameters of the adsorption were calculated from the Langmuir and Freundlich equations for Cd-IIP and NIP and are given in Table 1 and Table S2, respectively. The values of correlation coefficients (> 0.98) of the Langmuir model were a little higher than the values fitting the other two models in all three temperatures studies, indicating that the Langmuir mode was applicable to the adsorption data; the outer surface of the adsorbent is homogeneous and the adsorbate is adsorbed at well-defined sites which identify with the characteristics of the ion imprinting specificity. The values of q_m decreased with the increase in temperature, which was consistent with experimental data. The values of R_L and 1/n are all in the range of 0 to 1, confirming the favorable uptake of the adsorption process. Figure S2 shows the lower R_L values at higher initial concentrations of Cd(II) in solution, indicating that adsorption was more favorable at higher concentrations which was in accordance with the results obtained from the adsorption isotherms. In addition, adsorption on Cd-IIP was more favorable than on Cd-NIP at a constant concentration, suggesting that the Cd-IIP showed much more excellent adsorption performance than Cd-NIP.

The D–R isotherm is similar to the implication of Langmuir isotherm, which assumes the adsorption of single type of uniform pores. In this study, Langmuir mode was applicable to the adsorption data, here, D–R equation can be employed to distinguish physisorption of metal ions from their chemisorption. One of the best feature of the D–R equation lies on the fact that it is temperature-dependent. Combined with the data adsorption isotherms of Cd-IIP and NIP toward Cd(II), the adsorption capacity clearly varies with temperatures. The D–R isotherm model was applied to estimate the porosity apparent free energy, and the characteristics of adsorption^{30,31} which best fit the data are defined by the following equation:

$$\ln q_e = \ln q_m - K_{DR} \epsilon^2 \quad (8)$$

$$\epsilon^2 = RT \ln(1 + (1/C_e)) \quad (9)$$

$$E = (2K_{DR})^{-1/2} \quad (10)$$

where q_e (mg/g) and q_m (mg/g) are the equilibrium and theoretical maximum capacity, respectively; K_{DR} ((mol/J)²) is the activity coefficient related to the free energy of adsorption; ϵ is the Polanyi potential; R is the ideal gas constant (8.314 J·mol^{−1}·K^{−1}), T (K) is the absolute temperature, C_e is the equilibrium concentration; and E (J/mol) is the mean adsorption energy.

Adsorption energy is germane to the adsorption process: when E is less than 8 kJ/mol, physisorption is the major process, otherwise chemisorption is the predominant adsorption procedure.^{32,33} The correlation coefficient values of D–R model (> 0.96) are also high, suggesting that its fittings are reliable. Thus, for the adsorption energy (E) of Cd-IIP and NIP, shown in Table 1 and Table S2, both data values are less than 8 kJ/mol, suggesting that physisorption is the dominant adsorption mechanism.

3.4. Adsorption Thermodynamics. The thermodynamic parameters including standard free energy change ΔG^0 (kJ·mol^{−1}), enthalpy change ΔH^0 (kJ·mol^{−1}) and entropy change ΔS^0 (J·K^{−1}·mol^{−1}) can be calculated from the following equations:

$$\Delta G^0 = -RT \ln K \quad (11)$$

$$\ln K = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (12)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (13)$$

where R is the gas constant (8.314 J·mol^{−1}·K^{−1}), T is the absolute temperature, and K is the thermodynamic equilibrium constant in the adsorption process, which was determined using the method of Wu and Yu³⁴ by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e . Meanwhile, ΔS^0 and ΔH^0 are the intercept and slope, respectively, of the straight line which was plotted by $\ln K$ as a function of $10^3/T$.

The thermodynamic parameters of the sorption of Cd(II) onto the Cd-IIP and NIP were given in Table 2 and Table S3.

Table 2. Thermodynamic Parameters of Cd(II) Adsorption onto the Cd-IIP at Different Temperatures

T	ΔG^0	ΔH^0	ΔS^0
K	kJ/mol	kJ/mol	kJ/mol K
298	−16.20	−25.31	−30.59
308	−15.86		
318	−15.26		

The negative values of ΔG^0 suggested that the adsorption process was spontaneous with a high preference of Cd(II) for the Cd-IIP and NIP. The higher negative value of ΔG^0 reflects a more energetically favorable adsorption which was consistent with the adsorption isotherm results that showed that the optimal adsorption temperature is 298 K.³⁵ The negative values of the enthalpy change ΔH^0 indicated that the adsorption processes were exothermic. Normally, enthalpy value changes between 40 and 120 kJ/mol are attributed to chemisorption, otherwise the values indicate physisorption.³⁶ Therefore, the values of ΔH^0 (IIP: −25.31 kJ/mol, NIP: −17.18 kJ/mol) in this study suggested that the adsorption processes were regarded as physisorption, and the interactions between the polymeric materials and the cadmium ion are mainly

electrostatic (Coulombic interactions) and van der Waals. The negative value of ΔS^0 means a decrease in the freedom during the adsorption, which resulted in significant changes in the internal structure of the adsorbent during the adsorption processes.

3.5. Adsorption Kinetics. The time to reach equilibrium is an important parameter for evaluating the efficiency of adsorption. It can be observed from Figure 5 and Figure 3S

Figure 5. Kinetic adsorption cadmium on Cd-IIP at different initial Cd(II) concentrations. The inset is the fitting plots of the pseudo-second-order kinetic model for Cd(II) adsorption.

that the adsorption capacity of Cd(II) onto Cd-IIP and NIP increases rapidly during the initial 12 min; 8 min later the adsorption capacity slowed, then leveled off as equilibria were arrived at the different initial concentrations of Cd(II). The equilibrium adsorption capacity was greater with higher initial concentrations of Cd(II). The high initial adsorption rate may be due to the strong complexation, plenty of adsorption sites, the high affinity of imprinted cavities of Cd-IIP for Cd(II), and the geometric matching between Cd(II) ions and the imprinted cavities.

To further study the mechanism of adsorption and to determine its potential rate-controlling steps that contain the chemical reaction processes and mass transport, kinetic models including pseudo-first-order, pseudo-second-order, and Weber's intraparticle diffusion model have been employed to analyze the experimental data. These data can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (14)$$

$$\frac{t}{q_t} = \frac{1}{h_0} + \frac{t}{q_e} \quad \text{where, } h_0 = k_2 q_e^2 \quad (15)$$

$$q_t = k_i t^{0.5} + c \quad (16)$$

where t is the contact time (min), q_t and q_e are the individual amounts of Cd(II) adsorbed at an arbitrary time t and at

equilibrium (mg/g), k_1 (min^{-1}) is the pseudo-first-order rate constant, h_0 (mg/g min) is the initial adsorption rate, k_2 ($\text{g}/(\text{mg min})^{-1}$) is the pseudo-second-order rate constant, and k_i ($\text{mg/g min}^{0.5}$) is the rate constant for Weber's intraparticle diffusion model. The parameters of the adsorption were calculated from the Langmuir, Freundlich, and D-R equations for Cd-IIP and NIP.

The kinetic data with a good correlation clearly illuminates the mechanism of the adsorption of metal ions in the solid phase. The pseudo-second-order fitting plots of Cd-IIP and NIP are narrowed in Figure 5 and Figure 3S. The kinetic parameters of the adsorption were calculated from pseudo-first-order, pseudo-second-order, and Weber's intraparticle diffusion model for Cd-IIP and NIP and are presented in Table 3 and Table S4, respectively. In contrast with the pseudo-first-order model, high correlation coefficients are obtained (IIP: $R^2 > 0.995$, NIP: $R^2 > 0.997$). When the pseudo-second-order model is expanded to all concentrations, the calculated q_e is extremely close to the experimental data (q_{exp}). The initial high rate (h_0) of Cd(II) adsorption increases rapidly with an increase of C_0 of Cd(II).

Figure 6 and Figure S4 show the multilinear plots of Cd-IIP and NIP with Weber's intraparticle diffusion, which revealed

Figure 6. Fitting plots of intraparticle diffusion model for cadmium adsorption by Cd-IIP at different initial Cd(II) concentrations.

that there are two steps happening in the adsorption process. These two steps include film diffusion which is the diffusion of cadmium ions from solution to the external surface of the Cd-IIP and NIP (with particle adsorption at a site), and intraparticle diffusion, that is, ion diffusion into the interior of the adsorbent. The rate constants were listed in Table 3 and S4. It can easily be observed that k_{i1} shows an increase in the rate constant for film diffusion with an increasing initial concentration of cadmium, and that the value of k_{i2} was so small that the intraparticle diffusion in the adsorption process can be ignored. The plots in Figure 6 have no zero intercept,³⁷

Table 3. Kinetic Parameters of the Pseudo-first-order, Pseudo-second-order, and Weber's Intraparticle Diffusion Model for Cd-IIP

C_0	pseudo-first-order			pseudo-second-order			intraparticle diffusion		
	k_1	q_e	R^2	$k_2 \cdot 10^{-3}$	q_e	h_0	R^2	k_{i1}	k_{i2}
100	0.139	28.4	0.992	9.3	31.2	9.07	0.995	9.43	0
150	0.196	43.6	0.971	11.0	39.6	16.84	0.996	11.57	-0.091
300	0.181	46.2	0.971	8.9	46.5	19.16	0.997	13.34	0.039

suggesting that intraparticle diffusion was present, but it was not the rate-limiting step.

3.6. Selectivity of Cd(II)-IIP and NIP. Zn(II), Co(II), Pb(II), and Cu(II) are chosen as the competitor ions on account of their identical charge and similar size. Figure 7

Figure 7. Selectivity of Cd(II) adsorption by Cd-IIP and NIP.

shows the uptake of Pb(II), Zn(II), Co(II), Cu(II), and Cd(II) by Cd-IIP and NIP. It can be observed that Cd-IIP and NIP exhibit a much larger adsorption capacity for Cd(II) than for other ions and selectivity for other metal ions except other than Cd(II) is absent.

The distribution ratios, selectivity factors, and relative selectivity coefficients were calculated in Table 4. We can see

Table 4. Selective Adsorption Property of Cd-IIP and NIP

metal ions	Φ (pm)	$\log \beta_n$	Cd(II)-IIP		β	Cd(II)-NIP	
			K_D	α		K_D	α
Cd(II)	95	16.4	217.3			93.67	
Zn(II)	74	16.4	71.3	3.05	1.32	40.6	2.31
Pb(II)	119	18.3	79.1	2.75	1.64	55.9	1.68
Cu(II)	73	18.7	79.4	2.74	1.23	42	2.23
Co(II)	74.5	16.3	88.1	2.47	1.18	44.9	2.09

that the distribution ratio of the Cd-IIP for Cd(II) was much greater than that of the Cd-NIP. Furthermore, the relative selectivity factors of the ion-imprinted polymer for each individual metal ion were greater than 1.68. Each individual metal with its ionic radius (Φ) and the stability constants of its complexes with EDTA ($\log \beta_n$) is also listed in Table 4. The stability constants of dithizone are similar to those of EDTA because when the coordinating atoms are the same, there will be a similar ligand structure for the same metal. The above results implied that the imprinted cavities and specific binding sites in a predetermined orientation were formed in the Cd-IIP, and the sizes of Pb(II), Zn(II), Co(II), and Cu(II) do not match well with the cavity imprinted by Cd(II), although its stability constants higher than Cd(II), resulting in a high recognition ability and high selectivity of Cd-IIP for the Cd(II) ions.

3.7. Adsorption Mechanism. FTIR spectra (Figure 8a,b) were used to confirm the functional groups and surface

properties of the Cd-IIP, which was analyzed in the range of 400 to 4000 cm^{-1} both in the free state and loaded with Cd(II). We can clearly see that change in band shifts and the intensities decrease for several bands. The peaks (curve a) at 1161 cm^{-1} and 1259 cm^{-1} were the stretching vibration of the C–N bond in the N–C=S and C–N–N groups, the 1389 cm^{-1} peak was the C–N=N stretching vibration in dithizone. All three groups had shifted to 1163, 1261, and 1392 cm^{-1} , respectively (curve b), which was evidenced that the N groups were related to Cd(II) adsorption. The reason for the wavenumber increase is that the N donated the electron to the metal ion Cd(II) then generated an electron transition. Bands at approximately 2987 cm^{-1} and 3451 cm^{-1} were observed because of the stretching vibration of the N–H group in dithizone. The 3451 cm^{-1} peak that almost vanished is attributed to the H in the N–H group that was replaced by the metal ion Cd(II). A conclusion can be drawn, that the amino group is the major functional group involved in cadmium bonding.

XPS was further performed to confirm the adsorption mechanism. The typical XPS wide scan spectra for Cd-IIP are shown in Figure 8 panels c and d. Herein, the N 1s spectrum of the Cd-IIP (Figure 8c) could be decomposed into four peaks with the 398.48 eV peak representing N–N, the 399.39 eV peak representing N=N, the 400.39 eV carboxyl nitrogen peak as N–N–C₆H₅, and the 401.74 eV carboxyl nitrogen peak as N=N–C₆H₅. After adsorption (Figure 8d), the binding energy values of N–N, N=N, N–N–C₆H₅, and N=N–C₆H₅ groups increased to 398.57, 399.95, 400.95, and 401.9 eV, respectively, which indicates that the N groups are involved in Cd(II) adsorption. A lone pair of electrons from the N atoms is shared with Cd(II), thus the electron cloud density of the N atoms is decreased, especially the N atom of the N=N, N–N–C₆H₅, and N=N–C₆H₅ bonds, which obviously shift owing to their relatively stronger conjugation effect compared to that of the N–N. Hence, the adsorption of Cd(II) was followed by a charge transfer from these groups to Cd(II), which confirmed that the N–N, N=N groups served as the sorption sites.

3.8. Reusability Study and Application of Cd-IIP. The stability and reusability of Cd-IIP are key factors for improving the process economics (Figure 9); meanwhile, the applicability to real environmental water samples of the Cd-IIP is also necessary. The regenerated Cd-IIP was reused for five cycles of adsorption–desorption. It can be observed that the adsorption capacity of Cd-IIP was stable within the first three cycles with little decrease in the adsorption capacity for Cd(II), but that the adsorption capacity of Cd-IIP was approximately 22 % and 32 % loss in the fourth and fifth cycles, respectively. It can be concluded that Cd-IIP exhibits relatively good adsorption efficiency after regeneration, and could be used repeatedly.

To validate the applicability of the Cd-IIP for the removal of Cd(II) ions in real environmental water samples, lake water (Tianyi Lake, Nanchang) and river water (Ganjiang river, Nanchang) were selected and analyzed.³³ The lake water and river water were spiked with 10 mg/L of Cd(II), Pb(II), Zn(II), Co(II), and Cu(II), respectively. The several water samples (50 mL) were treated with 100 mg of Cd-IIP and Cd-NIP at an initial pH of 6.5 for 4 h. The Cd-IIP and NIP show almost 90 % and 46 % removal efficiency, respectively, which suggests that Cd-IIP has a strong anti-interference ability in real environmental water samples.

Figure 8. FT-IR spectra and N 1s of XPS spectra of the free (a) and loaded (b) Cd(II) onto Cd-IIP.

Figure 9. Reusability of Cd-IIP.

4. CONCLUSIONS

In the present work, a new Cd-IIP using MAA and dithizone as complexation agents was prepared for selective separation and decontamination of Cd(II) from aqueous and environmental samples. Both of these experiments demonstrated that several nitrogen functional groups were involved in the sorption of Cd(II) and that the Cd(II) adsorption on the ion-imprinted polymer was pH dependent. The adsorption isotherm data were better fitted to the Langmuir equation, indicating the formation of a monolayer coverage of Cd(II) on the ion-imprinted polymer surface and the adsorbate is adsorbed at well-defined sites. The better fit of the pseudo-second-order kinetic model suggested that the rate-limiting step may be chemical adsorption. Thermodynamic parameters manifested that the adsorption was a spontaneous, exothermic process. The relative selectivity coefficients for Cd(II)/Zn(II), Cd(II)/Cu(II), Cd(II)/Co(II) and Cd(II)/Pb(II) were greater than 1.68, indicating that the imprinting technology resulted in the increased affinity of the imprinted polymer for Cd(II) over other metal ions compared with the nonimprinted polymer. Moreover, the imprinted polymer had a superior reusability and stability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00494.

Chemical reagents and apparatus; methods of synthesizing the complexes; batch adsorption experiments; additional figures and tables (PDF)

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Notes

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