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Preparation and High Reusability of a Novel Acid-Resistant Magnetic Weak Acid Resin for Ni²⁺ Removal

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Ⓢ *Supporting Information*

ABSTRACT: A novel magnetic weak acid resin (MWA06) was successfully synthesized and characterized. To enhance the acid resistance and lipophilicity of the γ-Fe$_2$O$_3$ particles, a titanate coupling agent (TCA) was employed to modify the particle surface. Afterward, the resultant resin was obtained through copolymerization and hydrolysis reactions, with a specific saturation magnetization of 10.9 emu/g and weak acid cation exchange capacity of 8.44 mmol/g. Leaching tests in acid showed that the magnetic resin was stable at pH 2. The presence of Ca^{2+} in the solution had an obviously negative impact on the adsorption of Ni^{2+}, whereas Na$^+$ did not influence the adsorption process. The adsorption of Ni^{2+} was pH-dependent as the uptake capacity increased from 0.06 to 2.81 mmol/g with the pH rising from 2 to 6. The desorption efficiency was nearly 100% by using 0.01 M HCl solution as desorption agent. Moreover, MWA06 could maintain high adsorption capacities for at least 10 regeneration cycles, indicative of a good reusability.

1. INTRODUCTION

Heavy metal ions could cause serious environmental problems,[1,2] even at very low concentrations.[3] Therefore, much attention has been paid to the development of effective technologies for the treatment of heavy metal ions in aqueous solutions.

In recent years, various methods have been proposed for the removal of heavy metal ions in environmental samples, such as liquid–liquid extraction, precipitation, membrane separation, ion exchange, electrolysis, and physical adsorption.[4–11] Among these techniques, ion exchange has been considered to be a simple and effective approach for the elimination of heavy metal ions.[11–13] Cation-exchange resins, natural clinoptilolite, and some composites have been successfully used to remove heavy metal ions from aquatic solutions.[3,14–18]

For practical applications, ion-exchange resins are often packed in a fixed-bed column, through which the water passes to separate the heavy metal ions. However, the application of this technology is limited by the high reversed pressure and the large operation costs, which are only suitable for the treatment of wastewater with high concentrations and small fluxes.[19,20] Nevertheless, heavy metal ion pollution typically occurs at low concentrations in very large volumes of water, which requires novel methods with fast removal kinetics and easy operation property. Recently, several magnetic resins were developed and successfully applied for wastewater treatment.[19–22] Owing to the facile separation properties, magnetic resins could be used in small particle sizes to accelerate the adsorption process. Meanwhile, completely mixed contactors can be applied instead of fixed beds, which increase the flux and decrease the cost.

Previous studies showed that the magnetic weak acid resin MIEX-Na could be employed to remove Ca^{2+} and Mg^{2+} from water,[23] but the adsorption capacity quickly diminished after regeneration by a salt solution.[24] This result was mainly due to the fact that salt solution was a poor regeneration reagent for weak acid resins. In contrast, acidic solutions have been proven to be the most effective agents and are commonly used for cation desorption from weak acid resins.[12,16,25] However, the considerable corrosion of the magnetic particles in acid greatly impedes the application of magnetic resins for metal removal.

The specific objectives of this work were as follows: (1) synthesize a magnetic weak acid resin; (2) evaluate the acid resistance of the resulting resin; (3) investigate the effect of solution pH, ionic strength, and pore size of the resin on the adsorption behaviors; and (4) evaluate the reusability of the resultant beads. Ni^{2+} was employed as the target metal cation because of its extensive discharge from industry and its toxicity to organisms.[26,27]

2. EXPERIMENTAL SECTION

2.1. Preparation of Magnetic Weak Acid Resin. Industrial products of divinylbenzene (DVB; 63.6%), methyl acrylate (MA), γ-Fe$_2$O$_3$, and vinyltrimethoxysilane (VTS) were purchased from commercial vendors. The other chemicals used for the synthesis of magnetic weak acid resins were analytical grade. As shown in Supporting Information Scheme S.1, the synthetic reaction was performed in the following two steps.

2.1.1. Modification of γ-Fe$_2$O$_3$ Particles. The γ-Fe$_2$O$_3$ particles (20 g) were dispersed in methanol in the presence of VTS (0.3 g). Then, 30 mL of ammonium solution (25%, w/w) was added followed by 6 h of incubation at 318 K under vigorous agitation. Finally, the particles were separated with a magnet. After washing with methanol five times, the VTS-modified γ-Fe$_2$O$_3$ particles were dried at 338 K. The magnetic
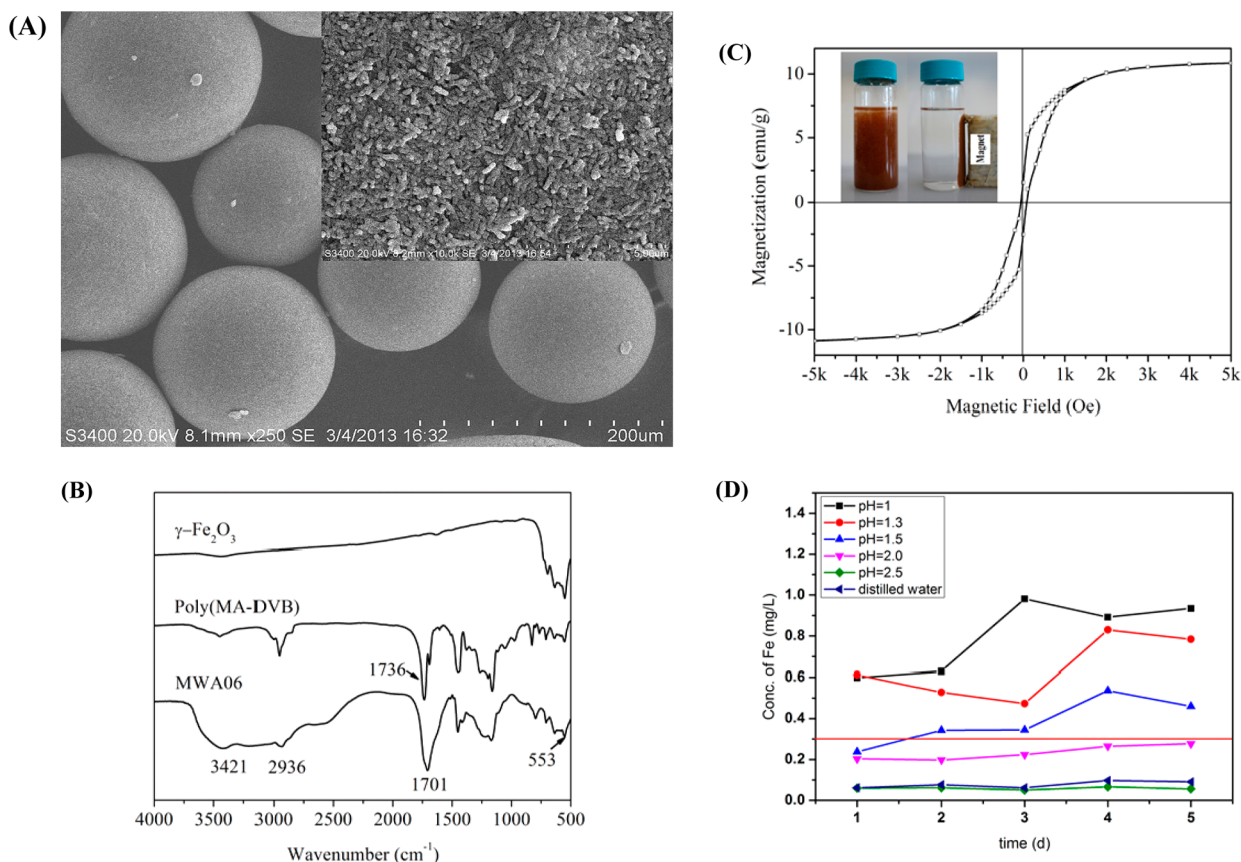
Figure 1. Characterization of the obtained magnetic weak acid resin, (A) SEM images, (B) FTIR spectra, (C) magnetization curves, and (D) concentration of Fe dissolved in acid solution.

particles were protected under a nitrogen atmosphere during the entire preparation process.

2.1.2. Preparation of Magnetic Poly(MA-co-DVB) Resin. The magnetic poly(MA-co-DVB) resin was synthesized through suspension polymerization. MA (84.3 g) and DVB (15.7 g) were mixed in a 1 L three-necked flask in the presence of the VTS-modified γ-Fe$_2$O$_3$ particles (20.0 g). Benzoyl peroxide (BPO, 1.0 g) was employed as the initiator. Subsequently, the aqueous dispersed phase (500 mL) containing 18 wt % NaCl and 1.2 wt % gelatin was transferred into the flask. The mixture was heated at 353 K for 18 h with vigorous agitation. After rinsing with methanol and deionized water, the obtained poly(MA-co-DVB) beads were dried at 333 K. For hydrolysis, the poly(MA-co-DVB) beads were fully swelled in methanol, and sodium hydroxide solution (20 wt %, 200 g) was added. The magnetic weak acid resin (MWA06) was then obtained after washing with deionized water to neutral pH and drying at 333 K.

2.2. Characterization. Scanning electron microscopy (SEM) analysis was conducted with an S-3400N II instrument (Hitachi, Japan) to observe the morphology of the obtained resin. The functional groups of the obtained resins were examined by Fourier transform infrared spectrophotometry (FTIR, Nexus870, Nicolet, USA). The magnetization curves of the magnetic resin were measured using a vibrating sample magnetometer (VSM, Quantum Design MPMS-5S). The surface area and pore size distribution were detected by nitrogen adsorption and desorption experiments using the BET equation, and all calculations were performed automatically using an accelerated surface area and porosimeter system (ASAP 2010, Micromeritics, USA).

2.3. Adsorption Assay. The magnetic weak acid resin was converted to the sodium form (MWA06-Na) by soaking in sodium hydroxide solution (2 wt %) for 30 min and washing to neutral pH with deionized water. Batch experiments were performed by introducing the resin (0.1 g) and 100 mL of Ni^{2+} solution into a series of 250 mL conical flasks. The flasks were then placed in an incubator shaker at a preset temperature and a shaking speed of 150 rpm. The 0.1 M HCl and NaOH solutions were employed to adjust the solution pH. For the kinetics studies, 500 mL of 1.0 mM Ni^{2+} solution were shaken with 0.1 g of magnetic resins at 150 rpm at 293 K in three conical flasks, and the solutions were sampled at different time intervals.

The resin was regenerated using acid and basic solutions as follows. At first, the resin was shaken for 2 h with 50 mL of hydrochloric acid (pH = 2), which converted the resin to the hydrogen form. Afterward, sodium hydroxide was added to reach a pH of 12 to transform the resin to the sodium form. Finally, the resin was rinsed to neutral pH with deionized water. To test the reusability of the magnetic resin, this adsorption–regeneration cycle was repeated 10 times.

In this work, the concentration of Ni^{2+} in the aqueous solution was determined using an atomic absorption spectrophotometer (Thermo ICE3500, USA).

3. RESULTS AND DISCUSSION

3.1. Characterization. The titanate coupling agent was employed to enhance the acid resistance and lipophilicity of the

γ-Fe$_2$O$_3$ particles. The poly(MA-DVB) beads were prepared via polymerization in the presence of coated magnetic particles. Subsequently, well-shaped beads with diameters ranging from 100 to 150 μm were obtained (Figure 1A) through the hydrolysis reaction of the poly(MA-DVB) beads. The presence of the γ-Fe$_2$O$_3$ particles in the resin skeleton resulted in the rough surfaces of the beads.

Figure 1B shows the FTIR spectra of the γ-Fe$_2$O$_3$ particles, poly(MA-DVB) beads, and the resultant MWA06 beads. Consistent with γ-Fe$_2$O$_3$, the absorption band at 553 cm^{-1} of poly(MA-DVB) and MWA06 was attributed to the Fe−O bond. The absorption band at 1736 cm^{-1} in the spectrum of poly(MA-DVB) corresponded to the stretching vibrations of the ester carbonyl groups, which shifted to 1701 cm^{-1} in the spectrum of MWA06. This shift confirmed the occurrence of the hydrolysis reaction.[11,12,28] The broad band at 3421 cm^{-1} in the spectrum of MWA06 was attributed to the carboxylic hydroxyl groups.

The magnetization curve of MWA06 is depicted in Figure 1C. The specific saturation magnetization (SSM) of MWA06 was 10.9 emu/g, which is sufficient for magnetic separation using an ordinary magnet.

To evaluate the acid resistance of MWA06, the beads were soaked in acid solution, and the concentration of dissolved Fe in the acid solution was detected. As shown in Figure 1D, the content of Fe in the solution increased with contact time at pH = 1.5. However, no significant increases in the Fe concentrations were observed when the solution pH was higher than 2. This result implied that the 0.01 M HCl solution (pH = 2) would not corrode the γ-Fe$_2$O$_3$ in the skeleton of the MWA06 beads if it was used as desorption agent.

3.2. Adsorption Kinetics. The pore size of the resin influences the adsorbate diffusion and further affects the adsorption kinetics.[20] Hence, a series of magnetic weak acid resins with diverse pore sizes were prepared using different porogen/monomer ratios.[29] The physicochemical properties of the obtained magnetic resin are listed in Table 1. MWA05, with

Table 1. Physicochemical Properties of the Employed Magnetic Weak Acid Resins

	MWA05	MWA06	MWA07
porogen/monomer ratio	0	3:10	1:1
WAEC^a (mmol/g)	2.94	8.44	8.63
Specific surface area (m^2/g)	2.19	1.89	3.67
average pore diameter (nm)	5.61	6.40	6.65
sphericity after osmotic-attrition (%)	89.71	84.26	51.62

^{a}Weak acid cation exchange capacity.

no porogen added during the preparation process, had a compact matrix and low average pore size. The addition of porogen would make the resin matrix more open and create abundant meso- and macropores,[30] rendering a larger average pore size. As a result, more functional groups inside the resin could be available. Therefore, the WAEC of the magnetic resin increased with the rise of porogen/monomer ratio. However, excessive functional groups in the channel of the resin might occupy the adsorption sites of N$_2$ during the nitrogen adsorption/desorption experiments, leading to the slight decrease of surface area for MWA06. On the other hand, the pore structure of MWA07 was more abundant resulting from the high porogen/monomer ratio of 100%. Hence, the

influence of functional groups on the surface area of MWA07 was not obvious.

The adsorbed amounts of Ni^{2+} on the magnetic weak acid resins with different pore diameters as functions of t and $t^{0.5}$ are depicted in Figure 2A,B, respectively. The pseudo-first-order
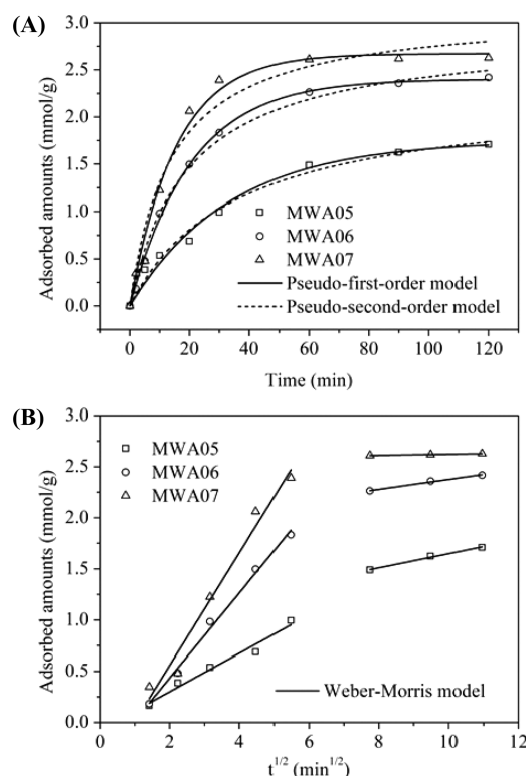
Figure 2. Effect of pore diameter on the adsorption of Ni^{2+}: (A) Langmuir and Freundlich model and (B) Weber-Morris model (0.1 g resin, C_0 = 2.5 mM, T = 293 K, pH = 5.5).

equation, pseudo-second-order equation, and Weber-Morris equation (Supporting Information Equations S.1 to S.5) were used to elucidate the adsorption behaviors on the three employed resins. The fitting coefficients are listed in Table 2. According to the correlation constants (r), the adsorption of Ni^{2+} fitted well with all three equations ($r > 0.96$). The value of $t_{1/2}$ (the time when the adsorption capacity reaches half of the equilibrium capacity) clearly decreased from MWA05 (35.81 min) to MWA07 (13.94 min), indicating that the highest adsorption rate was achieved with MWA07. Similarly, the initial reaction rates (h_0) increased in the order MWA05 < MWA06 < MWA07. These phenomena were both ascribed to the differences in the pore structures of the employed resins. The larger pore size meant less resistance for the diffusion of molecules in the pores of the adsorbent, which resulted in a faster sorption rate. The higher WAEC provided more adsorption sites for the adorbates. Therefore, the highest equilibrium adsorption capacity (q_e value) was obtained by MWA07. Larger intercept (I) of the Weber-Morris equation indicated a greater contribution of the surface sorption as the rate-controlling step.[31] Therefore, the trend of the intercept (absolute value of I, MWA05 < MWA06 < MWA07) confirmed that larger pore size was beneficial for adsorption.

However, as shown in Table 1, the sphericity of the resin at the porogen/monomer ratio of 1:1 (w/w) after osmotic attrition was very low, suggesting poor strength of the beads

Table 2. Kinetic Constants for the Adsorption of Ni^{2+} onto the Magnetic Weak Acid Resins

resin	pseudo-first-order model			pseudo-second-order model					Weber-Morris model (before 30 min)		
	$k_1/10^{-3}$	q_e	r	$k_2/10^{-3}$	q_e	h_0	$t_{1/2}$	r	K_{d1}	I_1	r
MWA05	29.91	1.75	0.9847	12.41	2.25	0.06	35.81	0.9867	0.19	−0.076	0.9654
MWA06	48.71	2.40	0.9989	17.76	2.89	0.15	19.48	0.9940	0.41	−0.393	0.9926
MWA07	64.40	2.67	0.9879	22.99	3.12	0.22	13.94	0.9655	0.55	−0.545	0.9665

with larger porogen ratio. Although the porogen/monomer ratio of MWA06 was lower than that of MWA07, MWA06 also contained a high WAEC and large pore diameter, which were both comparable to those of MWA07. Therefore, MWA06 resin was employed for further studies.

3.3. Isotherms. The equilibrium adsorption amounts of Ni^{2+} as a function of the equilibrium concentration of the metal ions are depicted in Supporting Information Figure S1. The adsorption capacities of Ni^{2+} onto the magnetic resin increased with temperature rise, which was in accordance with the principles of chemical adsorption. The most commonly used equations, the Langmuir and the Freundlich model (Supporting Information Equations S.6 and S.7), were employed to fit the isotherm data.

The fitting results are listed in Table 3. With higher values of correlation coefficient (r), the Langmuir model was considered

Table 3. Obtained Constants of Ni^{2+} Adsorption onto the Magnetic Weak Acid Resins for Langmuir and Freundlich Equations

	Langmuir Model			Freundlich Model		
T (K)	K_L (10^3)	Q_m	r	K_F	n	r
278	1.85	2.89	0.9510	2.94	48.65	0.8117
293	4.54	2.95	0.9363	3.03	46.38	0.8842
308	9.07	2.97	0.9371	3.04	51.68	0.8552

more suitable for describing the adsorption process of Ni^{2+}, which suggested a monolayer-type adsorption for the adsorption of the Ni^{2+} onto MWA06. The values of K_L (representing the affinity of adsorbent for the adsorbates) increased with increasing temperature, consistent with the tendency of Q_m (representing the maximum adsorption capacity).

3.4. Binary Competitive Adsorption. The influence of Na^+ and Ca^{2+} were investigated, as these cations represent the majority of alkali and alkaline earth metal ions in natural water and wastewater.[32] The results are depicted in Figure 3. The
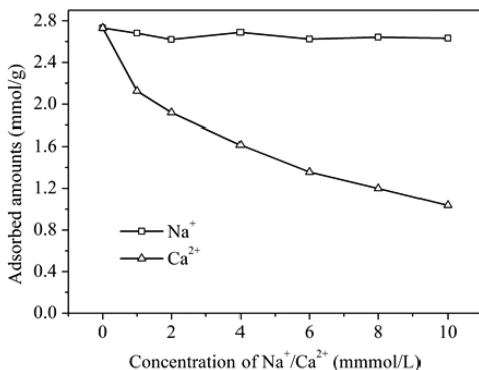

Figure 3. Effect of Na^+ and Ca^{2+} on the adsorption of Ni^{2+} by MWA06 (0.1 g resin, C_0 = 3.0 mM, T = 293 K, pH = 5.5).

results indicated that the adsorption capacities of MWA06 for Ni^{2+} were not influenced by increasing concentrations of Na^+ in the medium. Therefore, the MWA06 selectively adsorbed Ni^{2+} and strongly coordinated with it in a Na^+ solution. However, the adsorption of Ni^{2+} onto MWA06 was affected in the presence of Ca^{2+}. At Ca^{2+} concentrations ranging from 0 to 2 mM, the adsorption capacity of Ni^{2+} decreased from 2.73 mmol/g to 1.95 mmol/g. Consequently, the magnetic resin could be effectively used for Ni^{2+} removal from surface freshwater, in which the concentrations of Ca^{2+} generally range from 0.37 mM to 1.87 mM.[25] Nevertheless, when the concentration of Ca^{2+} increased to 10 mM, the adsorption capacity of Ni^{2+} decreased by 62.0%. This drastic decrease in adsorption capacity was likely due to the occupation of the adsorption sites on the resin surface by outer-sphere surface complexes formed by Ca^{2+} and water molecules.[33]

3.5. Effect of Solution pH. Solution pH is one of the most important factors that influence the form of adsorbent and the species of adsorbate. Hence, considering the stability limits of the magnetic weak acid resin (pH ≥ 2) and the precipitation limits of Ni^{2+} (pH = 7),[34] the influence of solution pH ranging from 2 to 6 was evaluated. As shown in Figure 4, the adsorption
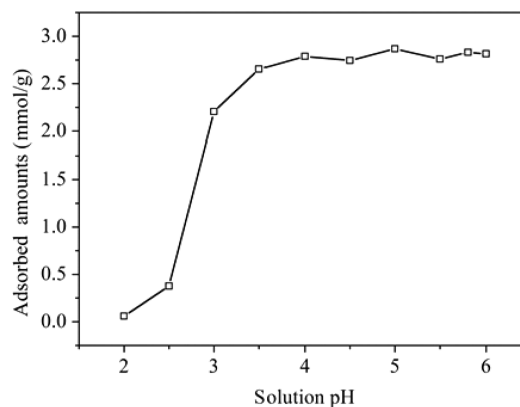

Figure 4. Influence of pH on the adsorption capacities of Ni^{2+} (0.1 g MWA06, C_0 = 3.0 mM, T = 293 K).

capacity of Ni^{2+} increased with increasing pH at lower solution pH and reached the maximum value of 2.81 mmol/g at pH 4. The low uptake capacity in acidic solutions was mainly due to the slight dissociation of the carboxyl groups on the resin and the competitive binding between the divalent ions and hydrogen ions for the binding sites on the magnetic adsorbent.[35] A negligible uptake capacity of 0.06 mmol/g was observed at pH 2, which suggested a potential regeneration method.

3.6. Desorption. It has been reported that acidic solutions and NaCl solutions are efficient for the desorption of weak acid resins.[16,22] In this work, the desorption efficiencies of a HCl solution and a NaCl solution were investigated. As shown in Figure 5, although the desorption efficiencies of Ni^{2+} increased
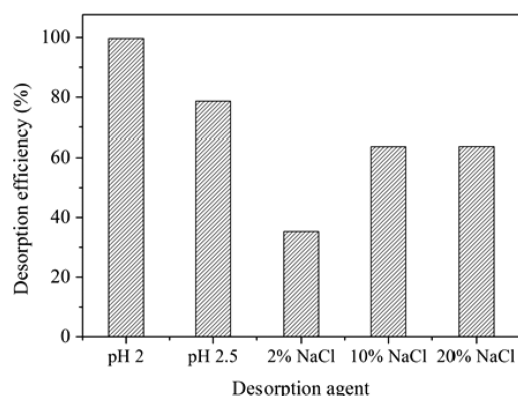
Figure 5. Desorption efficiencies by different agents.

with increasing concentrations of NaCl, the achieved results were unsatisfactory. The poor desorption performance of the NaCl solution was consistent with the noninfluence of Na^+ on the adsorption of Ni^{2+} (Figure 3). In contrast, the desorption efficiency was nearly 100% using HCl solution (pH 2), which was in accordance with the negligible adsorption capacity of Ni^{2+} in the same acidic solution (Figure 4). Therefore, the HCl solution at pH 2 was used as the desorption solvent.

3.7. Reusability. The reusability of the resin is one of the most important parameters to evaluate whether an adsorbent is appropriate for practical applications. The reusability of the MWA06 was investigated by repeating the adsorption/ regeneration process 10 times. The MWA06 resin was regenerated using a series of acid and base solutions as follows. The resin was stirred in HCl solution at pH 2, which converted the resin to the hydrogen form. Subsequently, sodium hydroxide was added until a pH of 12 was reached to convert the resin to the sodium form. Finally, the resin was washed to neutral pH using DI water. As shown in Supporting Information Figure S2, no appreciable loss of adsorption capacity was observed after 10 cycles, which indicated the perfect reusability of MWA06. Moreover, no obvious decrease of the specific saturation magnetization of the beads was observed after 10 times of repeated uses.

4. CONCLUSIONS

A novel magnetic weak acid resin with high cation-exchange capacity was successfully prepared and characterized in this work. The resulting magnetic beads could tolerate the erosion of 0.01 M acid (pH 2). The adsorption kinetics of Ni^{2+} onto the resulting magnetic resin followed both pseudo-first-order and pseudo-second-order equations. The sorption rate was closely associated with the pore size of the resin. Larger pore sizes meant less resistance for the diffusion of the molecules in the pores of the resin and faster sorption rates. The Langmuir equation was found to fit the isotherm data well, which indicated a monolayer adsorption of Ni^{2+} onto the MWA06. The maximum adsorption capacity of Ni^{2+} onto MWA06 was 2.97 mmol/g. Negligible effects of Na^+ were observed, whereas the presence of Ca^{2+} in the solution negatively impacted the adsorption of Ni^{2+}. Higher uptake capacities of Ni^{2+} onto MWA06 were obtained at higher pH values (pH between 4 and 6), and negligible adsorption was observed at pH 2. The 0.01 M HCl solution was found effective for nearly complete regeneration, and the novel magnetic resin could be reused for a minimum of 10 times with negligible decreases in adsorption capacity and saturation magnetization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Preparation steps of magnetic weak acid resin; adsorption isotherms; effect of regeneration cycles on the adsorption capacity; detailed explanation of pseudo-first-order, pseudo-second-order, Langmuir, and Freundlich equations. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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