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Synthesis of a new ion-imprinted polymer and its characterization for the selective extraction and determination of nickel ions in aqueous solutions

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ABSTRACT

A new ion-imprinted polymer (IIP) was synthesized by bulk polymerization from 2-vinylpyridine (the functional monomer), ethylene glycol dimethacrylate (EGDMA; the cross-linker), 2, 2´- azobisisobutyronitrile (the initiator), diphenylcarbazone (the ligand), and nickel nitrate (the template ion) in acetonitrile solution. The prepared IIP was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy, and studied for the preconcentration and determination of trace nickel ion from aqueous solutions using inductive couple plasma optical emission spectroscopy. The optimal pH value for the quantitative preconcentration was 6.0 and maximum sorbent capacity was 3.26 mg g^{-1}. Under the optimized conditions, the method had a linear analytical range from 0.5 to 50 μg L^{-1}. The detection limit, relative standard deviation, and recovery of the method were evaluated as 0.38 μg L^{-1}, 3.6% and 95–98%, respectively. The developed method was successfully applied to the selective extraction and determination of trace nickel in synthetic and real water samples and some medicinal plants with satisfactory results.

Keywords: Ion-imprinted polymer; Nickel; Inductively coupled plasma optical emission spectrometry; Extraction

1. Introduction

Heavy metals are natural components of the Earth's crust, which can accumulate in the environment. Many heavy metals are toxic and cause a potential risk for human health [1]. One of these elements is nickel with toxic and carcinogenic effects at elevated concentrations. It can cause a considerable health problem known as nickel eczema particularly in women [2]. Thus, determination of Ni(II) in biological and environmental samples is very important and need much more attention. Nickel determination could be carried out by

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graphite furnace atomic absorption spectrometry [3], flame atomic absorption spectrometry [3,4], electrothermal atomic absorption spectrometry [5], and inductively coupled plasma optical emission or mass spectrometry (ICP-OES/MS) [4,6,7]. To determine trace metals in aquatic environments by instrumental analysis, a separation and preconcentration method is commonly required because of low concentration of metal ions and presence of interferences [8]. Many separation and preconcentration techniques, such as solvent extraction [9,10], coprecipitation [11–14], liquid–liquid extraction [15], ion exchange [16,17], solid phase extraction (SPE) [18], and membrane filtration [19] have been developed for preconcentration of trace metals from matrices.

Ionic-imprinted polymers (IIPs) are the new improvement in the area of SPE. IIPs show very interesting characteristics such as high selectivity, low cost, high surface area, durability, and reusability. Because of this, recently, it has been widely used for separation and preconcentration in solid-phase extraction [20]. IIPs containing specific recognition sites are synthesized via copolymerization with functional and cross-linking monomers in the presence of imprint metal ion in the form of complex with a suitable ligand [20–22]. There are a number of previously published papers dealing with the preparation of IIPs for Ni(II) ion using different ligands such as hydroxyquinoline [23], or modified hydroxyquinoline [24] and its derivatives (mainly 5,7-dichloroquinoline) [25], dithizone [8], and alizarin red S [26].

In this work, a new Ni(II)–IIP was prepared by bulk polymerization method using diphenylcarbazone as ligand. There is no previous literature report on the use of diphenylcarbazone as a ligand in the preparation of nickel IIP. Characterization of the synthesized polymer was evaluated by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Effects of pH, extraction time, type and volume of eluant, and selectivity of polymer for Ni(II) ions were investigated. Ni(II)–IIP technique followed by ICP-OES was applied for preconcentration and determination of Ni(II) ions in synthetic and real water samples, and in some medicinal plants that are commonly used in traditional medicine in Iran.

2. Experimental

2.1. Chemicals

2-Vinyl pyridine, EGDMA, and diphenylcarbazone were obtained from Merck (Darmstadt, Germany). 2, 2-Azobis isobutyronitrile (AIBN) was purchased from Acros Organics (Morris Plains, NJ, USA). Water was obtained from a Milli-Q purification system (Purelab UHQ Elga). All solvents and other reagents used were of analytical grade and purchased from Merck (Darmstadt, Germany). A certified reference material (NCS ZC73036 Green tea obtained from National Institute of Standards and Technology, Beijing, China) was used to verify the accuracy of the results of analyses. Stock standard solutions of individual metals (1,000 or 10,000 mg L^{-1}) were supplied by Merck (Darmstadt, Germany). Stock solutions were diluted to 1 L with distilled water. More dilute standards were prepared daily by the dilution of these solutions. The herbal samples were obtained from institute of medicinal plants, ACECR.

2.2. Apparatus

FTIR spectra of grounded polymer were recorded on a Bomem FTIR MB 155S spectrometer (Canada) using KBr pellets in the range of 400–4,000 cm^{-1}. In all solutions, the pH was adjusted by a digital Metrohm pH meter (model 744) equipped with a combined glass–calomel electrode. Morphology of polymer was characterized by SEM (Philips XL30 scanning microscope, Philips, Netherlands). Samples were sputter coated with gold before the SEM measurement. An ICP-OES instrument (Varian 760-ES) was used for the determination of all metal ions. The operational conditions for ICP-OES and wavelength of analytical lines were in accordance with the manufacturer's instructions. Operating conditions for the ICP-OES instrument were forward power 1 kW, plasma flow rate 15 L min^{-1}, auxiliary gas flow rate 1.5 L min^{-1}, and nebulizer gas flow rate 0.75 L min^{-1}. The wavelengths used were as follows: Cu 327.395 nm, Co 238.892 nm, Ni 231.604 nm, Zn 213.857 nm, Mn 257.610 nm, and Pb 220.353 nm. A microwave oven equipped with PTFE vessels, (Berghof Speed wave (Germany)), was used for sample digestion. Ultra-pure deionized water was prepared by Basic 360 Series-Younglin, coupled with Aqua MAX-ultra 354.

2.3. Preparation of Ni(II) ion-imprinted polymer

The synthesis of Ni(II)–IIP was based on the bulk polymerization technique. In the first step, diphenylcarbazone (ligand, 4 mmol), 2-vinyl pyridine (functional monomer, 1 mmol), and acetonitril (polymerization solvent, 30 mL) were placed in a 100 mL volumetric flask and then $Ni(NO_3)_2$ (template, 0.5 mmol) was added slowly to this solution. The resulted mixture was stirred for 4 h at room temperature. In the second step, EGDMA (cross-linker, 20 mmol) and AIBN (Initiator, 0.8 mmol), were added to the solution and then stirred at room temperature. The solution was purged with a stream of nitrogen for 10 min to remove molecular oxygen, since it traps the radicals and retards the polymerization. Then the flask was sealed immediately and heated in an oil bath at 65℃ for 24 h to complete the polymerization. The prepared ion-imprinted polymer was dried at room temperature, crushed using a pestle and mortar, and then sieved to obtain a fine powder. The powders were washed with 1 : 4 (v/v) methanol/water to remove the unreacted materials and then by HNO_3 (0.1 M) for leaching of the imprint ions until the washing solution was free from Ni(II) ions. Finally, it was washed with double distilled water until neutral pH was achieved. The resulting powder was dried overnight. The non-imprinted polymer (NIP) was also prepared simultaneously as the same procedure, without Ni(II) ion. The scheme for preparation of Ni(II)–IIP is described in Fig. 1.

2.4. Batch rebinding experiments

Batch rebinding experiments were used to estimate the binding capacity of the ion-imprinted polymer. In order to extract Ni(II) ion by the IIP, 30 mg of the synthesized IIP was added in a volumetric flask (20 mL) containing Ni(II) ion in different concentrations (1–30 mg L^{-1}) in water. The mixtures were stirred 5 min at room temperature and then IIP particles were separated from the mixture by filtration. The free concentration of Ni(II) ion after the adsorption was recorded by ICP-OES at 231.604 nm. Three replicate extractions and measurements were carried out for each concentration. The IIP particles were washed with water (20 ml) and then leaching process was carried out by HNO_3 (5 mL, 0.1 M), while stirring for 5 min at room temperature. The amount of Ni(II) ion bound to the polymer was calculated by subtracting the concentration of free Ni(II) ion from the initial concentration.

2.5. Preparation of samples

For the decomposition of plant samples and certified reference material, about 0.1 g of the material was accurately weighed into a PTFE digestion vessel. Five milli liter of concentrated HNO_3 and 2 mL of concentrated H_2O_2 were added and waited for about 20 min. When the foam caused by organic matter decomposition disappeared, the vessels were closed, placed on the rotating turntable of the microwave, and then digestion was started as presented in Table 1. After cooling at room temperature, the extract was transferred into a volumetric flask and made up to 100 mL with deionized water.

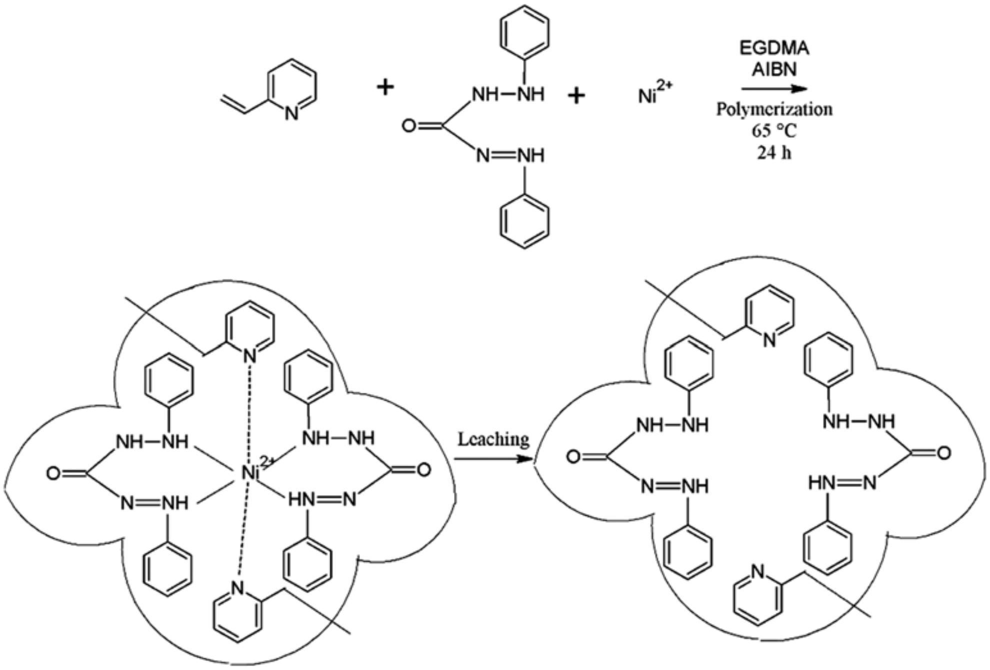

Fig. 1. The scheme for preparation of Ni(II)–IIP.

Table 1
Parameters for the microwave digestion

Time (min)	Temperature (˚C)	Pressure (bar)	Ramp (min)	Power (W)
10	160	50	15	40
5	175	50	15	50
1	50	50	1	0
1	50	50	1	0
1	50	50	1	0

The Ni(II)–IIP was also applied to the determination of nickel in synthetic and tap water samples.

For the preconcentration of Ni(II) ions, 100 mL of the aqueous solution of real and spiked samples with Ni(II) ions were adjusted to pH 6.0 and equilibrated with 30 mg of Ni(II)–IIP. The resulting suspension was stirred for 5 min and then leaching process was carried out by HNO_3 (5 mL, 0.1 M), while stirring for further 5 min.

The concentration of Ni(II) ions in leached solutions was determined by ICP-OES.

3. Results and discussion

3.1. SEM analysis

The morphology of the Ni(II)–IIP and NIP were assessed by SEM. Analysis of the SEM images (Fig. 2) indicated that IIP and NIP exhibited no detectable differences in appearance. As verified, owing to bulk method used for polymer synthesis, the particles of both IIP and NIP polymers have irregular shapes with heterogeneous surfaces.

3.2. IR spectra

The IR spectra of unleached and leached Ni(II)–IIP were recorded by using KBr pellet method (Fig. 3). Both IIPs have a similar IR spectrum, which indicates that all polymers have similar backbone but different intensity spectra. The N–H and C=N bands at 3,440.38 and 1,638.01 cm^{-1} in unleached IIP were shifted to 3,444.51 and 1,645.02 cm^{-1}, respectively, in leached IIP .The shift and decrease in strength of vibration can be attributed to bonding between the nickel with diphenylcarbazone. Different colors of the NIP (yellow) and imprinted polymer (purple) indicated the presence of template ion as a Ni(II)–diphneylcarbazone complex in the IIP matrix. Moreover, the change in color from purple to yellow is a clear result of desorption of the Ni(II) ions from the IIP particles after its leaching with a 0.1 M HNO_3 solution.

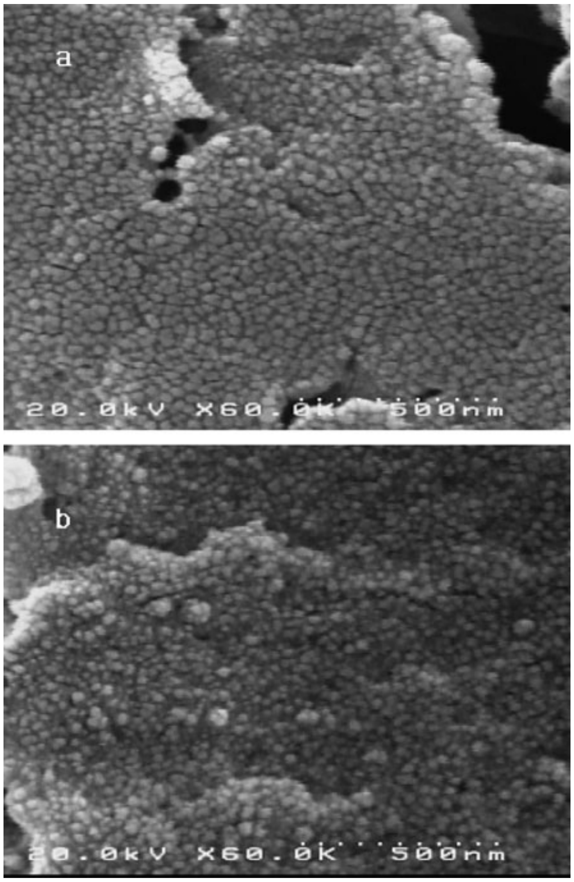

Fig. 2. Scanning electron micrograph of polymers: (a) IIP and (b) NIP.

3.3. Effect of pH on the extraction of Ni(II)

The pH was found to be the most important parameter for adsorption of metals on the ion-imprinted polymer. In an acidic environment, the nickel-imprinted sites of the polymer were occupied by protons rather than nickel ions, so that the polymer absorbs smaller amounts of nickel ions. As the pH increased, the protonation of ligand is suppressed and the condition becomes more favorable for sorption of

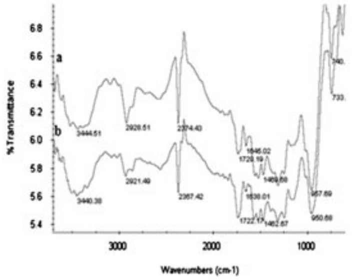

Fig. 3. The FT–IR spectra of leached (a) and unleached (b) Ni(II)–IIP.

Ni(II) ions to the imprinted polymer [27]. The effect of pH on the adsorption of Ni(II) was studied by mixing 30 mg of the sorbents with 20 mL Ni(II) ion solution (1 mg L^{-1}) in the pH range of 1.0–8.0. According to the results (Fig. 4), the maximum extraction of nickel ions was obtained at the pH of 6.0. The pH above 8.0 was not investigated because of the possibility of hydrolysis and precipitation of nickel ions.

3.4. Equilibrium sorption and desorption time

In a typical uptake kinetics test, 30 mg of the polymer was added to 20 mL Ni(II) aqueous solution (1 mg L^{-1}) at pH 6.0. The resulting suspension was stirred at different time intervals ranging from 2 to 10 min. As it was shown in Table 2, an optimum equilibration time of 5 min (98% extraction) was obtained for quantitative extraction of Ni(II) ion from solution into the sorbent, which could be attributed to the high surface area of imprinted polymer. In order to study the optimum desorption time, various times were examined (2–10 min). According to the results, extraction percent was increased up to 5 min and it was constant in longer times. Therefore, the best quantitative time for the elution of Ni(II) ions from the imprinted polymer was 5 min.

Table 2
Influence of sorption and desorption times on the extraction percent of Ni(II) ion using IIP and NIP particles

		Extraction(%) ± SD	
Parameter	Time (min)	IIP	NIP
Sorption	2	42 ± 1.2	22 ± 1.5
	3	69 ± 0.5	31 ± 0.9
	4	78 ± 0.8	35 ± 1.1
	5	98 ± 1.3	38 ± 0.6
	8	98 ± 0.8	42 ± 1.5
	10	98 ± 0.9	42 ± 1.2
Desorption	2	70 ± 1.2	28 ± 1.0
	3	89 ± 0.5	32 ± 1.2
	4	95 ± 0.8	35 ± 1.1
	5	98 ± 1.3	38 ± 0.9
	8	98 ± 0.8	41 ± 0.5
	10	98 ± 0.9	41 ± 1.0

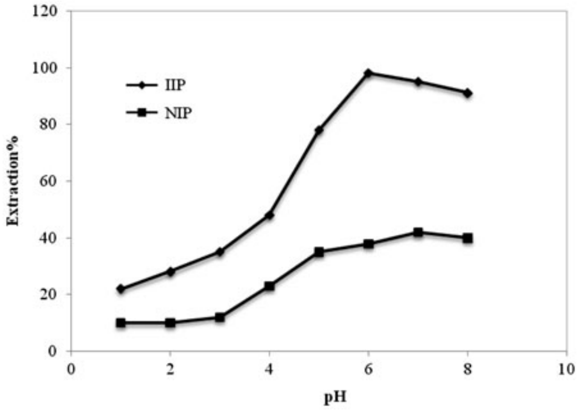

Fig. 4. Effect of pH on extraction of IIP and NIP particles in batch experiments with 30 mg of polymer particles; sample volume, 20 mL; Nickel ion concentration, 1 mg L^{-1}.

3.5. Choice of eluant solution

In order to obtain the best solvent for the elution of Ni(II) from IIP, 5 mL portions of 0.1 M HCl, 0.1 M HNO_3, and 0.1 M H_2SO_4 were used. The results showed that 0.1 M HNO_3 provided the best recovery among other solvents. HNO_3 was selected as eluant not only because of its better leaching characteristic over other two mineral acids, but also because of its compatibility with ICP-OES.

3.6. Adsorption capacity and adsorption isotherm

The capacity of the IIP is an important factor that establishes how much IIP is required to extract a specific quantity of ion from the solution. The sorption capacity (mg g^{-1}) of the IIP relative to the imprint metal ion was calculated as follows:

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

where C_i and C_e are the concentrations before and after extraction (mg L^{-1}), respectively, V is the volume of initial solution (mL), and m is the mass of IIP materials (g). According to batch rebinding results, the maximum amount of Ni(II) ion that can be absorbed by IIP was found to be 3.26 mg g^{-1} at pH 6.0. Fig. 5

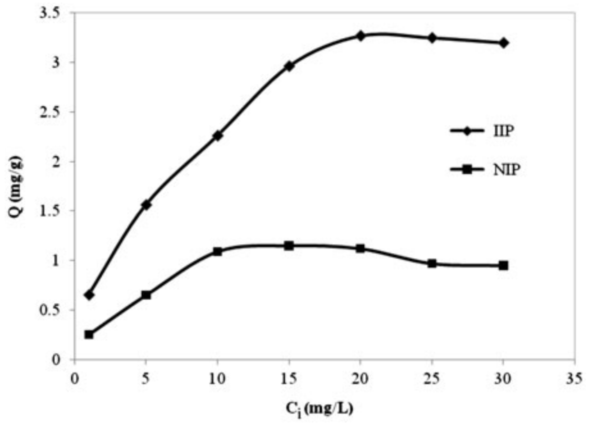

Fig. 5. Effects of initial concentration of Ni(II) ions onto the adsorption capacity of the IIP and NIP.

shows the effect of initial concentration of Ni(II) ions onto the adsorption capacity of the IIP and NIP. The amount of Ni(II) ions adsorbed per unit mass of the polymers increased with increasing initial concentration of Ni(II) ions, and reached a plateau at 20 mg L^{-1}. The high adsorption equilibrium capacity for IIP compared to NIP is due to the imprinted cavities and specific recognition sites created after removal of Ni(II) ion in the IIP, which are complementary to target ion in shape, geometry, and size, whereas no such specificity was found in NIP. The results indicate that imprinting play an important role in the adsorption behavior [28].

Adsorption isotherms measure the binding efficiency of a material over a range of analyte concentrations, and are commonly plotted as the binding capacity (Q) vs. the concentration of free analyte remaining in solution (C_e). Various models can achieve modeling of these equilibrium data [27]. Langmuir and Freundlich isotherm models are usually used to evaluate adsorption properties of IIPs. The Langmuir adsorption model is restricted to the formation of monolayer adsorption onto homogeneous binding sites [29,30]. The linear Langmuir model is expressed by the following equation:

$$C_e/Q = (1/Q_{\max})C_e + 1/bQ_{\max} \qquad (2)$$

where Q is the amount of Ni(II) ions adsorbed at equilibrium (mg g^{-1}), C_e is the final concentration of ion after rebinding experiment (mg L^{-1}), b is Langmuir constant (L mg^{-1}), and $Q_{\max}$ is the maximum adsorption capacity (mg g^{-1}).

The Freundlich model assumes heterogeneous adsorption and is applicable for multilayer coverage on adsorbent surface [31]. The Freundlich adsorption isotherm is expressed by the following equation:

$$\log Q = (1/n)\log C_e + \log K_f \qquad (3)$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The isotherm data were fitted with the above mentioned isotherm models and are shown in Figs. 6 and 7. The theoretical value of maximum adsorption capacity ($Q_{\max}$), Langmuir constant (b), and correlation coefficient (R^2) obtained from the Langmuir isotherm was found to be 3.49 mg g^{-1}, 0.51 L mg^{-1}, and 0.982. The maximum adsorption capacity determined from Langmuir plot was very close to the experimental value. The Freundlich constant (K_f), adsorption intensity (n), and correlation coefficient (R^2) were obtained to be 1.54, 4.25, and 0.962, respectively. Comparing the correlation coefficients of isotherms in fitting the adsorption data, it shows that Langmuir model provides better fitting for imprinted polymer.

3.7. Study of IIP selectivity

In order to study the selectivity of the imprinted polymer for Ni(II) vs. closely related ions, competitive adsorption of Ni(II) ion in the presence of Zn(II), Mn (II), Cd(II), Pb(II), Co(II), and Cu(II) from their binary mixtures was investigated in batch experiments. The initial concentrations of the pair of metal ions (1 mg L^{-1}) were extracted by 30 mg of imprinted material at pH 6.0. The distribution ratio (mL g^{-1}) of Ni(II) ions between the IIP and aqueous solution was evaluated by the following equation:

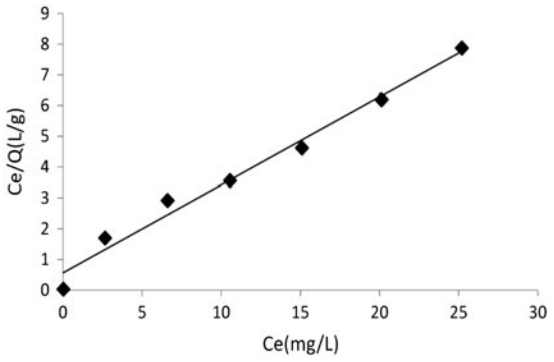

Fig. 6. Langmuir adsorption isotherm of Ni(II)–IIP.

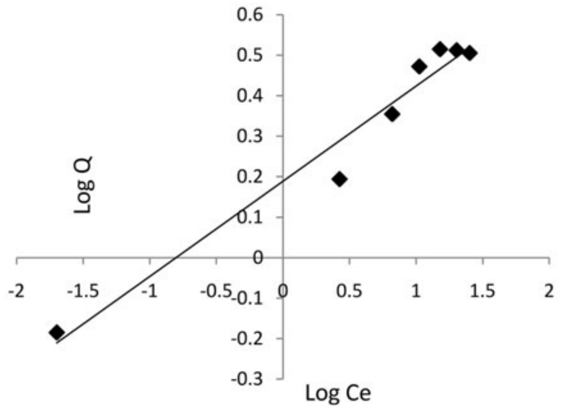

Fig. 7. Freundlich adsorption isotherm of Ni(II)–IIP.

Table 3
IIP and NIP selectivity studies for Ni(II) vs. closely related ions

Cation	K_d (IIP)[a]	K_d (NIP)	k (IIP)[b]	k (NIP)	k'[c]
Ni^{2+}	16,000	358.9	–	–	–
Zn^{2+}	299.5	272.3	53.4	1.3	40.5
Cu^{2+}	166.7	136.5	95.9	2.6	36.5
Co^{2+}	156.4	82.4	102.3	4.4	23.5
Pb^{2+}	90.9	74.1	175.9	4.9	36.2
Mn^{2+}	188.0	146.3	85.1	2.6	34.7

[a] Distribution ratio.
[b] Selectivity coefficient.
[c] Relative selectivity coefficient.

Table 4
Analysis of nickel ion in medicinal herbs and CRM

Sample	C_{added} ($\mu g\, g^{-1}$)	C_{found} ($\mu g\, g^{-1}$)[a]	Recovery %
Matricaria recutita (Asteraceae)	–	15.9 ± 0.7	–
	10	25.3 ± 0.9	97.8
Urtica dioica (Urticaceae)	–	25 ± 1.2	–
	10	34.4 ± 1.5	98.3
Hedera helix (Araliaceae)	–	17 ± 0.6	–
	10	25.9 ± 1.1	95.9
Cichorium intybus (Asteraceae)	–	14.2 ± 0.4	–
	10	23.1 ± 0.7	95.5
CRM (NCS ZC73036)	(real) 5.4 ± 0.4	5.3 ± 0.2	98

[a] Mean ± SD, $n = 3$.

$$K_d = (C_i - C_e)V/C_e m \tag{4}$$

where V is the volume of initial solution, m is the mass of IIP materials, C_i is the initial concentration in solution, and C_e is the final concentration of ion after rebinding experiment.

Selectivity coefficients for Ni(II) ions relative to foreign ions are defined as:

$$K_{\mathrm{Ni}^{2+}} = \frac{K_d^{\mathrm{Ni}^{2+}}}{k_d^{M^{n+}}} \tag{5}$$

where $K_d^{\mathrm{Ni}^{+2}}$ and $k_d^{M^{n+}}$ are distribution ratios of Ni(II) and foreign ion, respectively. The relative selectivity coefficient is defined as:

$$k' = k_{\mathrm{imprinted}}/k_{\mathrm{non-imprinted}} \tag{6}$$

where $k_{\mathrm{imprinted}}$ and $k_{\mathrm{non-imprinted}}$ are selectivity coefficients of the imprinted and NIPs, respectively [31]. The distribution ratios (K_d), selectivity coefficients (k), and relative selectivity coefficient (k') values of IIP and NIP material are listed in Table 3. According to the data shown in Table 3, prepared imprinted polymer has a high selectivity for Ni(II) ions.

Table 5
Determination of nickel ion in synthetic and real water samples

Sample	C_{added} ($\mu g\, L^{-1}$)	C_{found} ($\mu g\, L^{-1}$)[a]	Recovery %
Synthetic Sample [b]	0	0	–
	10	9.5 ± 0.1	95
Tap water	0	9.1 ± 0.2	–
	10	18.5 ± 0.1	96.8

[a] Mean ± SD, $n = 3$.
[b] Solution contains Cu^{2+}, Co^{2+}, Mn^{2+}, and Zn^{2+} ions of 10 $\mu g\, L^{-1}$ concentrations.

Table 6
Analytical parameters and application of different Ni(II)–IIPs

Ligand	Polymerization method	Detection system	Relative selectivity coefficient					Maximum capacity	LOD (μg L^{-1})	Matrix	Ref.
			k'_{Cu}	k'_{Zn}	k'_{Co}	k'_{Mn}	k'_{Pb}				
8-HQ[a]	Precipitation	ICP-OES	–	–	–	–	–	–	0.15	Sea water	[23]
MAH[b]	Dispersion	AAS	57.3	53.9	17.3	–	–	0.178 (m mol g^{-1})	0.3	Sea water	[2]
Dithizone	Bulk	AAS	54.3	–	21.6	–	–	1.3 (mg g^{-1})	1.6	Water samples	[8]
Vinylbenzoate	Bulk	AAS	111.1	78.6	91.6	–	–	1.51 (m mol g^{-1})	6	Sea water	[32]
5-VHQ[c]	Precipitation	ICP-OES	22.01	27.08	39.23	28.68	20.51	1.98 (mg g^{-1})	0.26	Sea water	[24]
Diphenylcarbazone	Bulk	ICP-OES	36.5	40.5	23.5	34.7	36.2	3.26 (mg g^{-1})	0.38	Plant and water	This work

[a] 8-hydroxyquinoline.
[b] Methacryloylhistidine.
[c] 5-vinyl-8-hydroxyquinoline.

3.8. Analytical performance of the method

The analytical performance of the present method was studied by the batch preconcentration procedure. The preconcentration procedure showed a linear curve over a concentration range of 0.5–50 μg L^{-1}. A good linearity with squared correlation coefficient (R^2) 0.999 was obtained. The enrichment factor, defined as the ratio of the slopes of the linear sections of the calibration curves after (i.e. Int = 100,153.9 C_{Ni} −0.405) and before (i.e. Int = 5,282.5 C_{Ni} −16.74) preconcentration process, is calculated as 100,153.9/5,282.5 = 18.96. Meanwhile, the preconcentration factor evaluated from the ratio of the sample volume (100 mL) to the eluant volume (5 mL) is 20. The limit of detection (LOD) of this method in the determination of nickel ion is defined as $C_{LOD} = 3S_b/m$, where S_b is standard deviation of the responses and m is the slope of the calibration curve after preconcentration; for a sample volume of 100 mL, it was found to be 0.38 μg L^{-1}. The relative standard deviation for six separate batch experiments (RSD) with a nickel concentration of 20.0 μg L^{-1} was 3.6%. The accuracy of the proposed method was evaluated by analyzing a certified reference material, NCS ZC73036, with a nickel concentration of 5.4 ± 0.4 μg g^{-1}. The nickel content obtained (mean ± SD, $n = 3$) was 5.3 ± 0.2 μg g^{-1}, which is not significantly different from the certified value. The recoveries of Ni(II) ions from the real and spiked samples varied in the range of 95–98% (Tables 4 and 5). Therefore, Ni(II)–IIP can be successfully applied to the preconcentration and determination of nickel ions in different real samples.

4. Conclusions

The ion-imprinted polymer technique is a useful method for extraction and preconcentration of metal ions from different matrices. The prepared Ni(II)–IIP has an increased selectivity toward Ni(II) ion over a range of competing metal ions. Performance of the method was excellent in extraction of trace amounts of Ni(II) ions from real samples. As a result, the LOD, RSD, selectivity, and maximum adsorption capacity of this method is comparable or better than some of the previously reported methods (Table 6).

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