Research Article

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Preparation and adsorption properties of Ni(II) ion-imprinted polymers based on synthesized novel functional monomer

<https://doi.org/10.1515/epoly-2021-0055>

received April 27, 2021; accepted June 22, 2021

Abstract: In this study, a novel functional monomer *N*-(1-(2,4-difluorophenyl)-2-(1*H*-1,2,4-triazol-1-yl)ethyl)acrylamide (NDTEA) was designed and synthesized, and was used to prepare Ni(II) ion-imprinted polymers (Ni(II)-IIPs). Sixteen kinds of Ni(II)-IIP (Ni(II)-IIP_{1–16}) and corresponding non-imprinted polymers (NIP_{1–16}) were prepared by precipitation polymerization method. After optimized condition experiment, Ni(II)-IIP₅ possessed maximum adsorption capacity and better imprinting factor under optimal experimental conditions which indicated by equilibrium adsorption experiments. The morphology and structural characteristics of Ni(II)-IIP₅ were characterized by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET). The adsorption selectivity of Ni(II)-IIP₅ was analyzed by ICP-OES, and the results showed that Ni(II)-IIP₅ had favorable selectivity recognition ability for Ni(II) when Cu(II), Co(II), and Cd(II) are used as competitive ions. The kinetic experiment indicated that the performance of Ni(II) adsorption on the surface of Ni(II)-IIP₅ obeyed the pseudo-first-order model, and adsorption equilibrium was attained after 15 min. Isothermal adsorption process fitted to Langmuir and Freundlich isothermal adsorption models, simultaneously. The results showed that Ni(II)-IIP₅ prepared by using a new functional monomer had better permeation selectivity and higher affinity for Ni(II), which also verified the rationality of the functional monomer design. At the same time, it also provided a broad application prospect for removal of Ni(II) in complex samples.

Keywords: Ni(II) ion, novel functional monomer, NDTEA, Ni(II) ion-imprinted polymer, selectivity

1 Introduction

Nickel (Ni) is a heavy metal material closely associated with human life, which possesses favorable characteristics of corrosion resistance and ductility, and has been widely used in steel, alloy manufacturing, electroplating, and batteries. Meanwhile, Ni is one of the trace elements necessary for organisms, but its availability is not up to the demand. Due to the serious problem of Ni pollution (1,2), it can damage kidney organs and cause irreparable harms to the physical health (3,4). Therefore, it is particularly important to develop a method for rapid and effective removal of Ni. In order to alleviate Ni ion pollution, many researchers have conducted a lot of explorations and experiments (5–7). The current conventional methods for treating Ni-containing wastewater are as follows: chemical precipitation (8–10), ion exchange (11,12), electrolysis (13,14), membrane separation (15,16), adsorption (17,18), etc. For example, Anna Wołowicz published an article in which they described an effective removal of Ni(II) from aqueous solutions with ion exchange resins (19).

Foong et al. demonstrated that heavy metal ion can be detected and separated by nanofiber membranes (20). Salama and co-workers proved that algae can remove heavy metal ions from various wastewater by adsorption process (21). The method of adsorption is effective and environmentally friendly, which has been widely used in the field of Ni-containing wastewater treatment in recent years (22,23). However, most adsorption processes are non-specific and have low selectivity for target ions. In view of the serious environmental pollution caused by Ni ion, there is an urgent need to find an adsorption separation material with high selectivity for Ni(II).

As an important developmental direction of molecular imprinting technology (24–26), metal ion imprinting technology (27) has vital academic and application value in various fields of environment and material science (28–32), for instance, solid phase extraction (33), sensor (34–36), membrane separation (37), etc. The concept of ion

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imprinting technology is that metal ion is used as template to form a chelate by combining with monomer through electrostatic and coordination actions. After polymerization, the template ions are eluted with acidic reagents. Finally, the imprinted material with three-dimensional pore structure corresponding to the target metal ion is prepared.

In this work, novel functional monomers are designed and synthesized to be used as monomers for preparing Ni ion polymers (Ni(II)-IIPs/NIPs). In the previous study of our research group (38), a novel functional monomer *N,N'*-(ethane-1,2-diyl)bis(2-methylacrylamide) (EBMA) was successfully prepared and applied to prepare ion-imprinted membranes of Cr(VI). In this study, a novel functional monomer *N*-(1-(2,4-difluorophenyl)-2-(1*H*-1,2,4-triazol-1-yl)ethyl)acrylamide (NDTEA) was designed and synthesized for recognizing Ni(II) ion in aqueous solution, using ethylene glycol dimethacrylate (EDMA) as cross-linker and 2,2'-azobis(2-methylpropionitrile) (AIBN) as initiator. Diverse parameters affecting the adsorbing capacity of polymers were optimized, such as the type and dosage of solvent, the dosage of functional monomer, cross-linker, etc.

The preparation of polymers with optimal conditions was characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET), and the selectivity of Ni(II)-IIP₅ was conducted by choosing Cd²⁺, Co²⁺, Cu²⁺ as competing ions. The polymer of Ni(II)-IIP₅ possesses positive specific selective recognition performance for Ni(II), and, therefore, it is expected to be used for separation and enrichment of Ni(II) in actual samples.

2 Experimental methods

2.1 Apparatus

A UV-2500 ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu, Japan) was used to detect metal ion concentration. The pH value was measured with a PHS-3C pH meter. XL 30esem-tm phenom electron microscope-energy spectrometer (Funer Scientific Instrument) was used to identify the surface morphologies of Ni(II)-IIP and NIP. The selectivity of polymer was validated by plasma emission spectrometer (ICAP 6000 series). The specific surface area of polymers were determined using NOVA2000e BET surface area analyzer (Quantachrome Instruments, USA). And the other apparatuses used were AS-series ultrasonic cleaning instrument (Tianjin, China); SHZ-82 Bath constant

temperature oscillator (Changzhou, China); DZKW S 4 electric-heated thermostatic water bath (Beijing, China); and analytical balance (Shanghai, China).

2.2 Materials

Nickel(II) chloride hexahydrate (98%, NiCl₂·6H₂O), chloride hexahydrate (99%, CoCl₂·6H₂O), copper chloride (99%, CuCl₂), cadmium chloride (99%, CdCl₂), AIBN (99%) and EDMA (98%) were purchased from Aladdin Bio-Chem Technology Co., Ltd, Shanghai. Methanol, ethanol absolute, isopropyl alcohol, acetonitrile, *N,N*-dimethylformamide, and acetic acid glacial were obtained from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. All reagents were of analytical grade. The laboratory water was deionized water.

2.3 Preparation of Ni(II) ion-imprinted polymer

2.3.1 Synthesis of novel functional monomer *N*-(1-(2,4-difluorophenyl)-2-(1*H*-1,2,4-triazol-1-yl)ethyl)acrylamide (NDTEA)

The synthesizing process of NDTEA is conducted according to the following steps:

2.3.1.1 Synthesis of compound 1

The process of synthesis can be seen from Scheme 1. The 2'-chloro-2,4-difluoroacetophenone and 1,2,4-triazole weighing 10 mmol and 30 mmol, respectively, were taken in a 50 mL round-bottom flask, added with 30 mL of anhydrous acetonitrile, and stirred overnight at room temperature. After the reaction was completed, the reactant was poured into 100 mL of cold water and stirred until solids precipitated. Afterwards filtration was performed with suction and the filter cake was washed three

Scheme 1: Synthesis of compound 1.

Scheme 2: Synthesis of compound 2.

times with water and dried. A light yellow solid of 1.87 g was obtained with yield up to 84%.

2.3.1.2 Synthesis of compound 2

The process of synthesis as can be seen from Scheme 2.

The prepared compound 1, ammonium chloride, and sodium cyanoborohydride were separately weighed for 10, 50, and 20 mmol, respectively, and taken in a 100 mL round-bottom flask, to which 50 mL of methanol was added later. The reaction was carried out at room temperature for 2 h and then heated to reflux for 12 h. After the reaction finished, the reactant was poured into 100 mL of cold water and stirred, and extracted with ethyl acetate. After the organic phase was dried over anhydrous sodium sulfate, it was filtered and concentrated to obtain 1.81 g of white solid with a yield of 81%.

The NMR data of the compound 2 are shown:

^1H NMR (400 MHz, CDCl_3) δ : 8.02(s, 1H), 8.20(d, $J = 5.4$ Hz, 2H), 7.82(s, 1H), 7.43–7.49(m, 1H), 6.86–6.91(m, 1H), 6.79–6.84(m, 1H), 5.34(d, $J = 7.5$ Hz, 1H), 4.85(br, 2H), 4.43–4.47(dd, $J = 2.6$ Hz, 2.6 Hz, 1H), 4.22–4.28(dd, $J = 8.2$ Hz, 8.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ : 164.2(d, $J_{\text{C-F}} = 12.1$ Hz), 161.7(d, $J_{\text{C-F}} = 11.8$ Hz), 160.9(d, $J_{\text{C-F}} = 11.7$ Hz), 158.4(d, $J_{\text{C-F}} = 11.7$ Hz), 151.8, 144.0, 128.7(q, $J_{\text{C-F}} = 5.8$ Hz), 123.5(d, $J_{\text{C-F}} = 13.7$ Hz), 112.0(q, $J_{\text{C-F}} = 3.4$ Hz), 104.3(t, $J_{\text{C-F}} = 25.3$ Hz), 66.6, 55.5.

2.3.1.3 Synthesis of compound 3

The process of synthesis as can be seen from Scheme 3.

The prepared compound 2 and potassium carbonate were weighed for 5 mmol and 10 mmol, respectively and taken in a 50 mL round-bottom flask, and was added with

Scheme 3: Synthesis of compound 3.

30 mL of anhydrous dichloromethane and 7.5 mmol of acrylic acid chloride under ice water slowly, and raised to room temperature for 5 h. After the reaction was detected by thin-layer chromatography, the reactant was poured into 100 mL of cold water and stirred for half an hour and dichloromethane (20 mL $\times$ 3) was extracted. The organic phase was dried over anhydrous sodium sulfate. It was then filtered and concentrated, and the residue was separated by column chromatography to obtain 1.21 g of red solid with 87% yield. The compound 3 is the new functional monomer synthesized for the preparation of polymers.

The NMR data of the compound 3 are shown:

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 8.43(s, 1H), 8.20(d, $J = 5.4$ Hz, 2H), 7.95(s, 1H), 7.73(s, 1H), 7.50–7.56(m, 1H), 7.18–7.23(m, 1H), 7.08–7.13(m, 1H), 5.93–6.02(dd, $J = 7.5$ Hz, 15.2 Hz, 1H), 5.71(d, $J = 15.3$ Hz, 1H), 5.34(d, $J = 10.6$ Hz, 1H), 5.16(s, 1H), 4.20(s, 1H), 4.16(s, 1H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ : 163.5(d, $J_{\text{C-F}} = 12.4$ Hz), 161.0(q, $J_{\text{C-F}} = 8.7$ Hz), 158.5, 158.4(d, $J_{\text{C-F}} = 12.1$ Hz), 151.7, 145.2, 129.8(q, $J_{\text{C-F}} = 6.2$ Hz), 128.8, 125.7(d, $J_{\text{C-F}} = 3.7$ Hz), 113.9, 112.1(t, $J_{\text{C-F}} = 3.6$ Hz), 104.3(t, $J_{\text{C-F}} = 25.7$ Hz), 65.3, 55.1, 51.9.

2.3.2 Preparation of Ni(II) ion-imprinted polymers

The major optimization of the preparation process can be seen in Table 1. Detailed procedure: 0.1 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (template ion) was weighed in a stoppering triangular conical flask and 0.4 mmol of novel functional monomer was

Table 1: Preparation of Ni(II)-IIP and NIP

Polymers	Types of solvent (v/v)	Ratio of solvent (v/v)	Dosage of functional monomer (mmol)	Dosage of cross-linker (mmol)
Ni(II)-IIP ₁	MeOH:H ₂ O	1:1	4	20
Ni(II)-IIP ₂	EtOH:H ₂ O	—	—	—
Ni(II)-IIP ₃	IPA:H ₂ O	—	—	—
Ni(II)-IIP ₄	DMF:H ₂ O	—	—	—
Ni(II)-IIP ₅	MeOH:H ₂ O	1:2	—	—
Ni(II)-IIP ₆	—	2:1	—	—
Ni(II)-IIP ₇	—	1:3	—	—
Ni(II)-IIP ₈	—	3:1	—	—
Ni(II)-IIP ₉	—	1:2	2	—
Ni(II)-IIP ₁₁	—	—	6	—
Ni(II)-IIP ₁₂	—	—	8	—
Ni(II)-IIP ₁₃	—	—	4	10
Ni(II)-IIP ₁₄	—	—	—	30
Ni(II)-IIP ₁₅	—	—	—	40
Ni(II)-IIP ₁₆	—	—	—	50

added to it. After dissolving with different solvents and then shaking at ambient temperature for 3 h, the Ni(II) ion and functional monomer were made to react completely; then 2 mmol of cross-linker EDMA and 15 mg of initiator AIBN were added to form a pre-polymerization solution which was transferred to an ampule and degassed for 5–10 min with ultrasonic. The solution was then placed in a constant temperature shaker at 60°C for 24 h. Finally, a 9:1 (v/v) methanol and acetic acid mixed solution was used to remove the template ions, eluted with methanol to neutral, and vacuum dried for 24 h and Ni(II)-IIPs were prepared. NIPs were also obtained under the same conditions, but without adding template ion. The process is shown in Scheme 4.

2.4 Adsorption experiments

The adsorption performance of Ni(II)-IIP₅ was assessed by a series of triplicate equilibrium adsorption experiments. Accurately weighed 0.0200 g of Ni(II)-IIP₅ and the corresponding NIP₅ were placed in a 25 mL stoppered conical flask, and 10 mL of the prepared Ni(II) solution was added. The reaction was placed in a thermostatic air bath shaker (at ambient temperature) for 12 h and filtered in a colorimetric tube. The concentration of Ni(II) was determined with an UV-Vis spectrophotometer which proceeded under corresponding wavelength conditions. Finally, the equilibrium adsorption capacity Q_e (mg/g) and the imprinting factor (α) were calculated according to Eqs. 1 and 2:

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\alpha = \frac{Q_{\text{IIP}}}{Q_{\text{NIP}}} \quad (2)$$

where Q_e (mg/g) is the equilibrium adsorption capacity, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of Ni(II) in solution, respectively, V (mL) is the volume of the solution, and M (g) is the mass of Ni(II)-IIP₅ and NIP₅.

2.5 Selectivity experiments

In order to obtain the selectivity of Ni(II)-IIP₅ for Ni(II) adsorption, Cu(II), Co(II), and Cd(II) were selected as competitive ions with the valence and ionic radius similar to that of the template ion Ni(II), and a mixed solution with an initial concentration of 100.00 mg/L was prepared. Twenty milligram of Ni(II)-IIP₅ were added to 10 mL of the above mixed solution and shaken at room temperature for 12 h. In addition, the adsorption capacity of each ion was measured, and the selective parameters, such as the distribution coefficient (K_d), selection factor (K), and relative selection factor (K'), of Ni(II) ions were calculated by the following Eqs. 3–5:

$$K_d = \frac{(C_0 - C_e)V}{wC_e} \quad (3)$$

$$K = \frac{K_d(\text{Ni(II)})}{K_d(M)} \quad (4)$$

$$K' = \frac{K_{\text{Ni(IIP)/M}}}{K_{\text{Ni(NIP)/M}}} \quad (5)$$

where K_d , K , and K' are the distribution coefficient, selectivity coefficient, and relative selectivity coefficient, respectively; C_0 and C_e are the initial and equilibrium concentrations of metal ions (mg/L); V is the volume of the solution (mL); w is the mass of Ni(II)-IIP₅; and M is the mass of each metal ion.

Scheme 4: Preparation of Ni(II)-IIP and NIP.

3 Results and discussions

3.1 The effect of polymer preparation conditions

3.1.1 The effect of solvent types

The purpose of solvent is to provide chemical environment for polymerization process, it not only influences the morphology of polymers but also impacts the chelating of functional monomers with the template before polymerization (39,40). Metal ions are soluble in water easily and difficult to dissolve in organic solvents, but functional monomers, cross-linker, and initiator are hardly soluble in water. However, the experiments required that the prepolymer which is formed by the template ion Ni(II) and the functional monomer and cross-linker coexisted homogeneously, so that the polymer can be maintained in binding sites during the polymerization process. Hence, the solvent must be a mixed solution which is composed of water and organic solvents. In this experiment, a mixed solvent of organic solvents (MeOH, EtOH, IPA, and DMF) and H₂O were used as the solvent in the volume ratio of 1:1. The experimental results are shown in Figure 1. The polymer with the best adsorption capacity and imprinting effect were prepared using MeOH/H₂O (v/v, 1:1) as the solvent, and the imprinting factor reached 1.27.

3.1.2 The effect of solvent ratio

The difference of solvent ratio mainly affected the tightness of the binding of the template ion and functional monomer. When the dosage of solvent was more or less in the preparation process, the texture of the prepared

Figure 1: Effect of the types of solvent on adsorption properties.

Figure 2: Effect of the ratio of solvent on adsorption properties.

imprinted polymer would be hard and dense or loose (40). Therefore, in this study, the polymer was prepared by changing the solvent ratio (methanol:water, v:v = 1:1, 1:2, 2:1, 1:3, 3:1). As shown in Figure 2, the solvent ratio of 1:2 (methanol:water, v/v) was the best preparation condition.

3.1.3 The effect of functional monomer dosage

The dosage of functional monomers had a crucial effect on the adsorption performance of the ion-imprinted polymers. When the dosage of the added functional monomers was too little, the degree of coordination between monomers and template ions would be insufficient, resulting in the reduction of the polymer recognition sites and selectivity; when the amount of functional monomer was too high, the prepared polymer was not conducive to specific recognition (41). Therefore, the polymer was prepared by changing the molar ratio of template ions to functional monomers (1:2, 1:4, 1:6, and 1:8), and the experimental results can be seen from Figure 3. The imprinting factors are 1.22, 1.96, 1.08, and 1.24 for molar ratios of 1:2, 1:4, 1:6, and 1:8, respectively, and the Ni(II)-IIP prepared with a molar ratio of 1:4 had preferable recognition performance. As a consequence, in the subsequent optimized experimental conditions, the molar ratio between the template ion and the functional monomer was 1:4 for synthesizing the polymer.

3.1.4 The effect of cross-linker dosage

One of the significant factors influencing the preparation of ion-imprinted polymers was the dosage of cross-linker. Its role was to fix the prepolymer formed by the template and monomer, by not only making the polymer to have a

Figure 3: Effect of the dosage of functional monomer on adsorption properties.

rigid structure and maintaining the recognition site after the template was eluted but also possessing certain chemical stability. The mass of cross-linker would slow the diffusion rate of the substrate into the polymer, which was not conducive for template mass transfer; nevertheless, a handful of cross-linker would cause the polymer to swell in the solution excessively, and reduce the selectivity of polymer to template ion (42). As shown in Figure 4, the imprinting factor reached 1.96 when the molar ratio of template ion and cross-linker was 1:20, and the recognition performance and adsorption capacity were favorable.

3.2 Equilibrium adsorption

3.2.1 Adsorption isotherm

Accurately weighed 20.00 mg of Ni(II)-IIP₅ and NIP₅ were taken in a series of triangular conical flasks, added Ni(II)

Figure 4: Effect of the dosage of cross-linker on adsorption properties.

solutions in a concentration range of 10.00–60.00 mg/mL, and the amount of imprinted polymer Ni(II)-IIP₅ and the corresponding NIP₅ were investigated for template ion Ni(II) in the solution with various concentrations, and the adsorption isotherm was drawn based on the experimental data (as shown in Figure 5).

It can be observed from the adsorption isotherm that the absorption capacity of Ni(II)-IIP₅ and NIP₅ strengthened with the increase in the concentration, and the adsorption amount of Ni(II)-IIP₅ in the range of 10.00–60.00 mg/mL of Ni(II) solution concentration was higher than the corresponding NIP₅ adsorption amount. This is because the adsorption of NIP₅ with template ions was non-specific mainly and there was no binding site, so the selectivity and adsorption capacity were weak. However, Ni(II)-IIP₅ contained holes that matched the size and configuration of the template ion, so it had better specific selective recognition performance.

In order to prove the adsorption performance of Ni(II) ion on the surface of Ni(II)-IIP₅, the experimental data were analyzed and they fitted the adsorption isotherm models of Langmuir, Freundlich, and Scatchard models. Its related linear fitting equation was expressed as follows:

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (6)$$

Freundlich isotherm:

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

where C_e is the concentration of Ni(II) ion at adsorption equilibrium, (mg/mL); Q_e and Q_m are the equilibrium adsorption capacity and maximum adsorption capacity of Ni(II) ions by imprinted polymer, respectively (mg/g);

Figure 5: The adsorption isotherm of Ni(II)-IIP₅ and NIP₅.

Figure 6: (a) Langmuir fitting isotherm of Ni(II)-IIP₅ and (b) Freundlich fitting isotherm of NIP₅.

K_L is the Langmuir constant; and n and K_F are the constants of Freundlich model.

The Langmuir and Freundlich isothermal adsorption models represented the monomolecular adsorption on heterogeneous surfaces and multimolecular adsorption on heterogeneous surfaces, respectively. The fitted curves are shown in Figure 6a and b. The relevant parameters of the fitted equation were calculated. It could be seen that the correlation coefficient obtained through the Langmuir and Freundlich adsorption isotherm models were both 1, indicating that Ni(II)-IIP adsorbed Ni(II) ions fitting the Langmuir and Freundlich isothermal adsorption models. Simultaneously, the result showed that monolayer adsorption and multimolecular layer adsorption were coexistent.

In addition, for demonstrating the binding properties of Ni(II)-IIP for Ni(II), the Scatchard isotherm adsorption model was proposed, and is expressed as Eq. 8.

Scatchard isotherm:

$$\frac{Q_e}{C} = \frac{Q_e - Q_m}{K_d} \quad (8)$$

where Q_e and Q_m are the equilibrium adsorption capacity and maximum adsorption capacity of Ni(II) ions by imprinted polymer (mg/g), respectively; C is the initial concentration (mg/mL) and K_d is the Scatchard constant.

The fitting plot of the Scatchard adsorption model is shown in Figure 7. The Scatchard curve of the Ni(II)-IIP was composed of two straight lines with a positive correlation. This showed that within the concentration range of this experiment, there were two different affinity binding sites in the adsorption process of Ni(II)-IIP₅. Among them, the K_d value of high affinity binding site was 79.30 mg/mL, and the K_d value of low affinity binding site was 305.26 mg/mL, the maximum apparent adsorption was due to the combined action of variety of sites.

3.2.2 Adsorption kinetics

Twenty milligram of Ni(II)-IIP₅ and NIP₅ were dropped into stoppered conical flask, to which 10.00 mL of 50.00 mg/mL Ni(II) solution was added with shaking at room temperature to measure the amount of change in substrate adsorption at different times. The kinetic adsorption curves of Ni(II)-IIP₅ and NIP₅ are shown in Figure 8. Ni(II)-IIP₅ adsorbed for Ni(II) in the first 5 min rapidly, and the adsorption speed of inter-ion slowed down significantly within 5–15 min, subsequently, it reached the adsorption equilibrium after 15 min. The reason of vast adsorption rate was because the surface of Ni(II)-IIP₅ had enough imprinting cavities to match Ni(II) at the initial stage, and the adsorption site had strong coordination with Ni(II) so that the diffusion resistance was small and mass transfer rate of Ni(II) ions was fast; whereas when the adsorption of the imprinted sites on polymer surface reached saturation, the resistance of the imprinted

Figure 7: Scatchard fitting isotherm of Ni(II)-IIP₅.

Figure 8: The kinetic adsorption curves of Ni(II)-IIP₅ and NIP₅.

ions to the internal transfer of Ni(II)-IIP₅ increased, causing adsorption rate of Ni(II)-IIP₅ for Ni(II) to decrease.

In order to investigate the adsorption kinetics of ion-imprinted polymers, pseudo-first-order kinetic model,

pseudo-second-order kinetic model, and ion diffusion models were used to fit experimental data to determine the kinetic process of adsorption. Its linear fitting Eqs. 9–11 are as follows:

Pseudo-first-order kinetic model:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \quad (9)$$

Pseudo-second-order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (10)$$

Ion diffusion model:

$$Q_t = K_p t^{1/2} + C \quad (11)$$

where Q_e and Q_t are the equilibrium adsorption capacity and adsorption capacity at time t of Ni(II) ions by imprinted polymer (mg/g), respectively; k_1 and k_2 are the rate constants of the pseudo-first-order and pseudo-second-order of these equations; K_p is the rate constant of ion diffusion model.

Figure 9: (a) Pseudo-first-order model, (b) Pseudo-second-order model, and (c) Ion diffusion model.

Table 2: Linear fitting parameters of adsorption kinetics of Ni(II)-IIP₅

Pseudo-first-order			Pseudo-second-order			Ion diffusion model		
Q_e (mg/g)	K_1	R^2	Q_e (mg/g)	K_2	R^2	K_p	C	R^2
5248.1	0.0046	0.99962	76.9	0.012	0.99011	72.86	368.32	0.88817

The fitting models of Ni(II)-IIP for Ni(II) adsorption is shown in Figure 9a–c, and the kinetic parameters were calculated from the equations fitted by the three models as shown in Table 2. It can be seen that k_1 is equal to 0.0046, correlation coefficient R^2 is 0.99962, and Q_e is 5248.10 mg/g. The pseudo-second-order kinetics model showed that k_2 is equal to 0.012, correlation coefficient R^2 is 0.99011, and Q_e is 76.90 mg/g; The ion diffusion model showed that K_p is equal to 72.86 and the correlation coefficient R^2 is 0.88817. The linear correlation coefficient of the curve fitted by the pseudo-first-order kinetic model was more than the others, which indicated that the process of adsorption was more consistent with the pseudo-first-order kinetic model.

3.2.3 Selectivity experiments

To evaluate the selectivity of Ni(II)-IIP₅ and NIP₅, Cu(II), Co(II), and Cd(II) ions which had similar charge numbers and ionic radius as that of the template ion were chosen as the competitive ions for the selective experiments. The data of K_d , K , and K' for Ni(II) ions as contrasted with other competing ions are shown in Table 3. Under the same experimental conditions, K_d values of Ni(II)-IIP₅ for Ni(II) ions were greater than that of NIP₅, while the K value of Ni(II)-IIP₅ was much greater than that of other competitive ions. The K' values of Ni²⁺/Cd²⁺, Ni²⁺/Co²⁺, and Ni²⁺/Cu²⁺ were 1.1, 1.07, and 1.08, respectively, which were more than 1. The results indicated that Ni(II)-IIP₅ had strong specific recognition for target ions Ni(II) as

Table 3: Parameters of ion competitive adsorption study for Ni(II)-IIP₅ and NIP₅

Metal ions	Ni(II)-IIP ₅		NIP ₅		K'
	K_d	$K_{Ni/M}$	K_d	$K_{Ni/M}$	
Ni(II)	2.076		1.918		
Cd(II)	0.532	3.902	0.540	3.549	1.100
Co(II)	1.623	1.279	1.618	1.186	1.079
Cu(II)	1.268	1.637	1.274	1.505	1.088

compared to other interfering ions, that is these data revealed that Ni(II)-IIP₅ had specific binding sites, which possessed favorable selectivity for Ni(II).

3.2.4 Effect of pH on adsorption of Ni(II)

The influence of pH is of vital importance for containing maximum adsorption with polymers (43,44). Hence, 20.00 mg of Ni(II)-IIP₅ and NIP₅ were immersed in 10 mL of 50.00 mg/L solution of Ni(II) under different pH conditions from 1–10 for 12 h. As can be seen from Figure 10, the curves of Ni(II)-IIP₅ and NIP₅ have similar trend. The adsorption capacity of Ni(II)-IIP₅ for Ni(II) decreased between the pH values of 1–3, it may ascribe to the higher concentration of H⁺ which produces competitive adsorption of Ni(II) and occupies the adsorption sites of Ni(II). The competitive ability of Ni(II) was reduced as the acidity of the solution decreased and the adsorption effect of Ni(II)-IIP₅ was obviously enhanced, maximum absorption capacity was obtained at pH = 4. This study also demonstrated that the adsorption amount would not have noticeable change with the increase in pH at 5–10; this range of pH has little impact on the adsorption process, and the Ni(II)-IIP₅ represents stable property. This research also illustrates that the preparation of Ni(II)-IIP₅ under optimal

Figure 10: Effect of pH on adsorption properties.

conditions has favorable stability with the range of alkaline, so it will be used in a wider application domain.

3.3 Characterization

3.3.1 SEM analysis

The morphological images of the Ni(II)-IIP₅, NIP₅, Ni(II)-IIP₅ after adsorption, and EDS analysis of loaded Ni(II) of Ni(II)-IIP₅ were characterized by SEM as shown in Figure 11a–d. There was significant difference in the surface morphology between Ni(II)-IIP₅ and NIP₅, wherein Ni(II)-IIP₅ exhibited porous and rough surface on account of imprinting of Ni(II) ion above polymer as shown in Figure 11a. Figure 11b shows an obvious relative flat surface and compact texture with less porous surface; however, an apparent increase in roughness and porous surface were observed after adsorption

of Ni(II) as shown in Figure 11c. Figure 11d expresses the EDS analysis of image (c). This indicates that the Ni ions were successfully adsorbed by Ni(II)-IIP₅.

3.3.2 BET analysis

The adsorption–desorption isotherms and surface properties which contained surface area (m²/g), average pore diameter (nm), and pore volume (cm³/g) of Ni(II)-IIP₅ and NIP₅ are shown in Figure 12a and b and Table 4, respectively. They were obtained by BET theory and Barrett–Joyner–Halenda (BJH) theory. It can be seen from the figure that the shapes of the adsorption/desorption isotherms of Ni(II)-IIP₅ and NIP₅ were fitted to the classic IV isotherms in the IUPAC classification method, which were typical characteristics of mesoporous materials. The pore size in Table 4 also proved that it was a mesoporous material. It could be seen that the BET surface area of Ni(II)-IIP₅

Figure 11: (a) SEM images of Ni(II)-IIP₅, (b) NIP₅, (c) Ni(II)-IIP₅ after adsorption, and (d) EDS analysis of image (c).

Figure 12: Nitrogen adsorption and desorption isotherm of Ni(II)-IIP₅ (a) and NIP₅ (b).

Table 4: Nitrogen adsorption data of Ni(II)-IIP₅ and NIP₅

Polymer	Surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
Ni(II)-IIP ₅	89.04	12.4	0.28
NIP ₅	67.36	8.18	0.14

and NIP₅ were 89.04 and 67.36 m²/g and pore volumes were 0.28 and 0.14 cm³/g, respectively. The parameters of Ni(II)-IIP₅ were all less than that of NIP₅. The results indicated that there was highly porous structure with imprinted material. After adsorption, the obvious changes in BET surface area, total pore volume, and average pore diameter were observed on Ni(II)-IIP₅ and NIP₅, indicating that Ni(II)-IIP₅ possessed the active sites which had identical shape and size of imprinting ion Ni(II) on adsorbent.

3.3.3 TGA analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique applied to material analysis extensively. In this experiment, the method of thermogravimetric was used to investigate the thermal stability of Ni(II)-IIP₅ and NIP₅ by the TGA curves. The analysis is carried out under conditions, such as temperature in the range of 40–600°C, nitrogen atmosphere, and the heating rate of 20°C/min.

The curve of TGA is shown in Figure 13. Ni(II)-IIP₅ and NIP₅ have similar linear trends, all of them have preferable stability in the range of 40–270°C which without apparent mass loss, it may cause by evaporation of water,

both of them with roughly trend weight loss from 270°C to 420°C. In this condition, it is possible that the framework of polymers was damaged at high degradation temperature and some organic components decomposed following the increase in the temperature. Calculated from the curve data that Ni(II)-IIP₅ and NIP₅ with total mass loss of 93% and 81% at the temperature of 420°C, respectively. The result indicated that both of them have a good thermal stability and these polymers will probably evaporate completely at temperature above 600°C. This provides a new mind for the preparation of a highly efficient and environmentally friendly adsorbent material that can be recovered at high temperature after repeated usage, which hardly causes secondary pollution.

Figure 13: TGA curve of Ni(II)-IIP₅ and NIP₅.

3.4 Regeneration and reusability

Regeneration and recyclability of adsorption material are often used to evaluate its properties. Excellent imprinted materials should not only have superior adsorption capacity but also have good regeneration performance, which is of great significance to reduce the cost of water treatment in actual production. In this study, the method of desorption and regeneration of adsorbent is carried out as follows: Ni(II)-IIP₅ after adsorption was dried and ground, and then reflux-extracted at a temperature of 70°C for 24 h, the mixed ratio of methanol and acetic acid with 9:1, after extraction and dried, and the regenerated adsorbent was obtained. As shown in Figure 14, the adsorption and desorption rates of Ni(II)-IIP₅ were 90% and 85% after first usage, respectively. And after using it a few times, Ni(II)-IIP₅ still maintained good adsorption performance, and the removal rate was still about 80%. It is shown that the number of regeneration did not affect the adsorption process, and the prepared Ni(II)-IIP₅ had a higher adsorption rate and stability for Ni ions.

3.5 Comparison with other methods

To attest the advantages of Ni-IIP₅, it was compared with other recent studies (45–50) with regard to maximum adsorption for recovery of Ni(II) as shown in Table 5. It can be seen that there exists difference in the adsorption capacity of Ni(II) wherein the adsorption materials were prepared by various methods. This study revealed that the prepared Ni(II)-IIP has a large amount of adsorption capacity by contrast, and the results indicated that Ni-IIP₅

Figure 14: Regeneration and reusability of Ni(II)-IIP₅.

Table 5: Comparison of adsorption capacity of nickel ion using different adsorbents

Adsorbents	Q_e (mg/g)	References
Magnetic imprinted polymer	158.73	(45)
Multi-wall carbon nanotube	115.8	(46)
Bentonite/GO composite	402.5	(47)
Clay	2,590	(48)
ZIF-8/Fly ash composite	93	(49)
Paper-based adsorbent	317.5	(50)
Ni(II) ionimprinted polymer	5,387	This work

can be a great potential adsorbent for heavy metal ion adsorption.

4 Conclusion

In this study, a favorable performance of Ni(II)-IIP (Ni-IIP₅) by using a novel functional monomer NDTEA had been prepared by precipitation polymerization method. The Ni-IIP₅ was adsorbed for Ni(II) in the solution containing Ni(II) which was obtained through optimizing various affecting parameters. It exhibited satisfactory adsorption ability, the high adsorption capacity and imprinting factor were 5387.00 mg/g and 1.96, respectively. The morphological structure and properties were characterized by SEM, BET, and TGA, and the result showed a series of excellent properties including thermal stability, porous structure, and specific selectivity identity with the performance of Ni-IIP₅ for Ni(II). The result simultaneously indicated that Ni-IIP₅ was a typical mesoporous material. The adsorption process of Ni-IIP₅ for Ni(II) was fitted with Pseudo-first-order adsorption models, and Ni-IIP₅ performed better selectivity with competing ions in the solution. These preferable properties would lead this imprinted polymer to have a potential application for separating and gathering Ni(II) in wastewater, and this novel functional monomer NDTEA exhibited an attractive application prospect in the functional adsorption material fields.

Acknowledgements: The authors acknowledge the financial support provided by the National Natural Science Foundation of China, also express sincere gratitude to co-authors who have made invaluable contributions, both directly and indirectly to my research.

Funding information: This work was supported by the National Natural Science Foundation of China (No. 21764008).

Author contributions: Li Zhao: methodology, writing – original draft, data curation; Xianzhi Hu: supervision,

validation; Futing Zi: supervision; Yingmei Liu: software; Deqiong Hu: investigation, data analysis; Peng Li: investigation; Huiling Cheng: project administration, funding acquisition, writing – review and editing.

Conflict of interest: Authors state no conflict of interest.

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Appendix

Compound 2: ^1H NMR (400 MHz, CDCl_3) δ : 8.02(s, 1H), 8.20(d, $J = 5.4$ Hz, 2H), 7.82(s, 1H), 7.43–7.49(m, 1H), 6.86–6.91(m, 1H), 6.79–6.84(m, 1H), 5.34(d, $J = 7.5$ Hz, 1H), 4.85(br, 2H), 4.43–4.47(dd, $J = 2.6$ Hz, 2.6 Hz, 1H), 4.22–4.28(dd, $J = 8.2$ Hz, 8.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 164.2(d, $J_{\text{C-F}} = 12.1$ Hz), 161.7(d, $J_{\text{C-F}} = 11.8$ Hz), 160.9(d, $J_{\text{C-F}} = 11.7$ Hz), 158.4(d, $J_{\text{C-F}} = 11.7$ Hz), 151.8, 144.0, 128.7(q, $J_{\text{C-F}} = 5.8$ Hz), 123.5(d, $J_{\text{C-F}} = 13.7$ Hz), 112.0(q, $J_{\text{C-F}} = 3.4$ Hz), 104.3(t, $J_{\text{C-F}} = 25.3$ Hz), 66.6, 55.5.

Compound 3: ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.43(s, 1H), 8.20(d, $J = 5.4$ Hz, 2H), 7.95(s, 1H), 7.73(s, 1H), 7.50–7.56(m, 1H), 7.18–7.23(m, 1H), 7.08–7.13(m, 1H), 5.93–6.02(dd, $J = 7.5$ Hz, 15.2 Hz, 1H), 5.71(d, $J = 15.3$ Hz, 1H), 5.34(d, $J = 10.6$ Hz, 1H), 5.16(s, 1H), 4.20(s, 1H), 4.16(s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 163.5(d, $J_{\text{C-F}} = 12.4$ Hz), 161.0(q, $J_{\text{C-F}} = 8.7$ Hz), 158.5, 158.4(d, $J_{\text{C-F}} = 12.1$ Hz), 151.7, 145.2, 129.8(q, $J_{\text{C-F}} = 6.2$ Hz), 128.8, 125.7(d, $J_{\text{C-F}} = 3.7$ Hz), 113.9, 112.1(t, $J_{\text{C-F}} = 3.6$ Hz), 104.3(t, $J_{\text{C-F}} = 25.7$ Hz), 65.3, 55.1, 51.9.

Figure A1: ^1H NMR spectra of compound 2.

Figure A2: ^{13}C NMR spectra of compound 2.

Figure A3: ¹H NMR spectra of compound 3.

Figure A4: ¹³C NMR spectra of compound 3.