

An Ion-imprinted Silica Gel Polymer Prepared by Surface Imprinting Technique Combined with Aqueous Solution Polymerization for Selective Adsorption of Ni(II) from Aqueous Solution

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Abstract A novel Ni(II) ion-imprinted silica gel polymer was prepared *via* the surface imprinting technique combined with aqueous solution polymerization by using 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) as a functional monomer for the selective separation of Ni(II) from aqueous solution. The sorbent showed good chemical and thermal stability. Kinetics studies indicated that the equilibrium adsorption was achieved within 10 min and the adsorption kinetics fitted well with the pseudo-second-order kinetic model. The maximum adsorption capacity of the ion-imprinted polymer towards Ni(II) at the optimal pH of 7.0 was 66.22 mg·g⁻¹. The relative selectivity coefficients of the sorbent were 9.23, 15.71, 14.72 and 20.15 for Ni(II)/Co(II), Ni(II)/Cu(II), Ni(II)/Zn(II) and Ni(II)/Pb(II), respectively. The adsorption isotherm fitted well with Langmuir isotherm model. The thermodynamic results indicated that the adsorption of Ni(II) was a spontaneous and endothermic process. The sorbent showed good reusability evidenced by six cycles of adsorption/desorption experiments. The precision of this method is satisfactory. Thus, the prepared sorbent can be considered as a promising sorbent for selective separation of Ni(II) in real water samples.

Keywords Ion-imprinted polymer; Ni(II) ion; Surface imprinting technology; Selective adsorption; Aqueous solution polymerization

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INTRODUCTION

Heavy metal ions are toxic and harmful to human beings, aquatic-life and environments. The toxicity of heavy metal ions is mainly due to their difficulty of biodegradation and easiness of accumulation in organisms' bodies^[1]. Nickel(II) is an essential trace element in the human body, but the higher concentration of Ni(II) can damage the central nervous system, leading to a variety of skin disease and cancers such as nickel-eczema among women^[2]. Therefore, removal of Ni(II) from aqueous solution has become a significant research project. Currently, there are various kinds of methods for removing heavy metal ions, including chemical precipitation, electrochemical treatment, ion exchange, flotation, membrane filtration, adsorption, coagulation and flocculation *etc*^[3]. Among these methods, the adsorption method is widely used due to its unique merits of easy operation, cost-effective, highly efficient process and sorbents' recyclability^[4]. However, conventional adsorbents lack the selectivity for specific metal ions.

Ion imprinted polymers (IIPs) as a new type of materials have attracted wide attention, which exhibit high adsorption

capacity and excellent selectivity for metal ions^[5–7]. IIPs were described by Nishide and Deguchi for the first time in 1976^[8]. They are similar to the molecular imprinted polymers (MIPs) but their targets (template) are inorganic ions^[9]. These materials are prepared by the polymerization between functional monomers and crosslinkers around the template ions, and then the template ions are leached, leaving the binding sites matched to the target ions in shape, size and chemical functionality^[10, 11]. Such imprinted polymers show remarkable recognition properties for the target ions. The conventional approaches for the preparation of IIP include bulk polymerization^[12], suspension polymerization^[13] and precipitation polymerization^[14]. Unfortunately, the obtained traditional imprinted materials display poor site accessibility to the target ions since the binding sites are completely embedded in the polymer matrix, which is unfavorable to the kinetics of sorption-desorption process^[15]. Surface imprinting technique is proposed to solve such difficulty. The point of this technique is to fix the complex of functional monomers and the target metal ions to the surface of matrix. The surface imprinted polymers prepared by this method have more accessible sites, fast binding kinetics and good selectivity^[16, 17]. Silica gel has been widely applied as a matrix for the surface imprinting material because of its excellent mechanical stability even under acidic conditions

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and easy modified silanol groups (Si—OH) on the surface of silica gel^[18]. To date, a large number of ion-imprinted silica gel sorbents have been prepared by surface imprinting technique for removing metal ions, such as AsO_4^{3-} , Fe^{3+} , Ni^{2+} , Cd^{2+} and Pb^{2+} ^[19–23] etc. In addition, a few Ni(II) ion surface-imprinted silica polymers have been prepared by surface imprinting technique, whose functional monomers or ligands are 3-aminopropyl trimethoxy silane^[17] and chitosan^[24].

As the literature reported, almost all of the surface imprinted polymers were prepared by bulk polymerization with organic solvents and porogens^[25, 26]. That is to say, the template metal ions are identified in the organic phase during the preparation process, but their cognition of target metal ions is in the water environment. According to the principle of similar dissolve mutually, the solubility of metal ions in water is much greater than that in organic solvents. Hence, the adsorption capacity of surface-imprinted polymers prepared by aqueous solution polymerization may be greater than that of the polymers prepared by bulk polymerization.

In the present study, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is selected as a water-soluble functional monomer to prepare the novel Ni(II) ion surface-imprinted polymer. AMPS is a borderline base that contains sulfonic acid ($-\text{SO}_3\text{H}$) groups and prefers to combine with borderline acid Ni(II) based on the Lewis theory of acids and bases. The surface imprinted silica gel polymer was prepared by aqueous solution polymerization for selective adsorption of Ni(II) from aqueous solutions. The characterization and adsorption properties of Ni(II) ion surface-imprinted silica gel polymer were studied and discussed in detail.

EXPERIMENTAL

Apparatus

The pH measurements were carried out with a pH meter (PHS-3C, Shanghai, China). Fourier transform infrared (FTIR) measurement was performed using a FTIR spectrometer (Nicolet iS10, Waltham, USA). The surface morphology measurement was conducted by scanning electron microscopy (SEM) (Quanta-250, FEI, USA). The thermal stability analysis was carried out with a thermo-gravimetric analyzer (TG/DTA 6300, SII, Japan). Surface areas were measured by a Brunauer-Emmett-Teller (BET) surface area analyzer (NOVA3200e, Quantachrome, USA). The concentration of metal ions was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Spectro Arcos, Spectro, Germany).

Chemicals and Reagents

Silica gels (60–100 mesh) were purchased from Ocean Chemical Company (Qingdao, China). 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and N,N' -methylenebisacrylamide (MBA) were purchased from Sigma-Aldrich (Milwaukee, USA). Ammonium persulfate (APS), sodium hydrogen sulfite (NaHSO_3) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Sinopharm (Beijing,

China). All other reagents were obtained from Beijing Chemical Plant (Beijing, China). All reagents were of analytical grade. All aqueous solutions were prepared using deionized water.

Real Water Sample Preparation

The standard solution of Ni (GBW080128) was purchased from National Institute of Metrology, Beijing, China. The real water samples were collected from tap water (the laboratory) and lake water (Beijing, China). All of the samples were filtered through a 0.22 μm polyethersulfone (PES) membrane and irradiated by UV light for 2 h, and then pH was adjusted to 7 by 0.1 $\text{mol} \cdot \text{L}^{-1}$ HNO_3 or 0.1 $\text{mol} \cdot \text{L}^{-1}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution and stored at 4 °C.

Synthesis of Ni(II) Ion-imprinted Silica Gel Polymer (IIP-AMPS/SiO₂)

Synthesis of *N*-propylmaleamic acid-functionalized silica gel (SG-PMA)

SG-PMA was prepared according to the described method in the previous report^[22]. Briefly, 5 g of SG-*N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (SG-AAPTS) and 2.5 g of maleic anhydride were dispersed in 100 mL of tetrahydrofuran with stirring at room temperature for 24 h. Then, the product was washed by tetrahydrofuran and ethanol successively, finally dried in vacuum at 60 °C for 12 h.

Synthesis of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂

The synthesis of Ni(II) ion-imprinted silica gel polymer was carried out by surface imprinting technique combined with aqueous solution polymerization. Firstly, 1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (template ion) and 12 mmol of AMPS (functional monomer) were dissolved in 50 mL of deionized water at room temperature. After stirring for 1 h, 1 g of SG-PMA was added and the mixture was stirred for 12 h. Then, 6 mmol of MBA (crosslinker) and 150 mg of APS and NaHSO_3 with the mass ratio of 2:1 (redox initiator) were added into the mixture that was stirred for 30 min under nitrogen atmosphere. The mixture was maintained at 40 °C for 12 h. After polymerization, the obtained polymers were filtered, washed with deionized water, and by adding 1 $\text{mol} \cdot \text{L}^{-1}$ HNO_3 to remove the template ion. Finally, the IIP-AMPS/SiO₂ was obtained by washing with deionized water to neutral and dried. The synthetic process of IIP-AMPS/SiO₂ is shown in Fig. 1.

The synthetic process of non-imprinted silica gel polymer (NIP-AMPS/SiO₂) was similar to the preparation of IIP-AMPS/SiO₂ without adding Ni(II) ion.

Batch Adsorption Experiments

Batch adsorption experiments were carried out by adding a certain amount of sorbent to a certain volume of metal ion solution, and the mixture was shaken for a certain time at 25 °C. The concentrations of all metal ions were determined by ICP-AES. Each adsorption experiment was conducted for three times. The adsorption capacity was calculated according to the following Eq. (1).

$$q = \frac{c_i - c_f}{1000W} \times V \quad (1)$$

where q ($\text{mg} \cdot \text{g}^{-1}$) is the adsorption capacity, c_i ($\text{mg} \cdot \text{L}^{-1}$) and

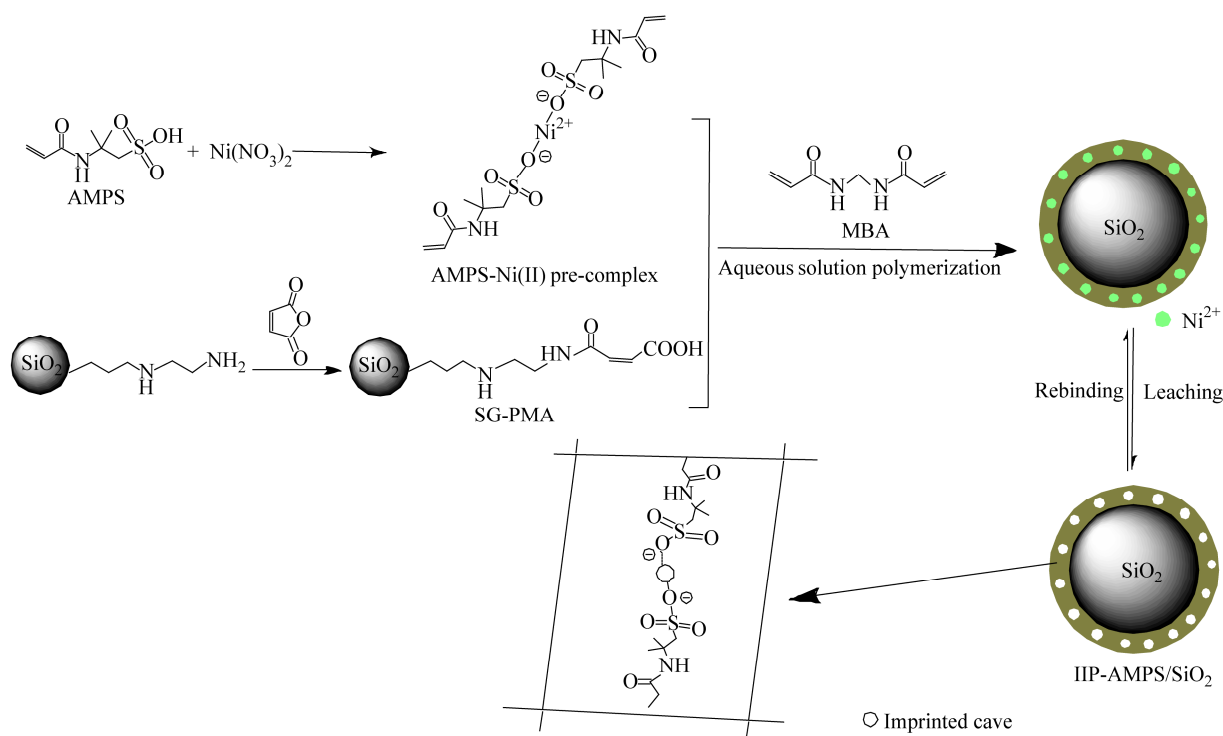


Fig. 1 The preparation of IIP-AMPS/SiO₂

c_f (mg·L⁻¹) are the initial and final concentrations of metal ions, respectively; V (mL) is the volume of the solution; and W (g) is the mass of sorbent.

The pH effect on Ni(II) adsorption was examined by adding 20 mg of sorbent into 20 mL of 100 mg·L⁻¹ Ni(II) ion solution with varying pH values at 25 °C for 2 h. The pH of solution was adjusted by HNO₃ and NH₃·H₂O solution. The effect of time required on Ni(II) adsorption was determined by adding 50 mg of sorbent into 50 mL of 100 mg·L⁻¹ Ni(II) ion solution at different contact time at 25 °C and pH = 7.0 for 60 min. Samples were taken out from the solution at different time intervals until saturation adsorption was achieved. In order to evaluate the effect of initial concentrations on Ni(II) adsorption, 20 mg of sorbent was added to 20 mL of Ni(II) ion solution with different concentrations (10–200 mg·L⁻¹) at 25 °C and pH 7.0 for 10 min.

Adsorption Selectivity Experiments

To the adsorption selectivity, 20 mg of the sorbent was added into 20 mL of 100 mg·L⁻¹ mixed solution of Ni(II), Co(II), Cu(II), Zn(II) and Pb(II) at pH = 7.0 for 10 min. The distribution ratio (D), the selectivity coefficient (k) and the relative selectivity coefficient (k') were calculated according to the following Eqs. (2)–(4)^[26].

$$D = \frac{(c_0 - c_e)}{c_e} \times \frac{V}{W} \quad (2)$$

$$k = \frac{D_{\text{Ni}}}{D_{\text{M}}} \quad (3)$$

$$k' = \frac{k_{\text{IIP}}}{k_{\text{NIP}}} \quad (4)$$

where c_0 (mg·L⁻¹) and c_e (mg·L⁻¹) are the initial and equilibrium concentrations of metal ions, V (mL) is the volume of metal ion solution, W (g) is the mass of sorbent, M represents other competitive metal ions.

Reusability Experiments

To examine the reusability, six cycles of repetitive adsorption/desorption experiments were conducted by using the same sorbent in conical flasks. In order to find a suitable stripping agent, five kinds of stripping agents, HCl (0.5 mol·L⁻¹, 10 mL), H₂SO₄ (0.5 mol·L⁻¹, 10 mL), HNO₃ (0.5 mol·L⁻¹, 10 mL), HNO₃ (1.0 mol·L⁻¹, 10 mL) and HNO₃ (2.0 mol·L⁻¹, 10 mL) solutions were selected to desorb the Ni(II) adsorbed on IIP-AMPS/SiO₂. For the adsorption experiments, 50 mg of IIP-AMPS/SiO₂ was equilibrated with 50 mL of 100 mg·L⁻¹ Ni(II) ions solution at pH = 7.0 and 25 °C for 1 h. After adsorption experiments, the sorbent was desorbed by 1 mol·L⁻¹ of HNO₃ solution for 1 h to remove Ni(II) ions adsorbed on the sorbent. Finally, the sorbent was filtered and washed with distilled water to neutral, dried under vacuum at 50 °C for 12 h before the next adsorption/desorption test.

RESULTS AND DISCUSSION

Characterization of Ni(II) Ion-imprinted Silica Gel Polymer FTIR spectra

Figure 2 gives the FTIR spectra of the three particles, SG-PMA, IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂. In the spectrum of SG-PMA, the sharp absorption bands at 1090

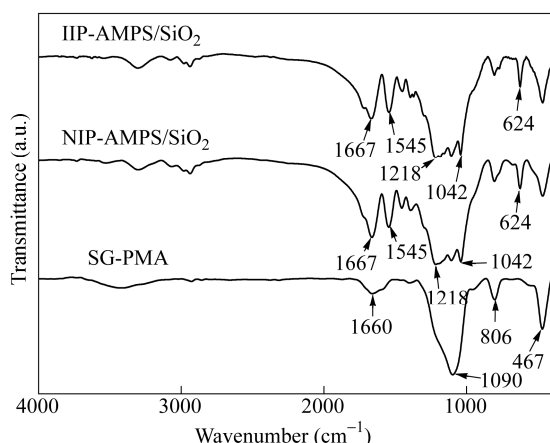


Fig. 2 FTIR spectra of SG-PMA, IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂

and 806 cm⁻¹ represented the C—N deformation vibration and Si—O stretching vibration, respectively, whereas the absorption peak at 467 cm⁻¹ was assigned to the bending vibration of Si—O—Si groups^[27]. The band at 1660 cm⁻¹ was ascribed to C=C stretching vibration from the group of —C(=O)—C=C—COOH^[28]. As compared with the spectrum of SG-PMA, two new bands at 1218 and 1042 cm⁻¹ appeared in the spectra of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂, which were ascribed to the asymmetric and symmetric stretching vibrations of SO₂ bond of sulfonic acid group. In addition, the band at 624 cm⁻¹ was assigned to the out-plane bending vibration of O—H bond of sulfonic acid group^[29]. Besides, two intense bands around 1667 and 1545 cm⁻¹ appeared; the former was attributed to the stretching vibration of C=O bond of amide group (amide I band), and the latter was associated to the in-plane bending vibration of N—H bond of amide group (amide II band)^[20]. The results showed that the polymerization of AMPS and MBA on the silica gel surface occurred and the Ni(II) imprinted layer on silica gel surface was formed.

Morphology study

Figure 3 presents the surface morphologies of SG-PMA and IIP-AMPS/SiO₂. Some notable changes in surface morphology of IIP-AMPS/SiO₂ were observed as compared to SG-PMA. The surface of SG-PMA (Figs. 3a and 3c) was flat and smooth, whereas the surface of IIP-AMPS/SiO₂ (Figs. 3b and 3d) was covered with many agglomerations and became irregular, rough and porous. It was caused by the imprinting polymerization of AMPS and MBA on the silica gel surface with Ni(II) ions as the template; after leaching Ni(II) ions, the porous imprinted layer contained a large number of binding cavities. The nanoporous structure on the surface of imprinted polymers plays an important role as the cognition site in the adsorption process. Therefore, the construction of nanoporous structure on the surface of adsorbent is a critical step.

Surface area and pore size analysis

The surface area was analyzed by Brunauer-Emmett-Teller (BET) method, and the pore size distributions were determined by Barrett-Joyner-Halenda (BJH) method. The

surface physical parameters of SG-PMA, IIP-AMPS/SiO₂, NIP-AMPS/SiO₂ and Ni(II)-loaded IIP-AMPS/SiO₂ are listed in Table 1. The surface area and pore volume of SG-PMA and IIP-AMPS/SiO₂ were different, which might be due to the polymer layer with nanoporous formed on the surface of SG-PMA after polymerization. The surface area and pore volume of IIP-AMPS/SiO₂ were 227.990 m²·g⁻¹ and 0.697 cm³·g⁻¹, respectively, higher than those of NIP-AMPS/SiO₂ (207.436 m²·g⁻¹ and 0.616 cm³·g⁻¹). It was possibly because the recognition cavities for Ni(II) were created on the polymer surface by imprinting process. In addition, the surface area and the pore volume of Ni(II)-loaded IIP-AMPS/SiO₂ (203.596 m²·g⁻¹ and 0.592 cm³·g⁻¹) were lower than those of IIP-AMPS/SiO₂, owing to the fact that nickel(II) ions entered the recognition cavities and combined with binding sites on the polymer surface. The result is consistent with the results of surface morphology study.

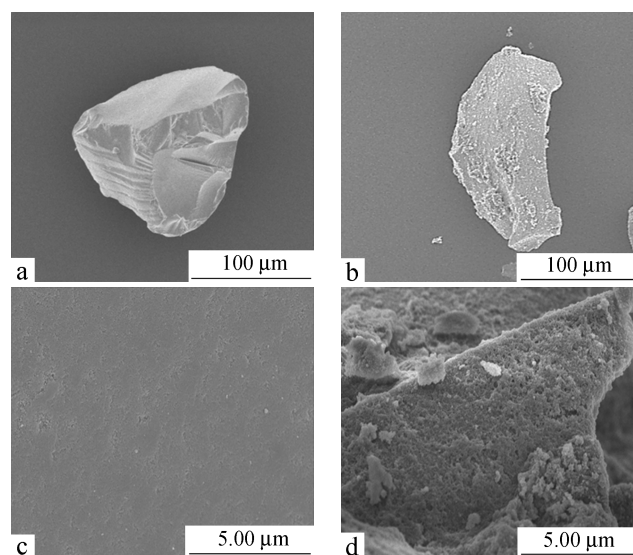


Fig. 3 (a) Low and (c) high-magnification SEM images of SG-PMA; (b) Low and (d) high-magnification SEM images of IIP-AMPS/SiO₂

Table 1 Surface physical parameters of SG-PMA, NIP-AMPS/SiO₂, IIP-AMPS/SiO₂ and IIP-AMPS/SiO₂ (loaded)

Sample	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Average pore diameter (nm)
SG-PMA	203.390	0.451	9.567
IIP-AMPS/SiO ₂	227.990	0.697	3.775
NIP-AMPS/SiO ₂	207.436	0.616	4.831
IIP-AMPS/SiO ₂ (loaded)	203.596	0.592	3.767

Thermal stability analysis

Thermal stability was investigated by thermogravimetric analysis (TGA) method with the temperature ranging from room temperature to 800 °C. The TGA curves of SG-PMA and IIP-AMPS/SiO₂ are shown in Fig. 4. For SG-PMA, the weight loss was about 5.8% when the temperature increased from room temperature to 150 °C, which was mainly owing to the loss of physical water. The weight loss of 18.3% from

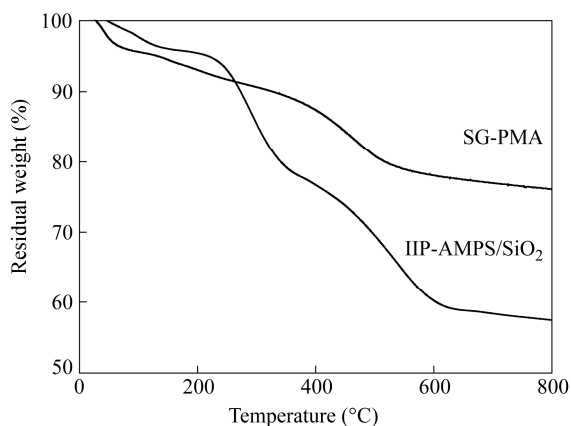


Fig. 4 TGA curves of SG-PMA and IIP-AMPS/SiO₂

150 °C to 800 °C was due to the decomposition of organic compounds grafted on the silica gel surface. For IIP-AMPS/SiO₂, a little weight loss of about 4.2% was observed from room temperature to about 160 °C at the first stage, which was mainly from the evaporation of physisorbed water. When the temperature was changed from 160 °C to 650 °C, the weight loss became fast and about 36.8% of weight loss was found. It might be due to the decomposition and degradation of poly(AMPS-co-MBA) coated on the silica gel surface. The results showed that the surface of silica gel was coated by a thin polymer layer, which was consistent with the results of surface morphology and BET measurements. Consequently, the prepared polymer possessed good thermal stability when the ambient temperature was lower than 200 °C.

Effect of the Solution pH

Considering the hydrolysis of Ni(II) ion at pH value over 8.0, the effect of solution pH on adsorption of Ni(II) ion was investigated at the pH values from 2.0 to 8.0. The results are presented in Fig. 5. It could be seen that the adsorption capacity of sorbent for Ni(II) increased from pH = 2.0 to pH = 4.0, then remained a constant value in the range of pH from 4.0 to 7.0, finally decreased at pH > 7.0. Below pH = 4.0, the low adsorption capacity was mainly on account of the protonation of active sites; more protons than metal

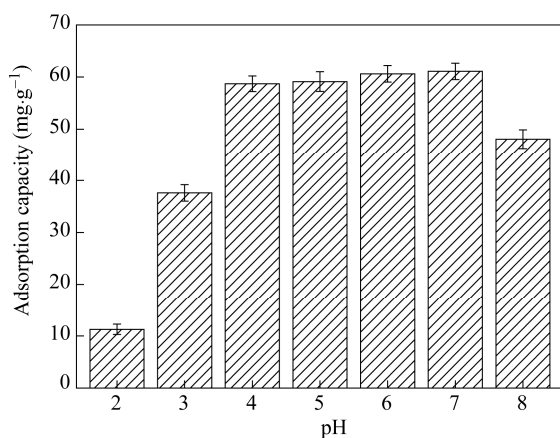


Fig. 5 Effect of pH on the adsorption of Ni(II) (sample volume: 20 mL, Ni(II) concentration: 100 mg·L⁻¹)

ions occupied the binding sites of polymer, leading to the weak adsorption for Ni(II). Over pH 7.0, some nickel(II) ions began to hydrolyze to form nickel hydroxide so that the concentration of free Ni(II) ion in the aqueous solution reduced, thereby, the adsorption capacity of the imprinted polymer decreased. It was obvious that the stable adsorption for Ni(II) appeared in the pH range of 4.0–7.0. At pH = 7.0, the maximum adsorption capacity of IIP-AMPS/SiO₂ was 61.09 mg·g⁻¹. In our case, pH value of 7.0 in aqueous solution was selected as the optimum pH in the follow-up experiments.

Adsorption Kinetics

The kinetic study is fundamental in evaluating the mechanism of interaction between the target metal ions and the sorbent. The effect of adsorption time on the adsorption of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ion was investigated (Fig. 6). The adsorption rate was fast in the initial stage, then became slow and gradually achieved the adsorption equilibrium in 10 min. We speculated that (1) in the initial stage, sufficient binding sites were available on the polymer surface, enabling Ni(II) to combine easily with sorbent; (2) after the fast adsorption stage, the external binding sites gradually got occupied by Ni(II) and the number of available binding sites decreased, so Ni(II) needed to diffuse into the interior of the sorbent for the further adsorption, leading to the slow adsorption rate until reaching the adsorption equilibrium^[22, 23].

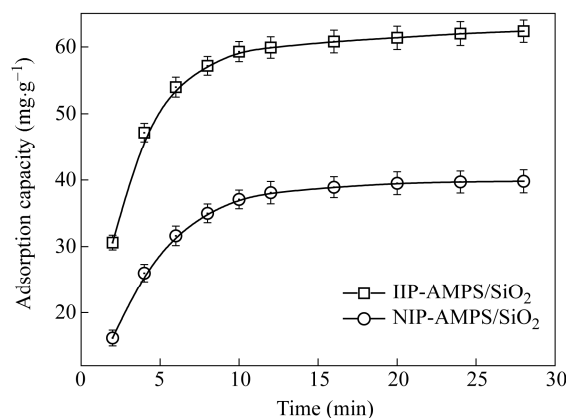


Fig. 6 Effect of time on the adsorption of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ions (sample volume: 50 mL, Ni(II) concentration: 100 mg·L⁻¹, pH = 7.0)

The pseudo-first-order kinetics model and pseudo-second-order kinetics model were used to further investigate the kinetic mechanism for Ni(II) ions adsorption. It is assumed that the adsorption process is conducted by the diffusion of ions through the boundary layer of sorbent surface for the pseudo-first-order kinetics model, and the adsorption process is controlled by diffusion step. For the pseudo-second-order kinetics model, the adsorption process is controlled by the chemical adsorption mechanism, which involves the electron sharing or electron transfer between adsorbent and adsorbate. The pseudo-first-order kinetics model and pseudo-second-order kinetics model are expressed as Eqs. (5) and (6)^[30]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where t (min) is the time, q_t ($\text{mg}\cdot\text{g}^{-1}$) and q_e ($\text{mg}\cdot\text{g}^{-1}$) are the amount of adsorption of Ni(II) ion at time t and at equilibrium, respectively, k_1 (min^{-1}) and k_2 ($\text{g}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$) are the rate constants of adsorption, respectively.

Figure 7 shows the plots of pseudo-first-order and pseudo-second-order models of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ion adsorption and Table 2 summarizes the kinetic parameters of the two models. The pseudo-second-order kinetics model can better describe the adsorption process of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ions because R^2_2 (> 0.99) for the pseudo-second-order kinetics model is better than R^2_1 for the pseudo-first-order kinetics model, and the calculated q_e values (69.64 and 47.98 $\text{mg}\cdot\text{g}^{-1}$) of the pseudo-second-order kinetics model are close to the experimental values (62.35 and 41.92 $\text{mg}\cdot\text{g}^{-1}$). It can be concluded that the adsorption of Ni(II) onto the surface of imprinted polymer is the chemical interaction^[31].

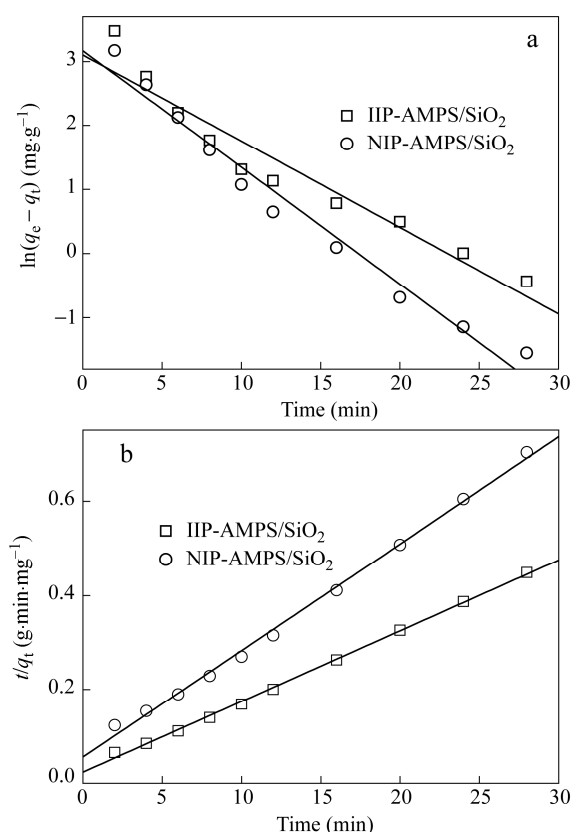


Fig. 7 (a) Pseudo-first-order and (b) pseudo-second-order kinetics of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ion adsorption

Maximum Adsorption Capacity and Adsorption Isotherms

The equilibrium adsorption isotherm is significant to describe the adsorption interaction between the adsorbates and adsorbents. The adsorption isotherm study was conducted at 25 °C and pH = 7.0 with the initial concentration of Ni(II) in the range of 10–200 $\text{mg}\cdot\text{L}^{-1}$. Figure 8 shows the effect of initial concentration of Ni(II) on the adsorption. It could be seen that the adsorption amount increased with increasing initial concentration, and the adsorption tended to saturation when the initial concentration reached up to 100 $\text{mg}\cdot\text{L}^{-1}$. The maximum static adsorption capacities of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ were 66.22 and 43.72 $\text{mg}\cdot\text{g}^{-1}$, respectively. The results indicated that both polymers exhibited high adsorption capacity, which could be attributed to the sulfonic acid functional groups grafted on the sorbent surface. Compared with NIP-AMPS/SiO₂, IIP-AMPS/SiO₂ had a higher adsorption capacity. The reason might be that there were more recognition cavities on the surface of IIP-AMPS/SiO₂ by ion imprinting, which enhanced the adsorption capacity for Ni(II) ions. In addition, the prepared IIP-AMPS/SiO₂ exhibited relatively high adsorption capacity for Ni(II) ions in comparison to other reported Ni(II) ion-imprinted sorbents (listed in Table 3)^[14, 17, 24, 32–34]. It may be explained by the following two reasons. Firstly, the functional monomer AMPS prefers to combine with borderline acid of Ni(II) because it is a borderline base which contains sulfonic acid ($-\text{SO}_3\text{H}$) groups according to the Lewis theory of acids and bases. The second reason is the advantage of aqueous solution polymerization. The solubility of Ni(II) ions in water is much better than that in organic solvents based on the principle of similar dissolve mutually, and the Ni(II) ions are recognized in the water environment during the preparation of IIP-AMPS/SiO₂,

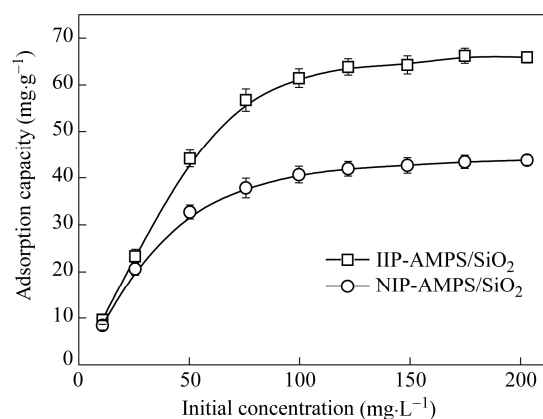


Fig. 8 Effect of Ni(II) initial concentration on the adsorption of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ (sample volume: 20 mL, pH = 7.0, adsorption time: 10 min)

Table 2 Adsorption kinetic parameters of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ion

Sorbent	$q_{e,\text{exp}}$ ($\text{mg}\cdot\text{g}^{-1}$)	Pseudo-first-order rate equation			Pseudo-second-order rate equation		
		k_1 (min^{-1})	$q_{e,\text{cal}}$ ($\text{mg}\cdot\text{g}^{-1}$)	R^2_1	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	$q_{e,\text{cal}}$ ($\text{mg}\cdot\text{g}^{-1}$)	R^2_2
IIP-AMPS/SiO ₂	62.35	0.1348	22.25	0.9197	9.611×10^{-3}	66.36	0.9984
NIP-AMPS/SiO ₂	41.92	0.1822	23.75	0.9717	9.205×10^{-3}	44.09	0.9962

Table 3 Adsorption capacity of Ni(II) onto various imprinted sorbents reported in the literature

Functional monomer	Polymerization method	Adsorption capacity (mg·g ⁻¹)	Ref.
3-Aminopropyltrimethoxysilane	Surface imprinting	12.61	[17]
Chitosan	Surface imprinting	38.49	[24]
Vinylbenzyliminodiacetic acid	Precipitation polymerization	12.00	[14]
1,5-Diphenylcarbazine	Precipitation polymerization	40.25	[32]
1-(Pyridin-2-yl)-N-(3-vinylbenzyl)methanamine	Suspension polymerization	11.74	[33]
2-Vinyl pyridine and Alizarin red S	Bulk polymerization	73.20	[34]
2-Acrylamido-2-methyl-1-propanesulfonic acid	Surface imprinting and aqueous solution polymerization	66.22	This work

thereby enhancing the affinity of the adsorbent for nickel ions from aqueous solution.

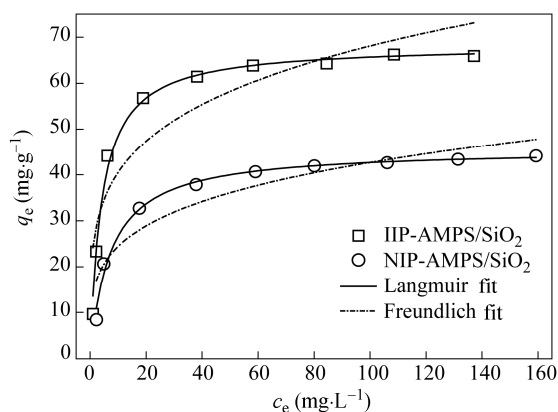
Moreover, Langmuir and Freundlich isotherm models were used to depict the adsorption process in this study. Langmuir and Freundlich isotherm models assume a monolayer adsorption on a homogenous surface or sorption on a heterogeneous surface, respectively. These isotherm models can be respectively expressed as the Eqs. (7) and (8)^[35]:

$$\text{Langmuir isotherm: } q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (7)$$

$$\text{Freundlich isotherm: } q_e = K_F c_e^{1/n} \quad (8)$$

where q_e (mg·g⁻¹) is the adsorption capacity of Ni(II) ion at equilibrium, c_e (mg·L⁻¹) is the equilibrium concentration of Ni(II) ion in the solution, q_m (mg·g⁻¹) is the maximal adsorption capacity of Ni(II) ion, K_L (L·g⁻¹) and K_F are the Langmuir and Freundlich adsorption equilibrium constants related to the affinity of binding sites, respectively, n is the Freundlich constant indicating the isotherm curvature.

The curves of adsorption isotherm models are presented in Fig. 9 and the parameters of two models are given in Table 4. It could be seen that the correlation coefficients (R^2) obtained

**Fig. 9** Langmuir and Freundlich isotherm models of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ions adsorption

from Langmuir model were closer to 1. Moreover, the maximum adsorption capacity (q_m) values of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ calculated from Langmuir model were closer to the experimental values. Therefore, Langmuir isotherm model can be used to depict the adsorption process, which indicates that the adsorption of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ions is a monolayer adsorption^[36].

Thermodynamic Study

The thermodynamic experiments were conducted at pH = 7.0 with the initial concentration of Ni(II) (100 mg·L⁻¹) in the temperature range of 25–45 °C. Figure 10 shows the effect of temperature on the adsorption of IIP-AMPS/SiO₂. The maximum adsorption capacity of IIP-AMPS/SiO₂ for Ni(II) ions increased from 62.79 mg·g⁻¹ to 70.14 mg·g⁻¹ when the temperature increased from 25 °C to 45 °C. The results indicated that the higher temperature was beneficial to the adsorption of Ni(II) ions. On one hand, it was probably because the higher temperature changed the pore size of the adsorbent, so that more nickel ions could diffuse into the interior of adsorbent. On the other hand, the higher temperature enhanced the chemical affinity of Ni(II) ions to the surface of sorbent, leading to some kind of chemical interaction in the adsorption process^[37].

In order to clarify the thermodynamics mechanism of the adsorption process, the related thermodynamic parameters were calculated. The free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were evaluated using the following Eqs. (9)–(11)^[38]:

$$K_c = \frac{c_{Ac}}{c_e} \quad (9)$$

$$\Delta G = -RT \ln K_c \quad (10)$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

where K_c is the equilibrium constant, c_{Ac} and c_e (mg·L⁻¹) are the Ni(II) equilibrium concentrations on sorbent and in the solution, respectively. R is the universal gas constant (8.314 × 10⁻³ kJ·K⁻¹·mol⁻¹) and T (K) is the absolute temperature.

Table 4 Adsorption isotherm parameters of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂ for Ni(II) ion

Sorbents	$q_{e,exp}$ (mg·g ⁻¹)	Langmuir isotherm			Freundlich isotherm		
		$q_{e,cal}$ (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	$1/n$	K_F (mg·g ⁻¹)	R^2
IIP-AMPS/SiO ₂	66.22	68.35	0.2452	0.9916	0.2254	24.11	0.8283
NIP-AMPS/SiO ₂	43.72	45.70	0.1399	0.9890	0.2423	13.98	0.8648

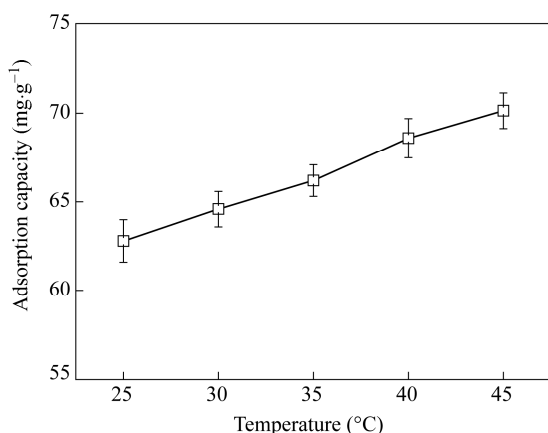


Fig. 10 Effect of temperature on the adsorption capacity of IIP-AMPS/SiO₂ for Ni(II) ions

The value of ΔG was calculated directly from the above relations. The values of ΔH and ΔS were calculated from the slope. The intercept of the plot of $\ln K_c$ versus $1/T$ is shown in Fig. 11 and the calculated values of thermodynamic parameters are given in Table 5. The positive value of ΔH indicated that the adsorption process of Ni(II) ions on IIP-AMPS/SiO₂ was endothermic and higher temperature was beneficial to the adsorption. The negative values of ΔG exhibited the feasibility and spontaneity of Ni(II) adsorption on the imprinted materials. The positive ΔS value indicated that the increase of randomness during the adsorption could be attributed to the release of water molecules when the Ni(II) ions was adsorbed on the surface of sorbent.

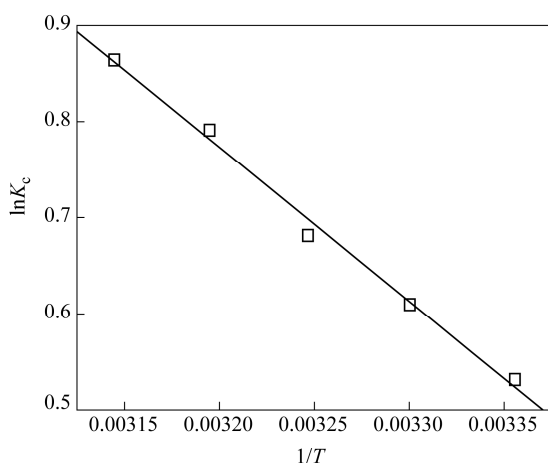


Fig. 11 Plot of $\ln K_c$ versus $1/T$ for Ni(II) ion adsorption on IIP-AMPS/SiO₂

Table 5 Thermodynamic parameters of IIP-AMPS/SiO₂ for Ni(II) ion

Temperature (K)	ΔG (kJ·mol ⁻¹)	ΔH (kJ·mol ⁻¹)	ΔS (J·mol ⁻¹ ·K ⁻¹)
298	-1.32	13.33	49.09
303	-1.51		
308	-1.69		
313	-1.96		
318	-2.14		

Adsorption Selectivity

To evaluate the selectivity of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂, the selective adsorption experiments were carried out in a mixed solution of Ni(II), Co(II), Cu(II), Zn(II), and Pb(II). They are chosen as the competitive ions due to the coexistence in natural sources. Table 6 summarizes the calculated data of the distribution ratio (D), the selectivity coefficient (k) and relative selectivity coefficient (k'). As listed in Table 6, the D value of IIP-AMPS/SiO₂ for Ni(II) was much higher than other competitive ions. On the other hand, the relative selectivity coefficients (k') for Ni(II)/Co(II), Ni(II)/Cu(II), Ni(II)/Zn(II) and Ni(II)/Pb(II) were 9.23, 15.71, 14.72 and 20.15, respectively, which were much higher than 1. It was noticeable that the imprinted silica sorbent had an ability for selective adsorption of Ni(II) ions in the presence of other interfering ions. In the present study, the sulfonic acid ($-\text{SO}_3\text{H}$) group grafted on the sorbent surface is borderline base and prefers to combine with borderline acid Ni(II) according to the Lewis theory of acids and bases. Although competitive ions Co(II), Cu(II), Zn(II) and Pb(II) are also borderline acids, IIP-AMPS/SiO₂ still exhibits high selectivity. This can be attributed to the following two reasons. One is the cavity size selectivity. The ionic radii of Ni(II), Co(II), Cu(II), Zn(II) and Pb(II) are 0.069, 0.065, 0.073, 0.074 and 0.119 Å, respectively. Cu(II), Zn(II) and Pb(II) with larger size than Ni(II) cannot enter the imprinted cavities of IIP-AMPS/SiO₂, while Co(II) with smaller size do not match the imprinted cavity. The other is the coordination geometry selectivity. IIP-AMPS/SiO₂ can provide sulfonic acid groups which coordinate with Ni(II) in a specific geometric space structure. Accordingly, despite the fact that many metal ions are borderline acid and have the high affinity with functional groups, the sorbent still exhibits high selectivity for Ni(II). The results indicate that coordination geometry selectivity may be the primary reason in the selective adsorption process.

Table 6 Selectivity parameters of IIP-AMPS/SiO₂ and NIP-AMPS/SiO₂

Metal ion	Distribution ratio D (mL·g ⁻¹)		Selectivity coefficient k		Relative selectivity coefficient k'
	IIP-AMPS/SiO ₂	NIP-AMPS/SiO ₂	IIP-AMPS/SiO ₂	NIP-AMPS/SiO ₂	
Ni(II)	15054.55	2005.25			
Cu(II)	449.71	553.15	33.48	3.63	9.23
Co(II)	283.54	593.17	53.09	3.38	15.71
Zn(II)	322.28	631.98	46.71	3.17	14.72
Pb(II)	229.23	645.30	65.68	3.26	20.15

Desorption and Reusability

The reusability of sorbent is an important factor since it affects the cost of application. In order to find a suitable eluent, five kinds of stripping agents, HCl ($0.5 \text{ mol}\cdot\text{L}^{-1}$, 10 mL), H_2SO_4 ($0.5 \text{ mol}\cdot\text{L}^{-1}$, 10 mL), HNO_3 ($0.5 \text{ mol}\cdot\text{L}^{-1}$, 10 mL), HNO_3 ($1.0 \text{ mol}\cdot\text{L}^{-1}$, 10 mL) and HNO_3 ($2.0 \text{ mol}\cdot\text{L}^{-1}$, 10 mL) solutions were used to desorb Ni(II) ions adsorbed on IIP-AMPS/ SiO_2 . It was found that the elution efficiency of HNO_3 solution was better than that of other stripping agents under the same concentration of $0.5 \text{ mol}\cdot\text{L}^{-1}$, and a high recovery (95%) was obtained when the concentration of eluent was raised to $1.0 \text{ mol}\cdot\text{L}^{-1}$. Therefore, 10 mL of $1 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 was used as the eluent.

In order to investigate the reusability of IIP-AMPS/ SiO_2 , six cycles of repeated adsorption/desorption experiments were conducted with the same sorbent. The results are shown in Fig. 12. It could be seen that the recovery of Ni(II) ions on IIP-AMPS/ SiO_2 was still maintained at about 90% after six adsorption-desorption cycles, indicating the prepared IIP-AMPS/ SiO_2 had good reusability for the adsorption of Ni(II) ions.

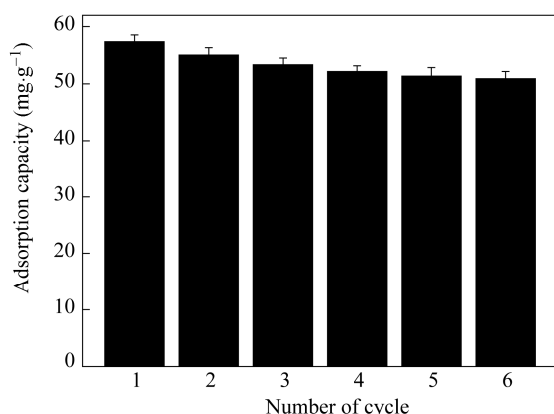


Fig. 12 Desorption and regeneration of IIP-AMPS/ SiO_2

Analytical Performance and Application of the Proposed Method

In order to evaluate the analytical performance of the proposed method, six portions of standard solutions of Ni(II) (GBW080128, $100 \mu\text{g}\cdot\text{L}^{-1}$) were enriched under the above optimal experimental conditions. The Ni(II) concentration was calculated to be $(103.45 \pm 2.64) \mu\text{g}\cdot\text{L}^{-1}$, which was in agreement with the certified value, and the relative standard deviation (RSD, %) of the method was 2.58%. The results indicated that the proposed method was suitable for detecting and analyzing Ni(II) in aqueous solution.

Furthermore, the proposed method was used for the analysis of trace Ni(II) in real water samples by using a standard addition method. The experiments were carried out by adding 20 mg of sorbent in the samples' solution (50 mL). As listed in Table 7, the adsorption efficiency of Ni(II) ions is over 95%, suggesting that the proposed method is suitable for the determination and adsorption of trace Ni(II) in natural water samples.

Table 7 Analysis of Ni(II) in real water samples

Sample	Added ($\mu\text{g}\cdot\text{L}^{-1}$)	Found ($\mu\text{g}\cdot\text{L}^{-1}$)	Recovery (%)
Tap water	0	0.68	—
	5	5.76	101.4
	10	9.94	95.2
	20	19.85	97.1
Lake water	0	1.63	—
	5	6.45	97.3
	10	11.76	101.1
	20	22.04	99.0

CONCLUSIONS

A new Ni(II) ion surface-imprinted silica gel sorbent was synthesized by surface imprinting technique combined with aqueous solution polymerization. The preparation method was easy to operate. The prepared sorbent exhibited excellent adsorption selectivity and higher adsorption capacity for Ni(II) as compared with other reported Ni(II) ion surface-imprinted sorbents. The maximum adsorption capacity of prepared sorbent towards Ni(II) was $66.22 \text{ mg}\cdot\text{g}^{-1}$ at the optimal pH of 7.0. The adsorption kinetics was fitted well with the pseudo-second-order kinetics model, and the adsorption isotherms followed Langmuir isotherm model. The thermodynamic study showed that the adsorption of Ni(II) on the obtained surface-imprinted silica gel sorbent was an endothermic and a spontaneous process. IIP-AMPS/ SiO_2 could be reused to adsorb Ni(II) from aqueous solutions, and the recovery of Ni(II) ions on IIP-AMPS/ SiO_2 was maintained at about 90% after six adsorption-desorption cycles. Furthermore, the sorbent could be utilized for the determination and adsorption of trace Ni(II) in natural water samples. In conclusion, the newly synthesized surface-imprinted silica gel sorbent is a promising candidate for selective separation of Ni(II) ions from aqueous solutions.

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