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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

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ABSTRACT

A new Cu(II)-imprinted sorbent has been prepared by using 5-methyl-2-thiozylmethacrylamide (MTMAAm). The monomer of Cu(II)–MTMAAm complex was synthesized and copolymerized in the presence of ethyleneglycol dimethacrylate cross-linker via bulk polymerization method. The resulting Cu (II)-imprinted polymer was characterized by FT-IR spectroscopy and scanning electron microscopy (SEM). Copper ions were removed from the polymer with 1.0 mol L^{-1} HNO_3 and determined by flame atomic absorption spectrometry (FAAS). The imprinted polymer showed higher selectivity for Cu(II) in comparison to the non-imprinted polymer. Relative selectivity coefficients (k') for Cu(II)/Zn(II), Cu(II)/Ni (II) and Cu(II)/Co(II) were 9.1, 14.8 and 26.6, respectively. The imprinted polymer was examined as a column packing material for solid phase extraction of Cu(II) from various matrices. The effects of solution pH, acid eluents and interfering ions were investigated. The poylmer possesses selective extraction of Cu (II) within pH range from 5.0 to 6.5. The relative standard deviation and limit of detection (3 s) of the method were evaluated as 1.4% and 0.9 μg L^{-1}, respectively. The accuracy of the method was verified by analysis of two certified reference materials (CWW-TM-D and SRM 3280) and then applied to the determination of Cu in seawater, lake water and tap water samples, and hemodialysis concentrates and multivitamin/multielement supplements.

1. Introduction

Solid phase extraction (SPE) is a widely used sample introduction approach for determination of trace elements by flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The principal advantages of SPE are twofold; (a) removal of matrix components and (b) enrichment of analytes of interest for sensitive detection [1,2]. In FAAS and ICP-AES, the preconcentration step improves the limit of detection for determinations at trace concentrations. Although ETAAS and ICP-MS possess higher sensitivity to achieve lower detection limits, they do suffer from spectral and non-spectral interferences in analysis of complex samples. Therefore, separation of an analyte from the matrix is frequently needed to alleviate the effects of interferences [3–6].

A wide range of sorbents, including chelating resin, silica gel, cellulose, activated carbon, and various biosorbents have been utilized in SPE applications [7–10]. These sorbents often lack the selectivity, although they could exhibit high sorption capacity, high surface area, and good chemical and physical stability [11,12]. In recent years, new materials with better selectivity have been synthesized and examined [13]. Molecularly imprinted polymers (MIPs) or ion-imprinted polymers (IIPs) have received significant attention as highly selective sorbents for the SPE of trace metal ions [14–17].

Molecular imprinting approach affords preparation of synthetic polymer receptors with enhanced selectivity for a target (template) molecule [18]. The synthesis of MIPs consists of three stages: (i) complexation of a template molecule with functional monomers, (ii) copolymerization of the monomers around the template using a cross-linking agent in the presence of an initiator, and (iii) leaching out of the template leaving behind binding sites that are complementary in size and shape to the template. An ion-imprinted polymer is obtained when a metal ion is used as template. Better selectivity is achieved when polymerization is carried out with complexes of metal ions with vinylated or non-vinylated ligand(s).

The choice of complexing ligand is important as it directly influences the selectivity of the sorbent. Coordination geometry,

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coordination number of the metal ion and the charge and size of the ion also influence the selectivity of IIPs [19,20]. Different approaches have been proposed for synthesis of IIPs, including crosslinking bifunctional reagents with linear chain polymers, chemical immobilization of vinylated ligands in the polymer matrix, surface imprinting by emulsion polymerization and trapping of a non-vinylated chelating agent inside the polymer matrix [21]. A number of different IIPs and their applications have been reported for selective separation and preconcentration of Pd(II) [15,16], Dy(III) [22,23], Er(III) [24], UO_2^{2+} [25–27], Cu(II) [28–36], Cd(II) [37], Ni(II) [38,39], Al(III) [40], Zn(II) [41], Pb(II) [42], Fe(III) [43], Cr(III) [44], Hg(II) [45], Ag(I) [46] and Sc(III) [47].

Aminothiazoles are known as biologically active compounds with a broad range of activity in the synthesis of antibiotics and dyes [48]. Various thiazole derivatives have shown herbicidal, anti-inflammatory, anti-microbial, or anti-parasitic activity [49]. The 2-thiozylmethacrylamide (or *N*-(thiazol-2-yl)methacrylamide) monomer possessing the thiozyl group forms strong, thermally stable complex with Cu(II) [50]. In this study, we report the synthesis of a novel ion-imprinted polymer with vinylated chelating agent of 5-methyl-2-thiozylmethacrylamide (MTMAAm). To the best of our knowledge, there is no previous literature report on the use of MTMAAm for preparation of a Cu(II)-imprinted polymer exhibiting high selectivity for separation of Cu(II) ions from aqueous solutions. The IIP was synthesized via bulk copolymerization of Cu(II)–MTMAAm complex with ethyleneglycol dimethacrylate (EGDMA) cross-linker in the presence of 2,2′-azobisisobutyronitrile (AIBN). After the removal of Cu(II) ions, the Cu(II)-imprinted polymer was used as a support material for solid phase extraction of Cu(II) for determination by FAAS. The experimental parameters affecting the extraction efficiency of Cu(II) from solutions were optimized. The selectivity of the polymer and its analytical merits were also discussed.

2. Experimental

2.1. Instrumentation

A PerkinElmer AAnalyst 800 flame atomic absorption spectrometer (Norwalk, CT, USA) equipped with a deuterium background correction system was used for determinations. The instrument was operated according to the guidelines of the manufacturer. A WTW inoLab model 720 digital pH meter (Germany) was used for pH measurements. The NMR (^{1}H) spectrum of the monomer was recorded on a Bruker Avance III 400 MHz NMR spectrometer (Karlsruhe, Germany) using dimethylsulfoxide (DMSO) as solvent and tetramethylsilane as internal standard. The Fourier transform infrared (FT-IR) spectra of the monomer, monomer-Cu complex, imprinted and non-imprinted polymers were recorded on a PerkinElmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA). Elemental analysis of the monomer-Cu complex was performed on a Leco CHNSO-932 auto microanalyzer (USA). The surface morphology of the polymers was examined using a Leo 440 scanning electron microscope (Leo Electron Microscopy Ltd., England).

2.2. Reagents

All glassware and plastic containers were cleaned in dilute (1:1) HNO_3 for 24 h and then rinsed with deionized water before use. Reagent grade chemicals were used in the synthesis of the imprinted polymer. Solutions were prepared with deionized water. The stock solutions of the metals were prepared by dissolving their nitrate salts in 1.0 mol L^{-1} HNO_3. The stock solutions of interfering ions were prepared from their high purity compounds (Merck, Germany). The pHs of the solutions were adjusted to the desired pH with buffer solutions of NaH_2PO_4/H_3PO_4 (pH 2–3), CH_3COONH_4/CH_3COOH (pH 4–6), NaH_2PO_4/Na_2HPO_4 (pH 7), and NH_3/NH_4Cl (pH 8). Methacryloyl chloride (Aldrich, USA) and 2-amino-5-methylthiazole (Alfa Aaser, Germany) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) (Acros Chemicals, USA) was purified by successive crystallizations in a chloroform-methanol mixture. Ethyleneglycol dimethacrylate (EGDMA) was obtained from Merck.

2.3. Synthesis of 5-methyl-2-thiozylmethacrylamide monomer

The synthesis of 5-methyl-2-thiozylmethacrylamide (MTMAAm) was performed according to the protocol reported in literature [51]. Under stirring, ice-cold solution of methacryloyl chloride (0.01 mol) in 10 mL dichloromethane was added dropwise to an ice-cold solution of 2-amino-5-methylthiazole (AMT) (0.01 mol) and triethylamine (0.03 mol) in 30 mL of dichloromethane at 0–5 °C. After addition, the reaction mixture was stirred for 12 h at room temperature, and then filtered and evaporated with a rotavapor. The resulting yellow product was recrystallized in ethanol with a yield of 54%.

The melting point for the monomer was determined to be 160–163 °C. Proton NMR (^{1}H NMR) obtained in DMSO revealed peaks (δ in ppm) at 1.9 (3H, CH_3), 2.3 (3H, CH_3), 5.6 (1H, CH_2), 6.0 (1H, CH_2), 7.2 (1H, CH) and 12.0 (1H, NH). FT-IR spectra exhibited bands at 3143 cm^{-1} (N–H amide), 3000–3100 cm^{-1} (C–H aromatic), 2920 and 2850 cm^{-1} (C–H aliphatic), 1669 cm^{-1} (C=O amide), 1630 cm^{-1} (CH_2=C–), 1556, 1527 and 1450 cm^{-1} (C=C aromatic), and 1152 cm^{-1} (C–O–C).

2.4. Synthesis of Cu(II)–MTMAAm complex

For the synthesis of Cu(II)–MTMAAm complex, 4.0 mmol (0.729 g) of 5-methyl-2-thiozylmethacrylamide was dissolved in 20 mL ethanol. A solution of 2.1 mmol (0.379 g) $CuCl_2 \cdot 2H_2O$ was added slowly into this solution with continuous stirring at room temperature. The reaction solution was stirred for 6 h until its color turned to green. The solvent was removed and the green solid was washed with a mixture of ethanol and acetonitrile. The yield was 0.623 g (62%). The decomposition temperature of the complex was measured to be 235 °C. The FT-IR spectrum showed peaks at 3364 cm^{-1} (N–H amide), 3000–3200 cm^{-1} (C–H aromatic), 2982 and 2932 cm^{-1} (C–H aliphatic), 1699 cm^{-1} (C=O amide) and 1630 cm^{-1} (CH_2=C–). The elemental composition was calculated to be $C_{16}H_{20}N_4O_2S_2CuCl_2$: 38.52% C, 4.04% H, 11.23% N, 12.85% S, 12.74% Cu. The experimentally determined values were 38.28% C, 3.78% H, 11.04% N, 11.14% S, and 12.67% Cu. It was reported that Cu (II) coordinated to the monomer through the nitrogen of thiazole ring and carbonyl oxygen [50].

2.5. Preparation of Cu(II)-imprinted and non-imprinted polymers

The synthesis of poly(EGDMA–MTMAAm/Cu(II)) particles was performed by bulk polymerization method as described below. About 1.0 mmol (0.4989 g) Cu(II)–MTMAAm complex was dissolved in 10 mL DMSO. To this solution, 12 mmol EGDMA (2.3 mL) and 0.15 mmol AIBN (25 mg) were added as cross-linker and free radical initiator, respectively. Nitrogen gas was purged into the solution for 5 min under stirring and then the reaction vial was sealed and kept at 70 °C for 12 h. Then, the temperature was raised to 80 °C and the polymerization was completed within 3 h. The resulting greenish material was transferred to another vial, thoroughly washed with water and dried at 60 °C for 24 h. The blocks of the polymer were ground and sieved to obtain a powdered material of 90–180 μm. The polymeric particles were washed with 1.0 mol L^{-1} HNO_3 several times to completely remove

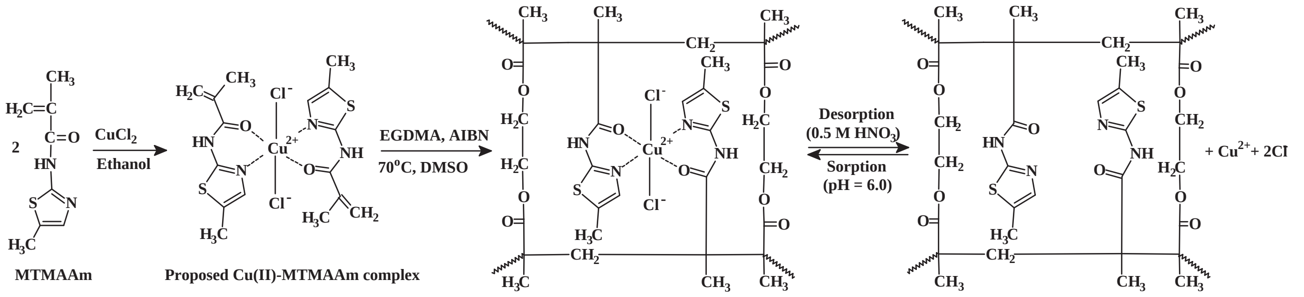

Fig. 1. Schematic representation of the synthesis of the Cu(II)–MTMAAm complex and Cu(II)–IIP, and the process of the sorption and desorption of the Cu(II) ions.

Cu(II) from the resin and finally with water to neutralize the particles. The resulting light yellow color polymeric particles (i.e., Cu(II)-free imprinted polymer) were dried at 60 °C. Non-imprinted polymer (NIP, poly(EGDMA–MTMAAm)) was prepared similarly with MTMAAm and EGDMA. A schematic representation for the preparation of Cu(II)–IIP and the processes of sorption and desorption of Cu(II) ions are presented in Fig. 1.

2.6. Procedure for solid phase extraction of Cu(II)

The Cu(II)-ion imprinted polymer (Cu(II)–IIP) was used as column filling material for solid phase extraction of Cu(II) from aqueous solutions. About 0.3 g of polymer was slurried in water and poured into a 10-cm long glass column (1.0 cm i.d.). A small amount of glass wool was placed at both ends to prevent the loss of polymeric particles during sample loading. The column was cleaned by treating successively with 2.0 mol L^{-1} HNO$_3$ and water, and conditioned by passing buffer solution (pH 6.0) prior to loading the sample solutions. Solutions of Cu(II) at pH 6.0 were passed through the column at a flow rate of 3 mL min^{-1}. The column was washed with 10 mL deionized water and the metal ions retained on the column were eluted with 10 mL of 0.5 mol L^{-1} HNO$_3$ at 3 mL min^{-1}. The concentration of the eluted metal ions was determined by FAAS. The recovery was calculated with the following equation [52]:

$$R\% = \left(\frac{C_2 - C_1}{C_0}\right) \times 100 \tag{1}$$

where $R\%$ is the percent recovery, C_0 (μg L^{-1}) is the concentration of the analyte added, C_1 (μg L^{-1}) is the concentration of the unspiked sample solution and C_2 (μg L^{-1}) is the concentration of the spiked sample solution.

2.7. Preparation of certified reference materials

The procedure was verified by analysis certified reference material of wastewater (CWW-TM-D, HPS Co., Charleston, USA) and multivitamin/multielement tablets (SRM 3280, Gaithersburg, MD, USA). The wastewater certified reference material was diluted to 1.0 L with deionized water and transferred to an acid-cleaned plastic container and stored for use. For analysis, 10 mL of diluted CWW-TM-D solution was taken and further diluted to 50 mL with deionized water. The pH was adjusted to pH 6.0.

For multivitamin/multielement tablets (SRM 3280), approximately 0.1 g portions were digested with 5 mL of concentrated HNO$_3$ and 3 mL of H$_2$O$_2$ in a 100-mL beaker on a hot plate at 150 °C. This procedure was repeated twice. After the digestion, the solution was filtered through a membrane filter into a 50-mL volumetric flask, completed to the mark with deionized water and then transferred to a polyethylene container for storage. A volume of 5.0 mL of the solution was taken, diluted to 50 mL with deionized water and the pH was adjusted to pH 6.0.

2.8. Preparation of water samples, hemodialysis solutions and multivitamin supplements

Cu(II) levels were determined in seawater, lake water and tap water samples and hemodialysis concentrates. Seawater samples were collected from the coastal city of Yumurtalık in Adana, Turkey. Lake water samples were collected from the Seyhan Dam Lake in Adana, Turkey. Tap water samples were obtained from our research laboratory. The water samples were acidified with HNO$_3$ to pH ~2 after collection. In the laboratory, they were heated at 80 °C for 30 min to destroy potential humic and fulvic acid complexes of the metals. Then they were cooled to room temperature and filtered through 0.45-μm cellulose acetate membrane filters to eliminate the insoluble particles. For lake water and seawater samples, a 50 mL of sample was taken and the pH was adjusted to pH 6.0. 500 mL of tap water sample was taken and the pH was adjusted to pH 6.0.

Diasol K2 Ac2 acidic hemodialysis solution (Lot No: 5) was purchased from a local drug manufacturing company. The concentrated solution (1.0 L) contained NaCl (214.77 g), KCl (5.22 g), $CaCl_2 \cdot 2H_2O$ (7.72 g), $MgCl_2 \cdot 6H_2O$ (3.55 g), CH_3COOH (4.20 g). A volume of 50 mL concentrated solution was taken and the pH was adjusted to pH 6.0 with 2 mol L^{-1} NH$_4$OH solution.

Three brands of multivitamin and multielement supplements (MMS$_1$–MMS$_3$) were purchased from local pharmacies. Digestions and sample preparations of the multivitamin and multielement supplements were performed similar to SRM 3280. A volume of 5.0 mL of the solution was taken, diluted to 50 mL with deionized water and the pH was adjusted to pH 6.0.

2.9. Selectivity experiments

Competitive sorption of Ni(II), Zn(II) and Co(II) in the presence of Cu(II) were investigated for both imprinted (IIP) or non-imprinted polymers (NIP). 50 mL aliquots of binary aqueous solutions (pH 6.0) of Cu(II)/Ni(II), Cu(II)/Zn(II) and Cu(II)/Co(II) containing 30 mg L^{-1} of each metal ion were passed through the column of appropariate polymer at a flow rate of 1.5 mL min^{-1} and then eluted with 50 mL of 1.0 mol L^{-1} HNO$_3$ at a flow rate of 1.0 mL min^{-1}. The concentration of the metal ions in the eluate was determined by FAAS. The distribution coefficient, selectivity and relative selectivity coefficients were determined for each polymer as described in the literature [38]. The distribution coefficient was calculated according to the equation below:

$$K_d = \left[\frac{C_i - C_f}{C_f}\right] \times \frac{V_s(\text{mL})}{\text{mass of polymer(g)}} \tag{2}$$

where K_d, C_i, C_f and V_s represent the distribution coefficient, the initial and the final concentrations of the metal ions, and the volume of solution, respectively. The selectivity coefficient for the binding of Cu(II) in the presence of competitor ions can be obtained from the equilibrium binding data according to Eq. (3):

$$k_{\mathrm{Cu(II)}/M(\mathrm{II})} = \frac{K_d(\mathrm{Cu(II)})}{K_d(M(\mathrm{II}))} \tag{3}$$

where k is the selectivity coefficient and M(II) represents Ni(II), Zn (II) or Co(II). The relative selectivity coefficient (k') can be defined according to Eq. (4). This equation allows an estimation of the effect of imprinting on the selectivity.

$$k' = \frac{k_{\mathrm{imprinted}}}{k_{\mathrm{non-imprinted}}} \tag{4}$$

where $k_{\mathrm{imprinted}}$ and $k_{\mathrm{non\text{-}imprinted}}$ are the selectivity coefficients of IIP and NIP, respectively.

3. Results and discussion

3.1. Characterization of IIP

The FT-IR spectra of unleached and leached Cu(II)-imprinted polymers are illustrated in Fig. 2a and b, respectively. As expected, both polymers exhibited similar spectral profiles. The presence of two low intensity peaks at about 2952 and 2988 cm^{-1} was attributed to C–H stretching of the –CH$_2$– and –CH$_3$ groups, respectively. The intense absorption centered at 1723 cm^{-1} was assigned to carbonyl groups from EGDMA, whereas the C–O vibration was observed at 1139 cm^{-1}. The weak absorptions at 1674 and 1680 cm^{-1} were associated to amide carbonyl groups from MTMAAm, while the peak at 1452 cm^{-1} was due to the –CH$_2$– and –CH$_3$ deformation. No absorption band was observed in the region of 1645–1630 cm^{-1} confirming the absence of vinyl groups in the polymers. This also confirmed the successful copolymerization of the vinylated MTMAAm ligand and EGDMA.

The SEM micrographs illustrating the morphologies of the polymers are shown in Fig. 3. The particles did not possess a definite shape, which was due to the bulk polymerization method used for the synthesis. It was reported that the variation in shape did not have any significant effect on sorption capacitiy of chemically imprinted polymers synthesized via bulk polymerization [32]. Similarly, the lack of spherical shape or morphological variations had no significant effects on the sorption properties of the imprinted polymer in this study. The polymers possessed a rough surface, which is an important parameter affording higher metal sorption capacity since it promotes the mass transfer rate of metal ions toward the polymer surface.

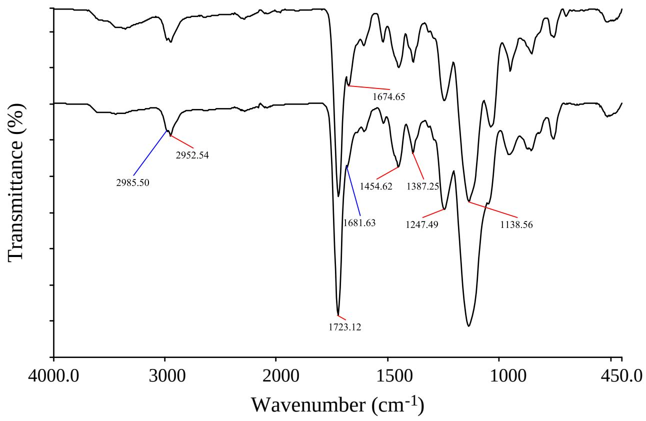

Fig. 2. IR spectra for unleached (a) and leached (b) Cu(II)-imprinted polymers.

3.2. Optimization of solid phase extraction with Cu(II)–IIP

3.2.1. Effect of pH

MTMAAm is immobilized on the polymeric network and is expected to show a pH-dependent complex formation with Cu(II) in solution. To elucidate the effect of pH on complexation, 0.2 mg L^{-1} Cu(II) standard solutions were prepared within a pH range from pH 2.0 to 8.0 and loaded onto the column. Percent recoveries for Cu(II) as a function of pH are shown in Fig. 4. At lower pHs (e.g., pH 2.0–3.0), the sorption of Cu(II) on the polymer was negligible, which was attributed to the protonation of the heterocyclic nitrogens and carbonyl oxygen in MTMAAm. With increasing pH, the protonation of the ligand was suppressed and conditions became favorable for the complex formation and sorption of Cu(II) by the imprinted polymer. The recoveries increased with increasing pH to pH 5 and remained constant up to pH 6.5, and then decreased with above pH 6.5. This pattern clearly showed that the complex formation between the ligand (e.g., MTMAAm) and Cu(II) was dependent on the acidity of the solution. Hence, pH 6.0 was selected as the optimum pH.

3.2.2. Investigating the eluent efficiency

The desorption process is limited by the kinetics and the strength of eluent-metal ion interaction as well as the type of eluent (acid) and its concentration. Nitric acid (HNO$_3$) and hydrochloric acid (HCl) solutions (10 mL) were investigated for desorption of Cu(II) from the imprinted sites on the polymer matrix. The concentrations of the acids were varied between 0.5 and 2.0 mol L^{-1}. The recoveries for Cu(II) ranged between 95 and 99% for both acid solutions. Dilute solutions of HNO$_3$ performed relatively better than those of HCl. Therefore, subsequent elutions were made using 0.5 mol L^{-1} HNO$_3$.

3.2.3. Effect of sample and eluent flow rates

The Cu(II) ions in the sample solution are retained on the column by complexing with the active sites along the imprinted polymer. To achieve quantitative sorption, the flow rate of the sample solution should be sufficiently low. Similarly, the eluent flow rate should be adjusted so as to ensure quantitative elution. The sample and eluent flow rates were examined between 1.0 and 6.0 mL min^{-1} for 50 mL of test solutions at pH 6.0. No significant variation was observed in the sorption of Cu(II) at sample flow rates as high as 6 mL min^{-1}. The recoveries were between 98 and 100%. Elution also occurred readily yielding recoveries of 98–101% at all flow rates. These results indicated that sorption and desorption kinetics of Cu(II) on the imprinted polymer were very fast. For the following experiments, the flow rates for sample and eluent were adjusted to 3 mL min^{-1}.

3.2.4. Effect of sample volume on preconcentration

The effect of sample volume on recoveries was examined for a volume of 50, 100, 250, 500, 750 and 1000 mL sample solution containing 20 μg of Cu(II) to elucidate the limit enrichment factor that could be achieved for preconcentration of Cu(II). The results indicated that volumes as high as 1000 mL could be loaded on the column with recoveries better than 96% (see Supplementary Fig. S1). The highest preconcentration factor was 100 from preconcentration of Cu(II) in 1.0 L solution into 10 mL dilute nitric acid solution.

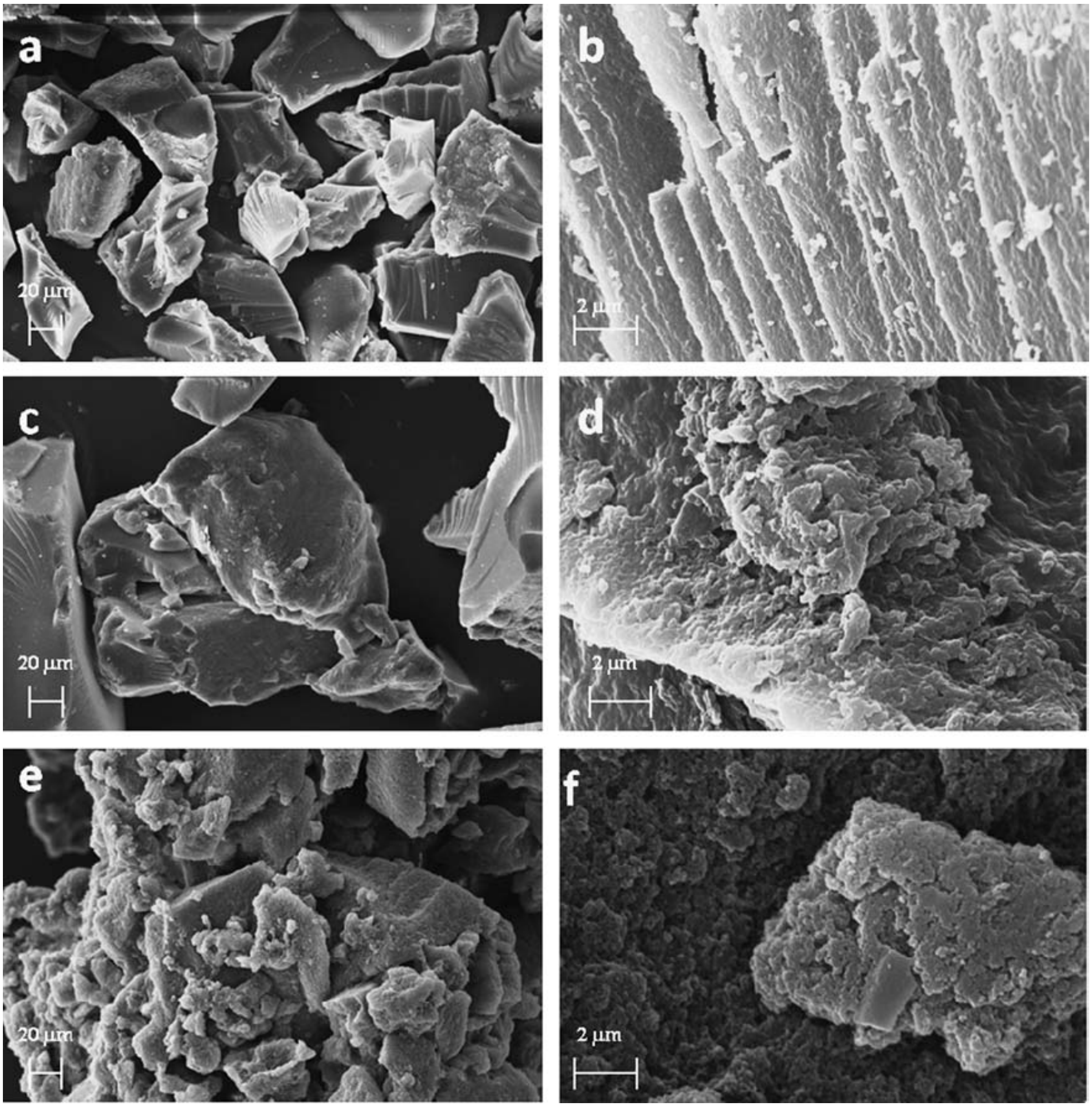

Fig. 3. SEM images of the unleached ((a) and (b)), leached ((c) and (d)) Cu(II)-imprinted, and non-imprinted ((e) and (f)) polymers. The images were amplified in 1000 × and 20.000 ×.

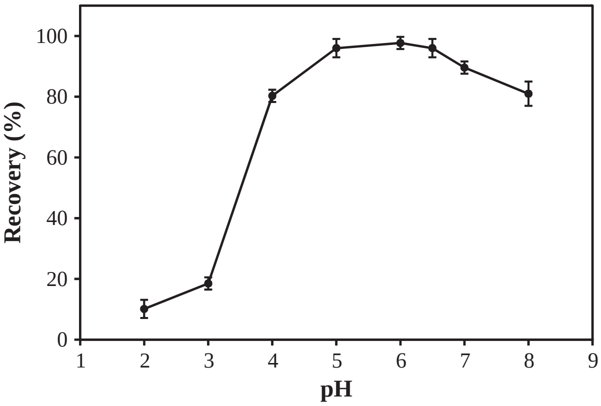

Fig. 4. Effect of pH on sorption of Cu(II) ions on IIP ($n=3$).

3.2.5. *Effect of foreign ions and selectivity study*

In ion-imprinted polymers, chelating sites (e.g., ligands) possess a uniform distribution and are selective to the imprint ion. Also, the cavities created after the removal of the template are complementary to the imprint ion in size and coordination geometries [29]. As a result, the IIPs are expected to possess good selectivity for sorption of their imprint ions. Conversely, the random distribution of ligand functionalities in polymeric network results in no specificity in the binding affinities of non-imprinted polymers [35].

The effect of foreign ions on the retention of Cu(II) ions was investigated individually by adding Na(I), K(I), Ca(II), Mg(II), Zn(II), Co(II), Ni(II) and Fe(III) ions to Cu(II) standard solution (0.2 mg L^{-1}). As can be seen in Table 1, quantitative sorption of Cu(II) ions could be achieved even in the presence of excess amounts of the interfering ions.

Competitive sorption of Cu(II)/Ni(II), Cu(II)/Co(II) and Cu(II)/Zn(II) pairs was investigated from their binary solutions to examine the selectivity of the imprinted polymer. It should be noted that the selected competitor ions possess the same charge and similar ionic radius as the Cu(II) [30]. Table 2 summarizes the distribution coefficients (K_d), selectivity coefficients (k) and relative selectivity coefficients (k') calculated using Eqs. (2)–(4), respectively. The results shown

Table 1
The effect of interfering ions on the retention of 0.2 mg L^{-1} Cu(II) ions ($n=3$).

Interferent ion	Added as	Concentration (mg L^{-1})	Recovery (%)[a]
Na(I)	NaCl	10,000	98 ± 2
K(I)	KNO_3	10,000	99 ± 2
Ca(II)	$Ca(NO_3)_2 \cdot 4H_2O$	10,000	99 ± 1
Mg(II)	$Mg(NO_3)_2 \cdot 4H_2O$	10,000	98 ± 1
Zn(II)	$Zn(NO_3)_2 \cdot 6H_2O$	10	100 ± 2
Co(II)	$Co(NO_3)_2 \cdot 6H_2O$	10	102 ± 2
Ni(II)	$Ni(NO_3)_2 \cdot 6H_2O$	10	98 ± 2
Fe(III)	$Fe(NO_3)_2 \cdot 9H_2O$	10	99 ± 3

[a] Avarage ± standard deviation.

Table 2
The effect of imprinting on the selectivity.

Metal ion	K_d (IIP) (mL g^{-1})	K_d (NIP) (mL g^{-1})	k (IIP)	k (NIP)	k'
Cu(II)	5005	359.1	–	–	–
Zn(II)	103.6	67.6	48.3	5.3	9.1
Ni(II)	116.9	125.4	42.8	2.9	14.8
Co(II)	23.2	44.3	215.7	8.1	26.6

in Table 2 clearly reveal that the ion imprinting effect of the polymer was due to MTMAAm as a vinylated chelating agent. The selectivity values for the imprinted polymer were 9.1, 14.8 and 26.6 times greater than those of the non-imprinted polymer for Cu(II)/Zn(II), Cu(II)/Ni(II) and Cu(II)/Co(II), respectively.

3.3. Sorption isotherm and sorption capacity

The sorption isotherm and sorption capacity of the Cu(II)–IIP were studied by using the proposed procedure at room temperature. 50 mL aliquots of sample solutions containing 0 to 80 mg L^{-1} Cu(II) were loaded onto the column. The retained Cu(II) was eluted with 0.5 mol L^{-1} HNO_3 and determined by FAAS. The mass of the metal ion bound per gram of the polymer (n, mg g^{-1}) was plotted as a function of initial metal ion concentration (C_i, mg L^{-1}) in the solution (see Fig. 5a). The sorption capacity (n_m) of the IIP for Cu(II) was obtained by using the Langmuir's Eq. (5) as shown below [9]:

$$\frac{C_e}{n} = \frac{1}{n_m \times K} + \left(\frac{1}{n_m}\right) C_e \tag{5}$$

where n is the mass of metal ion per gram of the polymer (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}) of metal ion in the solution, K is the binding equilibrium constant (L mg^{-1}), and n_m is the maximum sorption capacity of the polymer (mg g^{-1}). The plot of C_e/n against C_e would be a straight line (Fig. 5b) for which n_m and K can be obtained from the slope and intercept of the plot, respectively.

Langmuir sorption plots for Cu(II) obtained by the least-squares method were well-fitted with Eq. (5). The coefficient of determination ($r^2=0.9998$) indicated that Langmuir's isotherm was an adequate description of the sorption of Cu(II) on the IIP. The sorption capacity of the IIP for Cu(II) was calculated to be 5.2 mg g^{-1} (81.5 μmol g^{-1}) and the binding equilibrium constant was found to be 0.26 L mg^{-1} (1.65×10^4 L mol^{-1}).

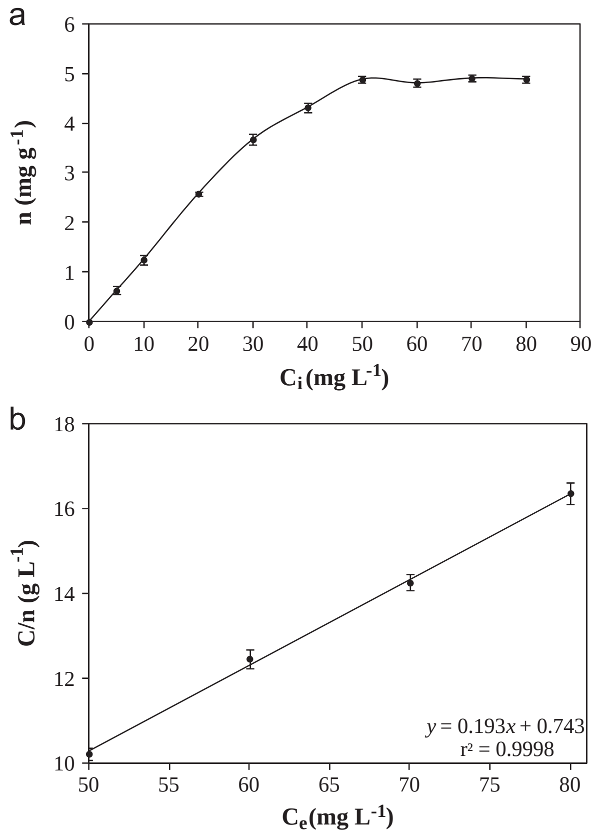

Fig. 5. Sorption isotherm (a) and Langmuir plot (b) for Cu on IIP ($n=3$).

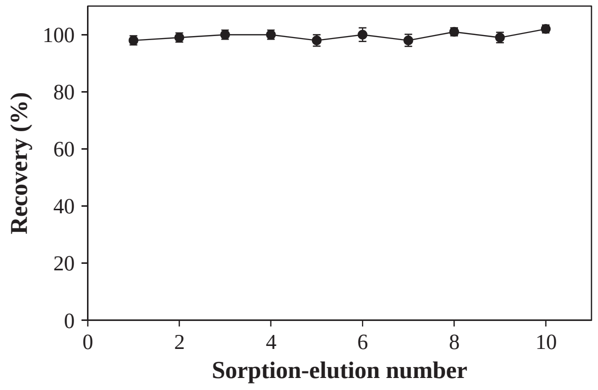

Fig. 6. Sorption and elution cycle of Cu(II)-imprinted polymer ($n=3$).

3.4. Effects of repeated use

In order to test the stability and reusability of the ion-imprinted polymer, the sorption–elution cycle was repeated 10 times by using the same IIP under the optimum conditions. In each cycle, 50 mL of 0.2 mg L^{-1} Cu(II) at pH 6.0 was passed through the column and then eluted with 10 mL of 0.5 mol L^{-1} HNO_3. The sorption–elution cycle of Cu(II)-imprinted polymer is shown in Fig. 6. The results clearly showed that the Cu(II)-imprinted polymer could be repeatedly used without any significant loss in the initial binding affinity. Mean recovery was 99.4 ± 1.3% at the 95% confidence level with a relative standard deviation (RSD) of 1.4% for 0.2 mg L^{-1} Cu(II).

3.5. *Evaluation of the method performance*

A limit of detection (LOD, 3 s) of 0.9 $\mu g\ L^{-1}$ was obtained for Cu(II) from the preconcentration of twenty blank solutions (pH 6.0). The accuracy of the method was verified by analysis of certified reference materials of wastewater (CWW-TM-D) and multivitamin and multielement tablets (SRM 3280). The results are summarized in Table 3. The results agreed with the certified values.

Table 3
Determination of copper in the certified reference materials (SRM 3280 and CWW-TM-D) and various water samples with the recoveries. Results are given as mean ± standard deviation of four replicate analyses for each sample. Spiked concentrations are 10 and 200 $\mu g\ L^{-1}$ for tap water and other water samples, respectively.

Sample	Determined		Certified value	Recovery (%)
	Unspiked sample	Spiked sample		
Tap water ($\mu g\ L^{-1}$)	4.1 ± 0.2	13.3 ± 0.8	–	92
Lake water ($\mu g\ L^{-1}$)	LOD <	199 ± 4	–	100
Seawater ($\mu g\ L^{-1}$)	LOD <	197 ± 3	–	98
Dialysis concentrate ($\mu g\ L^{-1}$)	LOD <	194 ± 5	–	97
Synthetic sample[a] ($\mu g\ L^{-1}$)	LOD <	201 ± 3	–	100
CWW-TM-D ($mg\ L^{-1}$)	0.98 ± 0.01	–	1.00	98
SRM 3280 ($mg\ g^{-1}$)	1.35 ± 0.02	–	1.40 ± 0.17	96

[a] Solution contains Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} ions at 10 $g\ L^{-1}$ concentrations.

Table 4
Determination of copper in multivitamin/multielement supplements. Results are given as mean ± standard deviation of four replicate analyses for each sample.

Sample	Content of copper ($mg\ g^{-1}$)		RSD (%)
	Declared by producer	Proposed method	
MMS_1	0.52	0.50 ± 0.01	2.0
MMS_2	0.92	0.91 ± 0.03	3.3
MMS_3	2.38	2.31 ± 0.02	0.9

The accuracy of the method was also tested through recovery studies with tap water, lake water, seawater samples, and dialysis concentrates and synthetic sample solution. The results are also summarized in Table 3. The recoveries of Cu(II) obtained from the real samples varied from 92 to 100%. These results clearly indicated that the MTMAAm containing imprinted polymer was suitable for solid phase extraction of Cu(II) from saline solutions.

Additionally, the method was applied to the analysis of multivitamin and multielement supplements (MMS_1–MMS_3) containing both major (Ca, Mg, P) and minor elements (Cu, Cr, Fe, Mn, Mo, Se, Zn). The data in Table 4 showed that the procedure could also be used for the determination of Cu(II) from samples that contain transition metals.

3.6. *Comparison with other Cu(II)–IIPs*

A comparison of various sorbents previously reported for Cu(II) with Cu(II)–IIP is provided in Table 5 with respect to the nature of ligand, polymerization method, relative selectivity coefficient and sorption capacity. The values for Cu(II)–IIP were comparable or better than some of the previously reported sorbents.

4. Conclusions

The preparation of IIPs via covalent binding of vinylated chelating agents in polymeric matrices is of special interest today. This approach provides spatially regulated sites in the polymer matrix. In this paper, we synthesized a novel ion-imprinted polymer using 5-methyl-2-thiozylmethacrylamide (MTMAAm) as a suitable vinylated chelating agent for selective separation and preconcentration of Cu(II) ions with EGDMA as a cross-linker. In comparison with non-imprinted polymer, the ion-imprinted polymer exhibits higher selectivity toward Cu(II) over the competing metal ions with similar ionic radii. Moreover, the Cu(II)-imprinted polymer shows high selectivity even in the presence of complex matrices, such as seawater and concentrated dialysis samples. The synthesized ion-imprinted polymer could be used as a column material in on-line or off-line solid phase extraction concerning ultra-trace level determination of Cu(II) by ICP-AES and ICP-MS.

Table 5
Comparison of the sorbent characteristics of different copper(II)-imprinted polymers.

Ligand	Polymerization method	pH	Relative selectivity coefficient			Sorption capacity ($\mu mol\ g^{-1}$)	Enrichment factor	Reference
			$k'_{Zn(II)}$	$k'_{Ni(II)}$	$k'_{Co(II)}$			
VP/DBDA15C4[a]	Bulk	7	16.1	11.3	13.9	75	100	[29]
MAH[b]	Dispersion	7	7.40	9.51	12.3	755	1024	[30]
CS[c]	Sol–gel	7	5.8	122.1	16.5	750	196	[31]
L[d]	Bulk	4	49.7	208.3	64.4	469	50	[32]
MAA/PAR[e]	Dispersion	7	N.R.[f]	16.96	19.34	37	250	[33]
MAA/diethylene triamine	Bulk	5	N.R.	1.6	3.1	1196	Not reported	[34]
AQ[g]	Precipitation	7	19.4	18.7	18.1	74	60	[35]
Salen[h]	Suspension	7	N.R.	N.R.	N.R.	114	16	[36]
MTMAAm	Bulk	6	14.8	9.1	26.6	82	100	This work

[a] 2-Vynylpyridine/5,6;14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane-5,14-diene.
[b] Metacryloylamidohistidine.
[c] Chitosan-succinate.
[d] (2Z)-*N*,*N*′-bis(2aminoethylic)but-2-enediamide.
[e] Metacrylic acid/4-(2-pyridylazo)resorcinol.
[f] Not reported.
[g] 1-Hydroxy-4(prop-2′-enyloxy)-9,10-anthraquinone.
[h] 2,2′-{Ethane-1,2-diylbis[nitrilo(E)methylylidene]}bis(6-allylphenol).

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.05.047.

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