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A nanostructure ion-imprinted polymer for the selective separation and determination of copper ions in aqueous solutions

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ABSTRACT

A new nanostructure Cu(II) ion-imprinted polymer (IIP) has been prepared using 1-(2-pyridylazo)-2-naphthol as a ligand. The Cu(II)–PAN complex was synthesized and polymerized in the presence of 2-vinylpyridine (the functional monomer), ethylene glycol dimethacrylate (the cross-linker) and 2,2´-azobisisobutyronitrile (the initiator) via precipitation polymerization using trapping method. The prepared IIP was characterized by FTIR spectroscopy, scanning electron microscopy, and transmission electron microscopy. The optimal pH value for the quantitative preconcentration was 6.0 and maximum sorbent capacity was 11.53 mg g^{-1}. Under the optimized conditions, the method had a linear analytical range from 1 to 50 μg L^{-1}. The detection limit, relative standard deviation, and recovery of the method were evaluated as 0.29 μg L^{-1}, 3.6, and 94–97%, respectively. The developed method was successfully applied to the selective extraction and determination of trace amount of copper ions in water samples and some medicinal plants by inductively coupled plasma-optical emission spectrometry.

Keywords: Adsorption; Copper ions; Ion-imprinted polymer; 1-(2-pyridylazo)-2-naphthol

1. Introduction

Extraction and determination of heavy metals in the aqueous environment is of increasing interest because of their high toxicity, their persistence and carcinogenic effect [1].

Determination of trace amounts of metals in a complex matrix by instrumental analysis often requires their preliminary concentration and separation, because of low concentration of metal ions and presence of interferences [2]. Various methods have been applied to remove toxic heavy metals, including solvent extraction [3,4], coprecipitation [5,6], liquid–liquid extraction [7], ion exchange [8,9],

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membrane filtration [10], and solid-phase extraction (SPE) [11].

Ionic-imprinted polymers (IIPs) are the new improvement in the area of SPE. IIPs have been investigated as highly selective sorbents for SPE in order to concentrate and clean up samples prior to analysis [12,13].

IIPs show very interesting characteristics, such as high selectivity, low cost, ease of preparation, high surface area, stability at high temperatures and pressures, durability and reusability. Because of this, IIPs recently have been widely used for separation and preconcentration in SPE [14]. IIPs containing specific recognition sites are prepared by the polymerization of a functional monomer with a crosslinker in the presence of a template metal ion to produce a three-dimensional polymer network [15–17]. The highest selectivity is achieved when template metal ions in the form of complex with suitable ligands are used in the polymerization process. Removal of the template ion results in a functional polymeric matrix with recognition sites that are complementary in size, charge, and coordination number to the template ion [18].

Copper as a heavy metal is an important element for most life forms as a micronutrient but is also toxic for many biological systems at high concentrations [19]. It is apparent that the free Cu(II) is highly toxic for marine organisms. The natural content of Cu(II) in seawaters is very low and varies in unpolluted regions in the range from 1 to 20 μg L^{-1} [20]. Environmental pollution agency (EPR) has established concentration action level as 1.3 ppm for public water supplies [21]. Therefore, the determination of copper in environmental samples is of great importance.

There are a number of previously published papers dealing with the preparation of IIPs for copper(II) ion using different ligands such as 5-methyl-2-thiozylmethacrylamide [22], 1-hydroxy-4-(prop-2´-enyloxy)-9,10-anthraquinone [23], 4-(2-pyridylazo) resorcinol [18,20], 1,4-dihydroxy-9,10-anthraquinone [24], 2,9-dim ethyl-1,10-phenanthroline [25], and 1-(2-pyridylazo)-2-naphthol [14].

In this work, a new nanostructure Cu(II)–IIP was prepared by precipitation polymerization method using 1-(2-pyridylazo)-2-naphthol. Characterization of the synthesized polymer was evaluated by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The effect of several variables on the separation and determination of Cu(II) ions was investigated. These variables included pH of solution, sorption and desorption time, type, and volume of leaching solution and the effect of coexisting ions on the extraction recovery. Adsorption isotherms and reusability of polymer were also investigated. Cu(II)–IIP technique followed by inductively coupled plasma-optical emission spectrometry (ICP-OES) was applied for selective separation and determination of Cu(II) ions in different types of water samples and some medicinal plants that are commonly used in traditional medicine in Iran.

2. Experimental

2.1. Chemicals

2-Vinyl pyridine, ethylene glycol dimethacrylate (EGDMA), and 1-(2-pyridylazo)-2-naphtholwere obtained from Merck (Darmstadt, Germany), 2,2-Azobis isobutyronitrile (AIBN) was purchased from Acros Organics (Morris Plains, NJ, USA). All solvents and other reagents used were of analytical grade and purchased from Merck (Darmstadt, Germany). A certified reference material CRM (NCS ZC73036 rice 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 were supplied by Merck (Darmstadt, Germany). The herbal samples obtained from institute of medicinal plants, ACECR.

2.2. Apparatus

FT-IR spectra of grounded polymeric samples were recorded on a Bomem FT-IR MB 155S spectrometer (Canada) using KBr pellets in the range of 400–4,000 cm^{-1}. pH of solutions was measured by digital Metrohm pH meter (model 744). Morphology of polymers was characterized by scanning electron microscopy (SEM, Philips XL30 scanning microscope, Philips, the Netherlands). Polymeric 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 manufacturer's instructions. Operating conditions for the ICP-OES instrument were forward power 1.2 kW, plasma flow rate 15 L min^{-1}, auxiliary gas flow rate 1.5 L min^{-1}, and nebulizer gas flow rate 0.85 $Lmin^{-1}$. 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 the digestion of medicinal plants samples. Ultrapure DI water was prepared by Basic 360 Series-Younglin coupled with Aqua MAX-ultra 354.

2.3. Preparation of Cu(II)–IIP

The Cu(II)–IIP particles were prepared by precipitation polymerization technique. In the first step, 0.25 mmol1-(2-pyridylazo)-2-naphthol (ligand), 2 mmol2-vinyl pyridine (functional monomer) were dissolved in 30 mL 1–1 of dimethyl sulfoxide (DMSO)-acetonitrile (polymerization solvent), and then, 0.25 mmol Cu $(NO_3)_2{\cdot}3H_2O$ (template ion) was added slowly to this solution. The resulted mixture was stirred for 4 h at room temperature in order to ensure the equilibration of the complexation reaction. In the second step, 20 mmol EGDMA (crosslinker) and 0.8 mmol AIBN (Initiator) 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°C for 24 h under magnetic stirring at 500 rpm to complete the polymerization. After polymerization, the excess amount of solvent was removed and the prepared polymer was washed with 1:4 (v/v) methanol/water to remove the unreacted materials and then by 1 M HNO_3 for leaching of the imprint ions until the washing solution was free from Cu(II) ions. Finally, it was washed with deionized (DI) water until neutral pH was achieved. The resulting powder was dried over night at room temperature. The nonimprinted polymer (NIP) was also prepared simultaneously as the same procedure except that Cu(II) did not exist in the polymerization mixture.

2.4. Preparation of sample and standard solutions

Plant samples and certified reference material (NCS ZC73036) were digested in a microwave digestion system. About 0.1 g of the material was accurately weighed into a PTFE digestion vessel. About 5 mL 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 according to the following program: step 1 (T, 160°C; ramp, 15 min; time, 10 min), step 2 (T, 175°C; ramp, 15 min; time, 5 min). After cooling at room temperature, the extract was transferred into a volumetric flask and made up to 100 mL with DI water.

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

Stock standard solutions of individual metals (1,000 or 10,000 mg L^{-1}) were diluted to 1 L with distilled water. More dilute standards were prepared daily by appropriate dilution of these solutions. All of these solutions were stored in ambient temperature.

2.5. Batch rebinding experiments

Batch-rebinding experiments were used to estimate the binding capacity of the IIP. In order to extract Cu(II) ion by the IIP, 30 mg of the synthesized IIP was added in volumetric flask (25 mL) containing Cu(II) ion in different concentrations (1–50 mg L^{-1}) in water. The pH of solutions was adjusted at 6.0 by adding 0.1 N sodium hydroxide and the resulted solutions were stirred for 30 min in room temperature using a magnetic stirrer. After centrifugation (5 min, 8,000 rpm), the free concentration of Cu(II) ion in the supernatant solution was recorded by ICP-OES at 327.395 nm. In desorption step, leaching of Cu(II) ions from IIP was performed by 5 mL of 0.1 M HNO_3, while stirring in room temperature. After 30 min, the concentration of Cu(II) ion in this solution was determined by ICP-OES.

The amount of Cu(II) ion bound to the polymer was calculated by subtracting the concentration of free Cu (II) ion from the initial concentration. Extraction percent of copper was calculated by the following equation:

$$\%E = \frac{(C_i - C_e)}{C_i} \times 100 \tag{1}$$

C_i and C_e are the concentrations of Cu(II) ion before and after extraction in the solution.

3. Results and discussion

Although one of the most established procedures for the preparation of IIPs is chemical immobilization of vinylated ligands interacting with metal ions, by crosslinking, a simpler method is trapping of nonpolymerizable ligand in polymeric matrixes. In this case, the ligand is not chemically bound to the polymer chain but embedded inside the polymer matrix through some trapping process [1]. The IIPs prepared by this technique were proved to have higher capacity and selectivity compared to those obtained by other methods [16].

In this work, the IIP was synthesized via precipitation polymerization of Cu(II)–PAN complex as a template using trapping method.

3.1. Preliminary complexation studies

In order to obtain the stoichiometry PAN complex with copper ion in dimethyl sulfoxide (DMSO) solution, the absorbance of the complex of PAN with copper ion was monitored as a function of ligand mole fraction during its titration with a 5.0×10^{-5} M of PAN and Cu (II) ion. The complexation is accompanied by a relatively strong shift of the absorption band of PAN, with a $\lambda_{\max} = 470$ nm toward longer wavelengths with a $\lambda_{\max} = 566$ nm. The stoichiometry of the complex was confirmed by the continuous variations method (Job's method). In this method, the total molar concentration of the two binding partners (e.g. a metal and a ligand) is held constant, but their mole fractions are varied. An observable that is proportional to complex formation (such as absorption signal) is plotted against the mole fractions of these two components. The maximum on the plot corresponds to the stoichiometry of the two species. The resulting mole ratio plot at 566 nm is shown in Fig. 1. The maximum absorbance at a $[Cu^{2+}]/([AQ] + [Cu^{2+}])$ ratio of 0.5 clearly indicates the formation of a 1:1 complex between Cu^{2+} and PAN.

3.2. Characterization of polymers

Different colors of the NIP (orange) and imprinted polymer (purple) indicated the presence of template ion as Cu(II)–PAN complex in the IIP matrix. Moreover, the change in color from purple to orange is a clear result of desorption of the Cu(II) ions from the IIP particles after its leaching with a 0.1 M HNO_3 solution.

The morphology of Cu(II)–IIP and NIP were assessed by SEM. Analysis of the SEM images (Fig. 2) indicated that the NIP surface is smoother than the IIP's. It is observed that, both IIP and NIP polymers have colloidal nanoparticles of 60–100 nm in diameter with irregular shapes. The IIP nanoparticles were also observed by TEM (Fig. 3). It is indicated that the mean size of the IIP particles is about 40 nm.

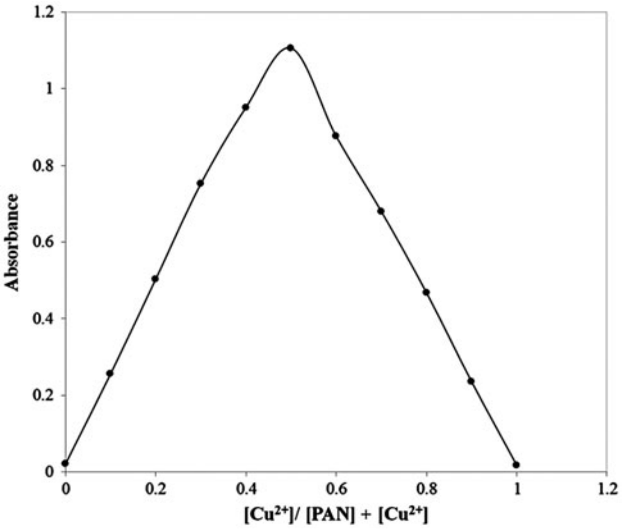

Fig. 1. Continuous variations plot for the complexation of Cu^{2+} with PAN determined by UV–vis spectrophotometry at 566 nm in DMSO solution.

The FT–IR spectra of unleached and leached Cu (II)–IIP were recorded by using KBr pellet method (Fig. 4). Both IIPs have a similar IR spectrum, which indicates that all the polymers have similar backbone, but they have different intensity spectra. The absorptions due to C–OH (3,746 cm^{-1}), C=O (1,744 cm^{-1}), C–O (1,244 cm^{-1}), C=C (1,513 cm^{-1}), and C–H bands (2,922 cm^{-1}) were observed. As can be seen in Fig. 4, the bands at 1,513, 2,922, and 3,746 cm^{-1} in unleached IIP were shifted to 1,521, 2,937, and 3,753 cm^{-1} in leached IIP. The shift and decrease in the strength of vibration can be attributed to bonding between the copper with PAN.

When the trapping method is used for the IIP preparation, it is expected that ligand remain entrapped inside the polymer during the leaching process. The similarities between the IR spectrums of PAN, unleached and leached IIPs suggested that the ligand is incorporated inside the polymer and leaching process does not affect the polymeric network.

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

PH was found to be the most important parameter for the adsorption of metals on the IIP. In an acidic environment, the copper-imprinted sites of the polymer are occupied by protons rather than copper ions, so that the polymer absorbs smaller amounts of copper ions. As the pH increased, the protonation of ligand is suppressed and condition becomes more favorable for the sorption of Cu(II) ions to the imprinted polymer [1]. The effect of pH on the adsorption of Cu(II) was studied by mixing 30 mg of the sorbents with 25 mL Cu(II) ion solution (1 mg L^{-1}) in the pH range between 1.0 and 8.0. The suspensions were brought to the desired pH by adding 0.1 N sodium hydroxide and 0.1 N nitric acid solutions. According to the results (Fig. 5), the maximum extraction of copper 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 Cu(II) ions.

3.4. Effect of sorption and desorption time

In several batch experiments, 30 mg of the polymer was added to 25 mL Cu(II) aqueous solution (1 mg L^{-1}) at pH 6.0. The resulting suspension was

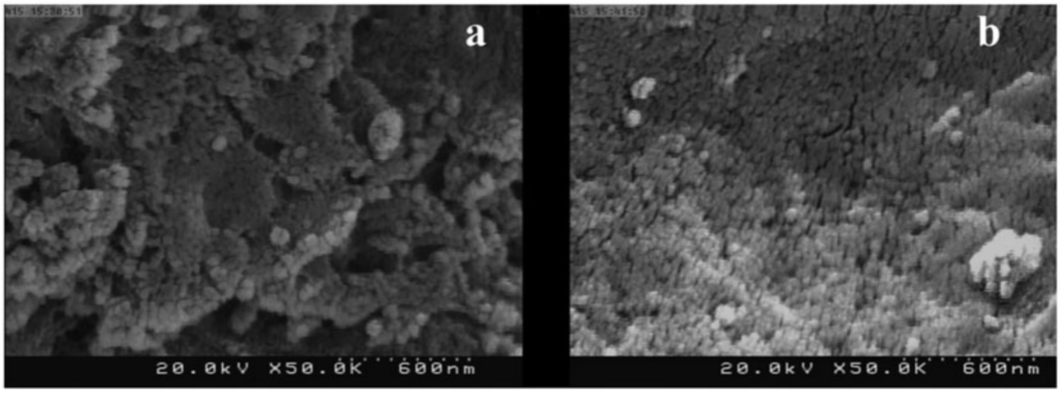

Fig. 2. Scanning electron micrograph of polymers: (a) Cu(II)–IIP and (b) Cu(II)–NIP.

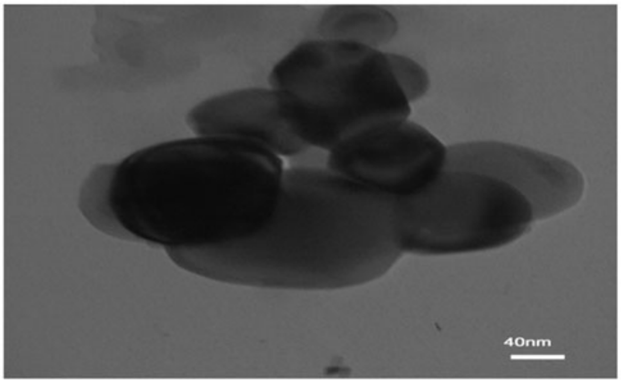

Fig. 3. TEM results of the Cu(II)–IIP nanoparticles.

stirred at different time intervals ranging from 5 to 45 min. After centrifugation, the concentration of Cu (II) ions in the supernatant solution was determined by ICP-OES. An optimum equilibration time of 30 min (98% extraction) was obtained for the quantitative extraction of Cu(II) ion from solution into the sorbent. In order to study the optimum desorption time, when the sorption process was completed, the solution was centrifuged. The supernatant solution was removed, and then, leaching of Cu(II) ions from IIP was performed by 5 mL of 0.1 M HNO_3. The resulting suspension was stirred for different times (5–45 min). After centrifugation, the concentration of Cu(II) ion in this acidic solution was determined by ICP-OES.

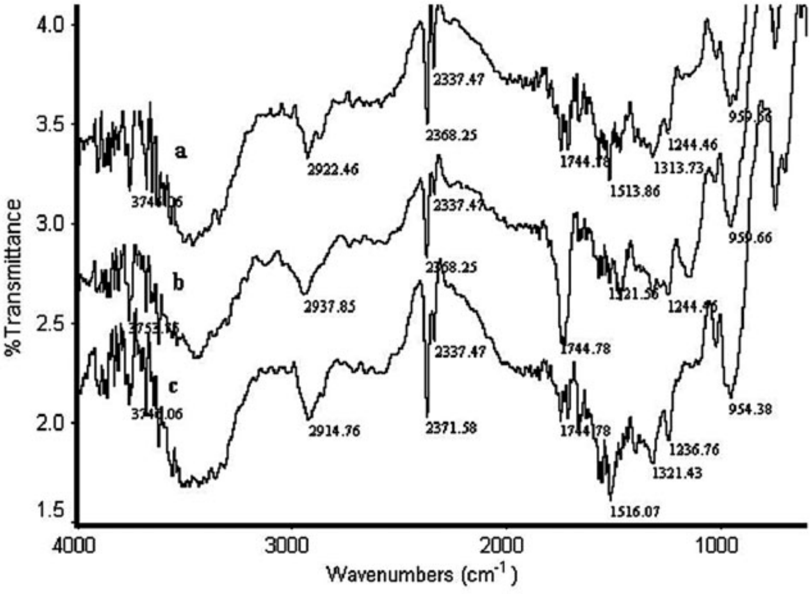

Fig. 4. The FT-IR spectra of unleached IIP (a), leached IIP (b), and PAN (c).

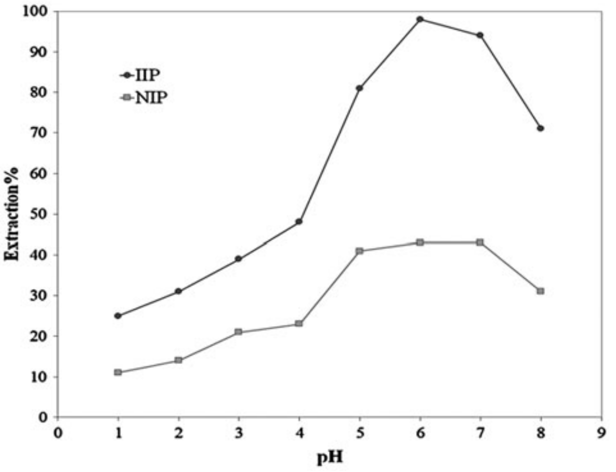

Fig. 5. Effect of pH on extraction of Cu(II)–IIP and Cu(II)–NIP particles in batch experiments with 30 mg of polymer particles; sample volume, 25 mL; Cu(II) ion concentration, 1 mg L^{-1}.

According to results, extraction percent was increased up to 30 min and it was constant in longer times. Therefore, the best quantitative time for the leaching of Cu(II) ions from the imprinted polymer was 30 min.

3.5. Choice of leaching solution

In order to obtain the best solvent for the leaching of Cu(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 leaching solution, not only because of its some better leaching characteristic over other two mineral acids but also because of its compatibility with ICP-OES.

3.6. Capacity and adsorption isotherms

The maximum experimental sorption capacity of the IIP and NIP was determined after saturation of the sorbents with copper ions under optimum conditions at room temperature. The sorption capacity (mg g^{-1}) of the polymers was calculated as follows:

$$Q = \frac{(C_i - C_e)V}{m} \tag{2}$$

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), m is the mass of IIP or NIP materials (g). According to batch rebinding results, the maximum amounts of Cu(II) ion that can be absorbed by IIP and NIP at pH 6.0 were found to be 11.53 and 4.32 mg g^{-1}, respectively. The effects of initial concentration of Cu(II) ions onto the adsorption capacity of the IIP and NIP were investigated. The resulting plot of Q vs. C_i showed that the amount of Cu(II) ions adsorbed per unit mass of the polymers increased with increasing the initial concentration of Cu(II) ions and reached a plateau, determining the adsorption capacity values. The high adsorption capacity for IIP compared to NIP is due to the imprinted cavities and specific recognition sites created after removal of Cu(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 demonstrate that imprinting play an important role in the adsorption behavior [12].

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 [1]. Langmuir and Freundlich isotherm models are usually used to evaluate adsorption properties of IIPs. According to the Langmuir adsorption model, the sorption process occurs in a surface monolayer of homogenous binding sites which number is fixed [26]. The linear Langmuir model is expressed by following equation:

$$C_e/Q = (1/Q_{max})C_e + 1/bQ_{max} \tag{3}$$

where Q is the amount of Cu(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 [24]. The Freundlich adsorption isotherm is expressed by following equation:

$$\log Q = (1/n) \log C_e + \log K_f \tag{4}$$

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. The theoretical value of maximum adsorption capacity (Q_{max}), Langmuir constant (b), and correlation coefficient (R^2), obtained from the Langmuir isotherm, were found to be 12.28 mg g^{-1}, 0.478 L mg^{-1}, and 0.995. The experimental value of sorption capacity is very close to the calculated value by Langmuir model. The Freundlich constant (K_f), adsorption intensity (n), and correlation coefficient (R^2) was obtained to be 3.549, 2.58, and 0.958, respectively. Comparing the correlation coefficients of isotherms in fitting the adsorption data shows that the Langmuir model provides better fitting for imprinted polymer (Fig. 6).

3.7. Selectivity studies

Competitive adsorption of Cu(II) ion in the presence of Zn(II), Mn(II), Cd(II), Pb(II), Co(II), and Ni(II) from their binary mixtures was investigated in batch experiments. The initial concentrations of pair of metal ions (1 mg L^{-1}) were extracted by 30 mg of polymers at pH 6.0. The distribution coefficient (mL g^{-1}) of Cu (II) ions between the polymer and aqueous solution was evaluated by following equation:

$$k_d = (C_i - C_e)V/C_e\, m \tag{5}$$

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 Cu(II) ions relative to foreign ions are defined as follows:

$$k_{Cu^{2+}} = k_d^{Cu^{2+}}/k_d^{M^{n+}} \tag{6}$$

where $k_d^{Cu^{2+}}$ and $k_d^{M^{n+}}$ are distribution coefficients of Cu (II) and foreign ion, respectively. The relative selectively coefficient is defined as:

$$k' = k_{\text{imprinted}}/k_{\text{non-imprinted}} \tag{7}$$

where $k_{\text{imprinted}}$ and $k_{\text{non-imprinted}}$ are selectivity coefficients of the imprinted and NIPs, respectively [24]. The distribution coefficients (k_d), selectivity coefficients (k), and relative selectively coefficients (k') values of IIP and NIP material were listed in Table 1. According to the data, prepared imprinted polymer has a higher selectivity towards Cu(II) ions than the non-imprinted one.

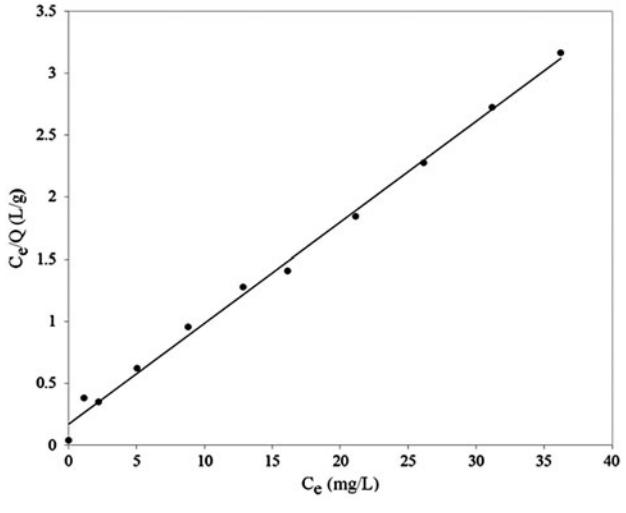

Fig. 6. Langmuir adsorption isotherm of Cu(II)–IIP.

3.8. Reusability

The reusability of an ion-imprinted adsorbent is important in terms of increasing its industrial efficiency at low costs [27]. In order to study the reusability of the prepared IIP, the sorption–desorption cycles were performed for six times using the same nanoparticles. Batch rebinding experiment was performed for initial copper ion concentration of 1 mg L^{-1}, under the optimal conditions. The relative standard deviations for six replicates were found to be 1.8%. The results showed that the Cu(II)–IIP could be repeatedly used without any significant loss in the initial binding affinity.

3.9. Evaluation of the method performance

Under the optimized conditions, the preconcentration procedure showed a linear curve within a concentration range of 1–50 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 calibration curves after (i.e. Int = 2.0022C_{Cu} + 47.282) and before (i.e. Int = 0.0993C_{Cu} + 50.858) preconcentration step, is calculated as 2.0022/0.0993 = 20.16. Meanwhile the preconcentration factor evaluated from the ratio of

Table 1
Cu(II)–IIP and Cu(II)–NIP selectivity studies for Cu(II) versus closely related ions

Cation	k_d (IIP)[a]	k_{id} (NIP)	k (IIP)[b]	k (NIP)	k'[c]
Cu^{2+}	9,583.3	532.8	–	–	–
Zn^{2+}	340.37	170.68	28.15	3.12	9.01
Ni^{2+}	182.93	102.1	52.39	5.17	10.13
Co^{2+}	489.42	324.07	19.58	1.64	11.94
Pb^{2+}	392.16	182.92	24.44	2.91	8.4
Mn^{2+}	248.92	182.92	38.5	2.91	13.18

[a] Distribution coefficient.
[b] Selectivity coefficient.
[c] Relative selectively coefficient.

Table 2
Determination of copper ion in medicinal herbs and CRM

Sample	C_{added} (μg g^{-1})	C_{found} (μg g^{-1})[a]	Recovery %
Matricariarecutita (Asteraceae)	–	12.9 ± 0.3	–
	10	21.8 ± 0.8	95.1
Urticadioica (Urticaceae)	–	15.2 ± 0.5	–
	10	24.4 ± 0.3	96.8
Hedera helix (Araliaceae)	–	13.5 ± 0.4	–
	10	22.7 ± 0.5	96.6
Cichoriumintybus (Asteraceae)	–	13.2 ± 0.6	–
	10	22.2 ± 0.5	94.9
CRM (NCS ZC73036)	(real) 1.7 ± 0.1	1.6 ± 0.05	94.1

[a] Mean ± SD, *n* = 3.

Table 3
Determination of copper ion in water samples

Sample	C_{added} (μg L^{-1})	C_{found} (μg L^{-1})[a]	Recovery %
Synthetic sample[b]	0	<LOD	–
	10	9.6 ± 0.1	96
Tap water	0	5.1 ± 0.2	–
	10	14.3 ± 0.1	94.7
Mineral water	0	13.2 ± 0.1	–
	10	22.1 ± 0.2	95.2

[a] Mean ± SD, *n* = 3.

[b] Solution contain Ni^{2+}, Co^{2+}, Zn^{2+}, and Mn^{2+} ions of 10 μg L^{-1}concentrations.

Table 4
Comparison of performance parameters of different Cu(II)–IIPs

Ligand	Polymerization method	Detection system	Relative Selectivity coefficient					Maximum capacity (mg g^{-1})	LOD (μg L^{-1})	Refs.
			k´ Ni	*k*´ Zn	*k*´ Co	*k*´ Mn	*k*´ Pb			
MTMAAm[a]	Bulk	FAAS	9.1	14.8	26.6	–	–	5.2	0.9	[22]
QZ[b]	Precipitation	ICP-AES	19.7	21.1	23.3	21.4	–	22.0	0.3	[24]
Salen[c]	Suspension	AAS	–	–	–	–	–	7.2	1.03	[28]
AQ[d]	Precipitation	ICP-AES	18.7	18.1	19.4	18	–	4.7	0.1	[23]
MAH[e]	Dispersion	FAAS	22.01	27.08	39.23	28.68	20.51	48	0.4	[29]
2,9-dimethyl-1,10-phenanthroline	Precipitation	FAAS	–	–	–	–	–	76.4	0.1	[25]
PAR[f]	Bulk	GF-AAS	2.47	3.37	3.37	–	–	0.3	3.0	[30]
PAN	Bulk	ETAAS	14.70	12.81	36.97	42.35	–	11.3	0.009	[14]
PAN	Precipitation	ICP-OES	10.13	9.01	11.94	13.18	8.40	11.5	0.29	This work

[a] 5-methyl-2-thiozylmethacrylamide.

[b] Quinizarin.

[c] 2,2-{Ethane-1,2-diylbis[nitrilo(E)methylylidene]}bis(6-allylphenol).

[d] 1-hydroxy-4-(prop-2_-enyloxy)-9,10-anthraquinone.

[e] Methacryloylamidohistidine.

[f] 4-(2-pyridylazo) resorcinol.

the sample volume (100 mL) to the leaching solution volume (5 mL) is 20.The limits of detection (LOD) and quantitation (LOQ)of this method are defined as $C_{LOD} = 3\ S_b/m$ and $C_{LOQ} = 10\ S_b/m$, where S_b is the standard deviation of 10 replicate blank signals and m is the slope of the calibration curve after preconcentration, for a sample volume of 100 mL, were found to be 0.29 and 0.88 μg L^{-1}. The relative standard deviation for six separate batch experiments (RSD) with a copper concentration of 25.0 μg L^{-1} was 3.6%.

3.10. Accuracy and analytical applications

The accuracy of the proposed method was evaluated by analyzing a certified reference material, NCS ZC73036 with a copper concentration of 1.7 ± 0.1 μg g^{-1}. The copper content obtained (mean ± S.D, $n = 3$) was 1.6 ± 0.05 μg g^{-1}, which is not significantly different from the certified value.

Finally, the proposed method has been applied for the determination of Cu(II) in different water and plant samples. The reliability of the method was checked by the analysis of the samples spiked with the known concentration of Cu(II).

For the preconcentration of Cu(II) ions, 100 mL of the aqueous solution of real and spiked prepared samples was adjusted to pH 6.0 and equilibrated with 30 mg of Cu(II)–IIP. The resulting suspension was stirred for 30 min, and then, leaching process was carried out by 5 mL 0.1 M HNO_3, while stirring for further 30 min. The concentration of Cu(II) ions in leached solutions were determined by ICP-OES and the results are summarized in Tables 2 and 3.

The recoveries of Cu(II) ions from the real and spiked samples varied in the range of 94–97%.Therefore, Cu(II)–IIP can be successfully applied to the preconcentration and determination of Cu(II) ions in different real samples.

4. Conclusions

The IIP technique is a useful method for extraction and preconcentration of metal ions from different matrixes. The prepared Cu(II)–IIP has an increased selectivity toward Cu(II) ion over a range of competing metal ions. Performance of the method was excellent in the extraction of trace amounts of Cu(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 4). The prepared IIP could be used as a sorbent in SPE concerning trace level determination of Cu(II) ion in water and medicinal plants samples.

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References

[1] C. Branger, W. Meouche, A. Margaillan, Recent advances on ion-imprinted polymers, React. Funct. Polym. 73 (2013) 859–875.
[2] M. Saraji, H. Yousefi, Selective solid-phase extraction of Ni(II) by an ion-imprinted polymer from water samples, J. Hazard. Mater. 167 (2009) 1152–1157.
[3] B. Holynska, B. Ostachowicz, J. Ostachowicz, L. Samek, P. Wachniew, A. Obidowicz, P. Wobrauschek, C. Streli, G. Halmetschlager, Characterisation of ^{210}Pb dated peat core by various X-ray fluorescence techniques, Sci. Total Environ. 218 (1998) 239–248.
[4] D. Kara, M. Alkan, Selective preconcentration, separation and speciation of ferric iron in different samples using N,N´-bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane, Talanta 55 (2001) 415–423.
[5] Z.-S. Chen, M. Hiraide, H. Kawaguchi, Preconcentration of trace heavy metals in water by coprecipitation with magnesium oxinate for electrothermal atomic absorption spectrometry, Mikrochim. Acta 124 (1996) 27–34.
[6] O.D. Uluozlu, M. Tuzen, D. Mendil, M. Soylak, Coprecipitation of trace elements with Ni^{2+}/2-Nitroso-1-naphthol-4-sulfonic acid and their determination by flame atomic absorption spectrometry, J. Hazard. Mater. 176 (2010) 1032–1037.
[7] Y.J. Park, D.J. Fray, Separation of zinc and nickel ions in a strong acid through liquid–liquid extraction, J. Hazard. Mater. 163 (2009) 259–265.
[8] Ü. Beker, F. Güner, M. Dizman, A. Erciyes, Heavy metal removal by ion exchanger based on hydroxyethyl cellulose, J. Appl. Polym. Sci. 74 (1999) 3501–3506.
[9] R.-S. Juang, Y.-C. Wang, Use of complexing agents for effective ion-exchange separation of Co(II)/Ni(II) from aqueous solutions, Water Res. 37 (2003) 845–852.
[10] U. Divrikli, A.A. Kartal, M. Soylak, L. Elci, Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations, J. Hazard. Mater. 145 (2007) 459–464.
[11] A. Bagheri, M. Behbahani, M.M. Amini, O. Sadeghi, M. Taghizade, L. Baghayi, M. Salarian, Simultaneous separation and determination of trace amounts of Cd (II) and Cu(II) in environmental samples using novel diphenylcarbazide modified nanoporous silica, Talanta 89 (2012) 455–461.
[12] Z. Li, J. Li, Y. Wang, Y. Wei, Synthesis and application of surface-imprinted activated carbon sorbent for solid-phase extraction and determination of copper (II), Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 117 (2014) 422–427.

[13] K. Ramakrishnan, T. Prasada Rao, Ion imprinted polymer solid phase extraction (IIP-SPE) for preconcentrative separation of erbium(III) from adjacent lanthanides and yttrium, Sep. Sci. Technol. 41 (2006) 233–246.

[14] H. Fazelirad, M.A. Taher, H. Ashkenani, Use of nanoporous Cu(II) Ion imprinted polymer as a new sorbent for preconcentration of Cu(II) in water, biological, and agricultural samples and its determination by electrothermal atomic absorption spectrometry, J. AOAC Int. 97 (2014) 1159–1166.

[15] H. Ashkenani, M.A. Taher, Determination of cadmium (II) using carbon paste electrode modified with a Cd-ion imprinted polymer, Microchim. Acta 178 (2012) 53–60.

[16] T.P. Rao, R. Kala, S. Daniel, Metal ion-imprinted polymers—Novel materials for selective recognition of inorganics, Anal. Chim. Acta 578 (2006) 105–116.

[17] N. Ashouri, A. Mohammadi, M. Shekarchi, R. Hajiaghaee, H. Rastegar, Synthesis of a new ion-imprinted polymer and its characterization for the selective extraction and determination of nickel ions in aqueous solutions, Desalin. Water Treat. 56 (2015) 2135–2144.

[18] I. Dakova, I. Karadjova, V. Georgieva, G. Georgiev, Synthesis and application of vinylpyridine containing ion-imprinted copolymer gel microbeads for Cu(II) solid-phase extraction, J. Sep. Sci. 35 (2012) 2805–2812.

[19] M. Faraji, Y. Yamini, S. Shariati, Application of cotton as a solid phase extraction sorbent for on-line preconcentration of copper in water samples prior to inductively coupled plasma optical emission spectrometry determination, J. Hazard. Mater. 166 (2009) 1383–1388.

[20] I. Dakova, I. Karadjova, I. Ivanov, V. Georgieva, B. Evtimova, G. Georgiev, Solid phase selective separation and preconcentration of Cu(II) by Cu(II)-imprinted polymethacrylic microbeads, Anal. Chim. Acta 584 (2007) 196–203.

[21] D.K. Singh, S. Mishra, Synthesis of a new Cu(II)-ion imprinted polymer for solid phase extraction and preconcentration of Cu(II), Chromatographia 70 (2009) 1539–1545.

[22] V. Yılmaz, O. Hazer, Ş. Kartal, Synthesis, characterization and application of a novel ion-imprinted polymer for selective solid phase extraction of copper(II) ions from high salt matrices prior to its determination by FAAS, Talanta 116 (2013) 322–329.

[23] M. Shamsipur, A. Besharati-Seidani, J. Fasihi, H. Sharghi, Synthesis and characterization of novel ion-imprinted polymeric nanoparticles for very fast and highly selective recognition of copper(II) ions, Talanta 83 (2010) 674–681.

[24] M. Shamsipur, A. Besharati-Seidani, Synthesis of a novel nanostructured ion-imprinted polymer for very fast and highly selective recognition of copper(II) ions in aqueous media, React. Funct. Polym. 71 (2011) 131–139.

[25] H. Ebrahimzadeh, M. Behbahani, Y. Yamini, L. Adlnasab, A.A. Asgharinezhad, Optimization of Cu(II)-ion imprinted nanoparticles for trace monitoring of copper in water and fish samples using a Box–Behnken design, React. Funct. Polym. 73 (2013) 23–29.

[26] M. Ahamed, A. Mulaba-Bafubiandi, L. Marjanovic, X. Mbianda, Ion imprinted polymers for the selective extraction of silver(I) ions in aqueous media: Kinetic modeling and isotherm studies, React. Funct. Polym. 73 (2013) 474–483.

[27] S. Özkara, M. Andaç, V. Karakoç, R. Say, A. Denizli, Ion-imprinted PHEMA based monolith for the removal of Fe^{3+} ions from aqueous solutions, J. Appl. Polym. Sci. 120 (2011) 1829–1836.

[28] A. Tobiasz, S. Walas, B. Trzewik, P. Grzybek, M.M. Zaitz, M. Gawin, H. Mrowiec, Cu(II)-imprinted styrene–divinylbenzene beads as a new sorbent for flow injection-flame atomic absorption determination of copper, Microchem. J. 93 (2009) 87–92.

[29] R. Say, E. Birlik, A. Ersöz, F. Yılmaz, T. Gedikbey, A. Denizli, Preconcentration of copper on ion-selective imprinted polymer microbeads, Anal. Chim. Acta 480 (2003) 251–258.

[30] D.K. Singh, S. Mishra, Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer, J. Hazard. Mater. 164 (2009) 1547–1551.