Selective Solid-phase Extraction of Cu²⁺ by a Novel Cu(II)-imprinted Silica Gel

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A new Cu(II)-imprinted salen functionalized silica gel adsorbent was synthesized by surface imprinting technique and was employed as a selective solid phase extraction material for Cu²⁺ removal from aqueous solutions. The samples were characterized by FT-IR, ¹HNMR, ¹³CNMR, CHNS and DTG techniques. The BET surface area of the silica gel was also determined. The adsorbent was then used for removal of Cu²⁺ from aqueous solutions under different experimental conditions. It was concluded that the synthesized imprinted silica gel had higher selectivity and capacity compared to the non-imprinted silica gel and the maximal adsorption capacity of 67.3 and 56.5 mg.g⁻¹ was obtained respectively for ion-imprinted and non-imprinted adsorbents. The relative selectivity factor (β) of 50.32 and 31.94 was obtained respectively for Cu²⁺/Ni²⁺ and Cu²⁺/Zn²⁺ pairs. The dynamic adsorption capacity of the imprinted adsorbent was close to the static adsorption capacity due to the fast kinetic of adsorption. Furthermore, the ion-imprinted adsorbent was recovered and repeatedly used and satisfactory adsorption capacity with acceptable precision was obtained. Each experiment was repeated at least for three times and the mean and the standard deviation for each measurement were calculated. The applicability of the method was examined for Zayandehrood water as real sample. Acceptabe standard deviation was obtained.

Keywords: Surface imprinting; Salen-functionalized; Copper; Solid-phase extraction.

INTRODUCTION

As the result of industrial activities development, the amount of transition metals released into the environment has increased continuously. It has been proved that large amounts of many heavy metals such as copper, zinc, lead, cadmium and mercury seriously affect environment health because of their toxicity, accumulation in the food chain and persistence in nature. Since copper and its compounds are widely used as chemical materials in modern society, they are widespread in natural waters and soils. Several industries, for example, dyeing, paper, petroleum, copper/ brass plating and copper-ammonium rayon, release undesired amounts of Cu²⁺ into the environment. High Cu concentration in soils causes delay in flowering and fruiting and low seed set.^{1,2} It is also toxic to fish life even at low concentrations. Copper contaminant in soil and water system can eventually impact human health through the food chain. The health impact includes hepatic, cirrhosis, anemia, unusual symptoms of the nervous system and vascular sclerosis.³ Consequently, development of reliable methods for removal and determination of copper in real samples is of particular significance. Traditional separation methods for metal ions are liquid-liquid extraction, co-precipitation and ion-exchange. These methods often require large amounts of high purity organic solvents some of which are harmful to health and cause environmental problems.⁴ Solid-Phase Extraction (SPE) is widely used as a powerful and fast emerging sample preparation technique for separation or enrichment of selected analytes. SPE is based on the distribution of analyte between an aqueous solution and adsorbent by mechanisms such as adsorption, co-precipitation, complex formation and other chemical reactions. Comparing with the traditional enrichment procedure such as liquid-liquid extraction, SPE is considered to be superior due to its simplicity, rapidity, environmental and economical friendly, minimal cost owning to low consumption of reagents, absence of emulsion, flexibility, ease of automation, safety with respect to hazardous materials and the ability to combine with different modern detection technique.⁵ The choice of adsorbent is a key point in SPE, because it can control the analytical parameters such as selectivity, affinity, and capacity. An efficient adsorbing material should possess a stable and insoluble porous matrix having suitable active groups that interact with selected metal ions. Silica gel is an ideal support for organic groups, because it is thermally, mechanically and chemically stable and non-swelling material.⁶ However, the basic disadvantage of these adsorbents is the lack of metal selectivity

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which leads to other species interfering with the target metal ion. Moreover, matrix of environmental samples is too complex and separation of trace elements in complicated matrix is interfered by other species. So the selective separation of cations is of great significance. Ion-imprinting, is an effective technique for recognition of template metals. In recent years, a lot of ion-imprinted polymer (IIPs) have been prepared and used for selective solid phase extraction and enrichment of metal ions.^{7,8} However, with the usage of ion-imprinted polymers, the kinetics of the adsorption and desorption is unfavorable.⁹⁻¹¹ This may be interpreted that the templates and functionality are totally embedded in the polymer matrix. So the mass transfer is slow. Surface imprinting technique, to brief, is localizing of binding sites to the surface of high accessibility. Ion-imprinted adsorbents prepared by this technique show many advantages including high selectivity, more accessible sites, fast mass transfer and fast binding kinetics. Therefore, intensive researches have been performed in recent years. Wang et. al prepared an ion-imprinted thiol functionalized silica gel sorbent for selective separation of mercury ions.¹² Hu and coworkers prepared Cr(III)-imprinted silica gel and the material was successfully applied to the speciation of trace chromium in environmental samples.¹³ Pd-imprinted functionalized silica gel showed high selectivity for palladium(II) preconcentration.¹⁴ Chang et al synthesized a surface imprinted amino-functionalized silica gel material for selective solid-phase extraction of Zr(IV).¹⁵ Surface imprinting technique was also used for selective separation of Cu²⁺. The synthesize of a Cu(II)-imprinted sorbent by surface imprinting and functionalizing by N-[3-(trimethoxysilyl)propyl] ethylenediamine (TPED) on silica gel surface has been reported.¹⁶ Gue and coworkers synthesized a new Cu(II) ion-imprinted diethylenetriamine (DETA) modified silica gel sorbent by surface imprinting technique.¹⁷ The choice of a complexing ligand is of great importance here, as it directly influences selectivity of the adsorbent. Effectiveness of a surface imprinted adsorbent in rebinding metal ions has been attributed to the complexation chemistry between the ligand which supported onto the silica-gel surface and the target ion. Also the coordination geometry and the coordination number of a metal ion together with the charge and the size of the target ion play an important role in obtaining selectivity. Schiff bases may be perspective complexing ligand for ion-imprinting purposes due to their complexing abilities toward heavy metals. They have been applied as modifying agents for adsorption of various metal ions.¹⁸⁻²³ In this study a new Cu(II)-imprinted silica-gel was synthesized by functionalization of silica gel surface by salen-Cu complex the ion imprinted adsorbent was used for removal of Cu^{2+} from aqueous solutions and the effect of imprinting process on the selectivity of the adsorbent was examined.

EXPERIMENTAL SECTION Chemicals and reagents

Cu(OAC)₂.H₂O, Ni(NO₃)₂.6H₂O, Zn(NO₃)₂.4H₂O, 4-hydroxysalicylaldehyde, 1,2-diamino ethane, silica gel (5-40 μ m particle size, and 3-chloropropyltrimethoxysilane were received from Merck. All solvents; such as methanol, ethanol, toluene, diethyl ether and chloroform were purchased from Merck. For preparation of the solutions double distilled water was used.

Apparatus and instruments

FT-IR spectra (4000-400 cm⁻¹) were recorded on FT-IR, Perkin Elmer 65, using KBr pellets. A PG instrument Ltd, T70 UV-Vis spectrometer was used to provide the UV-Vis spectra of the synthesized ligand and complex. A 3505 Jenway digital pH meter was used for the pH adjustments. A flame atomic adsorption spectrometer (A. Analyst 300 Perkin Elmer flame) was used for determining the concentration of Cu(II), Ni(II) and Zn(II). Hollow cathode lamps were used as the radiation sources at 324.8 (Cu), 232.0 (Ni) and 213.9 nm (Zn). TG-DTG measurements were performed on a Setaram TG-DSC thermal analyzer. A ¹³CNMR spectrometer (Bruker DPX400 ¹³CNMR) was used to prepare the ¹³CNMR spectrum of the synthesized ligand. The ¹HNMR Spectrumeter (Bruker ¹HNMR 100 MHz) was used to obtain the ¹HNMR of the synthesized ligand. ElementarVarioEl III (CHNS) analyzer was used to examine the elemental composition of the synthesized ligand and complex. The specific surface area of the silica gel was determined by the Brunauer-Emmett-Teller (BET) method by using a Quantachrome apparatus.

Activation of silica gel

Silica gel is an amorphous inorganic polymer having siloxane groups (Si-O-Si) in the bulk and silanol groups (Si-OH) on its surface. The silanol groups facilitate the introduction of the organic groups which covalently bind to the silica surface. Commercial silica gel contains a low concentration of surface silanol groups suitable for modification. Silica gel surface was activated before modification to increase the surface silanol groups and removal any adsorbed impurities. Hydrochloric acid was used for the activation of silica gel. To activate the silica gel surface, 5.000 g of silica gel was mixed with 50 mL of 6 M hydrochloric acid. The mixture was refluxed for 8 hours. The solid was filtered and thoroughly washed with doubly distilled water. Activated silica gel was dried at 110 °C for 6 hours. The specific surface area of the silica gel was determined by N_2 adsorption. to be 450 m².g⁻¹. Preparation of chlorofunctionalized silica gel

To prepare the chlorofunctionalized silica gel 5.000 g of activated silica gel was dispersed into dry toluene (50 mL) and then 10 mL 3-chloro propyltrimethoxysilane (CPTS) was added in one portion. The mixture was refluxed for overnight under nitrogen atmosphere. The product was filtered off, washed with dry toluene, ethanol and diethyl ether respectively and dried under vacuum at 70 °C for 6 hours.²⁴

Preparation of N,N'-bis(4-hydroxysalicylidene)ethylene-1,2-diamine; H₂[(OH)₂-salen]

The stoichiometric amount of 4-hydroxysalicylaldehyde (0.02 mol, 2.760 g) dissolved in methanol (25 mL) was added drop-by-drop to 0.01 mol, 0.6 g of 1,2-diaminoethane solution dissolved in 25 mL methanol. The mixture was refluxed for 4 hours and a bright yellow precipitate of symmetrical Schiff base ligand; H₂[(OH)₂-salen]; was obtained. The yellow precipitate was separated by filtration, washed with cold methanol and dried. It was then re-crystallized from methanol to remove the unreacted materials. The Schiff base ligand was characterized by CHN analysis, UV-vis spectroscopy, FT-IR spectroscopy and ¹H and ¹³CNMR spectroscopy.²⁵ Anal. Calculated for Schiff base ligand: C, 63.99; H, 5.37; N, 9.33; found: C, 63.69; H, 5.53; N, 9.64.

Synthesis of [Cu((OH)₂-salen)]

A flask containing a stirred suspension of copper(II) acetate mono hydrate (3.192 g, 0.016 mol) in methanol (100 mL) was warmed to 50 °C. Then N,N'-bis(4-hydroxysalicylidene)ethylene-1,2-diamine; H₂[(OH)₂-salen], (4.800 g, 0.016 mol) was added in one portion, and the resulting brown suspension was then refluxed for 8 hours. The mixture was cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give brown crystalline [Cu((OH)₂-salen)] which was purified by re-crystallization from chloroform. This Schiff base complex was characterized by CHN analysis, UV-vis spectroscopy, FT-IR spectroscopy.²⁶ Anal. Calculated for [Cu((OH)₂-salen)]: C, 52.83; H, 4.43; N, 7.70; found: C, 52.36; H, 4.38; N, 7.61.

Preparation of Cu(II)-imprinted and non-imprinted silica gel adsorbents

At the first step, to anchor the copper(II) complex onto the silica gel surface, 2.190 g (0.006 mol) of synthesized copper(II) salen complex was dispersed in dry toluene (50 mL) and warmed to 60 °C with continuous stirring. Then 1.000 g of chlorofunctionalized silica gel was added in one portion. The mixture was refluxed under nitrogen atmosphere for overnight. The resulting product was filtered, washed with dry toluene, ethanol and

Amount of complex (mmol)	Cu content (mg/g)	Cu content (meq/g)
1	40.01	1.26
4	90.28	2.91
6	106.82	3.36
8	110.05	3.37

Table 1. Cu content of each solid product

diethyl ether, and then dried at 50 °C for 6 hours. The un-reacted complex was extracted by soxhelet (in toluene) for 8 hours. The covalently anchorage of the complex to the silica-gel surface was confirmed by wet and thermal analyses. Different amount of complex was immobilized on silica gel surface, in order to investigate its optimal quantity. The Cu content of the solid product which was determined by FAAS, represents the amount of complex supported on silica gel surface. This also shows the maximum accessible adsorption capacity of the synthesized adsorbent. Table 1 shows the Cu content of the products.

According to this data, 6 mmol of complex was selected as the optimal amount of Cu-complex for the synthesis process. The elution of copper ions acting as a template in the salenfunctionalized silica gel was examined by different solvent; including NH₃, EDTA and HNO₃. 0.1 mol. L⁻¹ nitric acid was the most effective eluent. At the second step, 0.200 g of silica gel supported by [Cu((OH)₂-salen)] was shaken with 0.1 mol.L⁻¹ HNO₃ for 4 hours to remove metal ions and leave Cu(II)-imprinted silica gel adsorbent. The solid product was filtered under reduced pressure and washed with 0.1 mol.L⁻¹ HNO₃ and doubly distilled water respectively. The Cu(II)-imprinted silica gel adsorbent was characterized by FT-IR spectroscopy and thermal analysis. The same procedure was repeated for preparation of non-imprinted silica gel but H₂[(OH)₂-salen] was used instead of [Cu((OH)₂salen)]. In each preparation about 1.5 g of the adsorbent was obtained. Since we needed more than 30 g of material, the procedure was repeated more than 20 times and the products were characterized according to the same procedures.

Static adsorption expriments

To perform the static adsorption, 0.200 g portion of Cu(II)-imprinted or non-imprinted adsorbent was transferred into a polyethylene bottle previously cleaned with detergent and doubly distilled water. Then 20 mL of standard solution of Cu²⁺ was added and the pH was adjusted with HCl and NaOH. The mixture was shaken for 5 min. The solid was separated by filtration and centrifugation. The concentration of the metal ion, in the initial and the final solutions was directly determined by FAAS and the adsorption capacity was measured.

Effect of pH

In order to investigate the effect of the pH on Cu^{2+} adsorption, according to the static procedure, 0.200 g of Cu(II)-imprinted or non-imprinted adsorbent was equilibrated with 20 mL of Cu^{2+} solution (1000 ppm) at different pH. The mixture was filtered and the concentration of Cu^{2+} in the filtrate was determined. *Effect of contact time*

0.200 g portion of Cu(II)-imprinted or non-imprinted adsorbent was equilibrated with 20 mL of Cu²⁺ solution (1000 ppm) at optimized pH of 5 for different contact time. After separation the concentration of Cu²⁺ in the filtrate was determined.

Selectivity

In order to determine the selectivity of the method, the solutions containing known concentration of Cu^{2+} and competitive ions were prepared. The solutions were equilibrated with 0.200 g portion of Cu(II)-imprinted or non-imprinted adsorbent for 5 min. The mixture was filtered and the concentration of Cu^{2+} was determined in the filtrate. Five real samples from different location of Zayandehrood river were taken and 20 mL of each sample was mixed with 0.200 g of the Cu(II)-imprinted sorbent. After equilibration, the adsorbent was separated and the adsorbed metal ions were eluted with 0.1 M HNO₃. The concentration of Cu^{2+} was measured by Flame Atomic Adsorption Spectrometer.

Reusability of the adsorbent

To test the reusability of the imprinted adsorbent, it was subjected to eight adsorption-elution cycles. Adsorption cycles were adjusted at optimized conditions and the elution operations were carried out by shaking 0.200 g portion of the adsorbent with 25 mL of 0.1 mol.L⁻¹ HNO₃ for 4 hours. At the end of each cycle the amount of Cu²⁺ was measured in the eluted solution.

Dynamic adsorption procedure

A glass column (50 mm in length and 7 mm in inner diameter) was cleaned with detergent and doubly distilled water. 500 mg portion of Cu(II)-imprinted adsorbent in water was transferred into the column. A small amount of glass wool was placed at both ends of the column to prevent loss of the adsorbent particles during sample loading. Before use, the column was washed successively with doubly distilled water. A solution containing 20 mg.L⁻¹ of Cu²⁺ was allowed to pass through the column. The sample flow rate was adjusted at 0.1 mL.min⁻¹ and each 10 mL of the effluent was collected for determination the Cu⁺² concentration.

RESULTS AND DISCUSSION

Characterization

UV-Vis spectra

UV-Vis spectra of the synthesized ligand and the complex have been prepared in ethanol (Fig. S1). Elec-

tronic spectrum of the ligand exhibits two bands at 280 and 310 nm which could be respectively assigned to intra ligand $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions. All these bands shifted to higher wavelength, indicating the restructuring of the ligand after coordination with the metal ion.

The electronic spectrum of this kind of Schiff base, which are widely used as chelating agents, are relevant due to the possibility of finding them in the solid state and/or in solution as keto-amine or phenol-imine tautomer. In the solid state salicylaldimine Schiff bases tend to form (N...H-O) or (N-H...O) types of hydrogen binding, respectively. In many cases in solution, both types of hydrogen bonds have been observed indicating phenol-imine, O-H...N, keto-amine, O...H-N, tautomerism. Polar solvents such as EtOH, favor the formation of the keto-amine. The interaction of enol-imine with a hydrogen bond forming solvent would presumably reduce the O-H bond strength and facilitate proton transfer to the nitrogen center. Thus, the band in 385 nm is assigned to $n \rightarrow \pi^*$ transition of keto-amine tautomeric structure of ligand. Addition to these bands, the electronic spectra of complex contain a weak broad band in the 560 nm which assigned to $d \rightarrow d$ transition of the metal ion. Appearance of a weak band due to charge transfer transition, underneath of $n \rightarrow \pi^*$ transition (as a shoulder at 360 nm) in the electronic spectrum of the complex, makes this band broad.^{27,28}

¹H and ¹³CNMR Spectra

The ¹H and ¹³CNMR spectra of the ligand have been recorded in DMSO-d6 as solvent (Fig. S2 and S3). It is important to emphasize the ¹HNMR resonance of the ortho OH group at 13.7 ppm is attributed to the presence of inter molecular hydrogen bounding. The singlet at 9.9 ppm can be assigned to the para OH proton. The single-proton resonance in the ¹HNMR spectrum of the ligand near 8.3 ppm has been assigned to the azomethine group proton. The multiples at 6.1-7.1 ppm can be attributed to the protons of the aromatic ring. In addition, the CH₂ groups are observed at 3.7 ppm. The ¹³CNMR spectral data of the ligand confirms the results of the ¹HNMR spectrum. The greatest downfield peak in 168 ppm, is likely to arise from the HC=N. The peak in 157.1 ppm is due to carbon atoms which are attached to the hydroxyl groups. The signal at 56.1 can be attributed to the carbon atoms of the CH_2 groups.^{29,30}

FT-IR

The FT-IR spectrum of $H_2[(OH)_2$ -salen] and [Cu-((OH)_2-salen)] are shown in Fig. S4. The band appeared at

3400-3600 cm⁻¹ is assigned to v_{O-H} stretching. The band at 2751 cm⁻¹ is assigned to OH group (ortho position) associated inter-molecularly with the nitrogen atom of CH=N group. This band disappeared in the FT-IR spectrum of the complex. The sharp strong band observed at 1642 cm⁻¹ in ligand spectrum is assigned to the azomethine group vibration. This band is slightly shifted to lower frequencies in the complex indicating that the imine nitrogen atom is coordinated to the Cu^{2+} ion. In the spectrum of the complex, the medium or weak bands observed at 564 and 473 cm⁻¹ can be respectively attributed to (Cu-O) and (Cu-N) mods. FT-IR spectrum of the activated silica gel includes the bands at 1099 and 956 cm⁻¹ which indicated respectively Si-O-Si and Si-OH stretching vibrations. The most informative spectroscopic data to elucidate anchoring of $H_2[(OH)_2$ -salen] and $[Cu((OH)_2$ -salen)] on the silica gel surface obtained from the comparison of the set of FT-IR spectra including activated silica gel (SG), SG-H₂[(OH)₂salen] and SG-[Cu((OH)₂-salen)], imprinted and non-imprinted silica gel adsorbent^{31,32} (Fig. S5).

Thermal analysis

TG and DTG curves of imprinted and non-imprinted silica gel adsorbent are shown in Fig. 1. The weight loss occurred in temperature range of 225-227 °C reflects the surface grown salen groups. This could confirm the covalent anchoring of functional group on silica gel surface. That one in temperature range of 88-90 °C corresponds to the loss of humidity.

Batch adsorption experiments *Effect of pH*

Complex formation between salen immobilized on the silica-gel surface and copper ions was expected to be pH dependent. For this reason pH influence on the Cu^{2+} ad-



Fig. 1. TG-DTG curves of Cu(II)-imprinted (a) and Non-imprinted silica gel (b).

sorption by Cu(II)-imprinted and non-imprinted silica gel adsorbent was tested (Fig. 2). At low pH ranges due to the protonation of the active sites, the Cu²⁺ adsorption is lowered. The maximal complex formation was observed at pH 5. Considering the ksp of Cu(OH)₂ (4.8×10^{-20}), the solubility of Cu²⁺ at pH = 5 was 4.8×10^{-2} M (3050 ppm), while at pH = 6 it reduced to 4.8×10^{-4} M (30.50 ppm). The optimized concentration was 1000 ppm, therefore, the pH above 5 could not be used.

Kinetic of the reaction

Figure 3 shows that an equilibrium time of about 5 min was required for complete adsorption process. As the time of 50% adsorption $(t_{1/2})$ was less than 1 min. It means that the sorption rate is very fast. This kind of fast kinetic adsorption is due to accessibility of active sites on the surface of the adsorbent.³⁴

Static adsorption capacity of Cu(II)-imprinted and non-imprinted adsorbent

The adsorption capacity is an important factor because it determines how much adsorbent is required to



Fig. 2. Effect of pH on sorption of the Cu(II) by Cu(II)imprinted and non-imprinted silica gel.



Fig. 3. Effect of stirring time on the Cu(II) sorption by Cu(II)-imprinted and non-imprinted silica gel.

quantitatively extract the analyte from a given solution. As can be seen from Figure 4, the amount of Cu²⁺ ions adsorbed per unit mass of ion-imprinted or non-imprinted adsorbent increased till plateau values were obtained. The static adsorption capacity of the Cu(II)-imprinted and non-imprinted silica gel for Cu²⁺ sorption were calculated 67.3 mg.g⁻¹ and 56.5 mg.g⁻¹, respectively. Wu et al. used imprinted silica gel modified by N-[3-(trimethoxy-silyl)propyl]ethylenediamine (TPED) for removal of Cu²⁺ from aqueous solutions. Their reported adsorption capacity was higher than the value of this work, but the selectivity was lower.¹⁶ Gue et al also use diethylenetriamine imprinted silica for Cu²⁺ adsorption. The adsorption capacity of 41.1 mg.g⁻¹ and selectivity coefficient of 411 was reported.¹⁷ The reported adsorption capacity of different imprinted material used for adsorption of a variety of cations was always lower than the value obtained in this work.¹⁸⁻⁴⁷ Furthermore the Cu(II)-imprinted silica gel prepared in this work showed faster adsorption kinetic and higher selectivity value for the studied cations.

Selectivity of the Cu(II)-imprinted adsorbent

The Zn^{2+} and Ni^{2+} ions were chosen as the competitive species because these ions have similar charge, ionic radius and properties. Additionally they exist in real and environmental samples together. Tolerance limit of Cu(II)imprinted and non-imprinted adsorbent are listed in Table 2. The tolerance limit is defined as the ion concentration causing a relative error $\geq 5\%$ in adsorption of Cu⁺². The tolerance limits of the investigated competitive ions of nonimprinted adsorbent are 55 and 65 fold of Cu(II)-imprinted one (Table 2).



Fig. 4. The effect of Cu(II) initial concentration on adsorption capacity.

Table 2. Tolerance limits (ppm)

Metal ion	Cu(II)-imprinted adsorbent	Non-imprinted adsorbent
Ni(II)	10100	180
Zn(II)	8000	120

Adsorption capacity, distribution ratio, the selectivity factor of Cu^{+2} with respect to Ni^{+2} and Zn^{+2} and the relative selectivity factor were calculated by following equations.³⁵

$$Q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$D = \frac{Q}{C} \tag{2}$$

$$\frac{\alpha_{Cu}}{M} = \frac{D_{Cu}}{D_{Lu}} \tag{3}$$

$$\beta = \frac{\alpha_I}{\alpha_N} \tag{4}$$

where *Q* represents the adsorption capacity (mg.g⁻¹), C_0 and C_e represent the initial and equilibrium concentration of metal ion respectively (mg.L⁻¹), W is the mass of the adsorbent (g), and V is the volume of metal ion solution (L), D_{Cu} and D_M represent the distribution ratios of Cu⁺² and Ni⁺² or Zn⁺² (mL.g⁻¹), $\alpha_{Cu(II)/M(II)}$ is the selectivity coefficient with respect to competitive ion, α_I and α_N represent the selectivity factor of Cu(II)-imprinted and non-imprinted salen-functionalized silica gel adsorbent respectively. The calculated D values for Cu^{2+} is high, while significantly lower for Ni^{2+} and Zn^{2+} . The β values for Ni^{+2} and Zn⁺² are 50.32 and 31.94 respectively which are greater than one (Table 3). This means that Cu(II)-imprinted adsorbent has higher selectivity for Cu⁺² adsorption than nonimprinted one.³⁶ Thus Cu(II)-imprinted adsorbent can be used for removal of Cu²⁺ in the presence of high concentrations of Zn⁺² and Ni⁺².

There are two possible factors for the selectivity of Cu(II)-imprinted salen functionalized silica gel adsorbent.

Table 3. Selectivity of Cu⁺² ions on imprinted and non-imprinted silica gel sorbent

Competitive ion	$\alpha_I{}^a$	$\alpha_N{}^b$	β^{c}
Ni(II)	566.53	11.26	50.32
Zn(II)	350.49	10.97	31.94

^a: selectivity factor of Cu(II)-imprinted silica gel adsorbent

^b: selectivity factor of non-imprinted silica gel adsorbent

^c: the relative selectivity factor (α_{I}/α_{N})

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Table 4.	Ionic	radii	of Zn ²⁺ .	, Ni ²⁺	and	Cu ²⁺
				/		

Cation	Radius (pm)	
Cu ²⁺	73	
Zn^{2+}	74	
Ni ²⁺	69	

One is the functional group inherent selectivity; salen ligand has good affinity toward Cu^{2+} .

The second is the coordination-geometry selectivity that means the Cu(II)-imprinted adsorbent can provide the ligand groups in a suitable way required for coordination of Cu^{2+} ion.³⁷ The selectivity factor of Cu(II)-imprinted adsorbent with respect to Ni²⁺ were higher than Zn²⁺. This is attributed to similarity of the ionic radius of Zn²⁺ and Cu²⁺ which intensified the interfering effect of Zn²⁺ (Table 4).

The applicability of the method for real samples was successfully examined for analysis of cooper in aqueous solutions taken from different location of Zayandehrood river (Table 5). In Zarinshahr sample due to the presence of many industrial factories including Isfahan Steel Factory, higher concentation of the Cu^{2+} was observed. The standard deviation between 1.84-2.94 was obtained which was acceptable for the method.

Precision of the method

Under the optimized conditions, twelve replicate samples were examined by static method. The mean quantity of adsorbed Cu^{2+} was 67.28 mg.g⁻¹. The relative standard deviation of the adsorption capacity was 1.56% which indicated that the method had good precision.

Reusability of the adsorbent

Adsorption capacity of the Cu(II)-imprinted silica gel was determined for eight consecutive recycling. The decrease on the adsorption capacity was attributed to the separation of loosely bonded ligands but the ligands which are covalently anchored to the surface were not separated, hence the capacity remained constant after seventh regeneration cycle. The variation in adsorption capacity within 8 adsorption-desorption cycles are displayed in Figure 5.

These results showed that the synthesized Cu(II)-imprinted adsorbent can be used repeatedly with satisfactory adsorption capacity (Table 6).

Dynamic adsorption capacity of Cu(II)-imprinted adsorbent

Figure 6 shows the breakthrough carve of the Cu(II)imprinted adsorbent. The calculated total dynamic capacity was 65.4 mg.g⁻¹. For column operation, breakthrough ca-

Table 5. Cu²⁺ concentration and standard deviations of real samples

Region	Cu(II) concentration (ppm)	Standard deviation (ppm)
ZamanKhan	67.28	2.08
Zarinshahr	342.50	2.94
Ziyar	78.30	2.08
Ejieh	29.39	1.89
Varzaneh	35.73	1.94

Table 6. Extraction recyclability through eight adsorption/elution cycles

Adsorption recycle	Adsorption capacity (mg.g ⁻¹)	Recovered capacity (mg.g ⁻¹)	Standard deviation of capacity (mg.g ⁻¹)
1	67.28	100.0	1.08
2	64.01	95.2	0.94
3	63.94	95.0	1.08
4	62.69	93.2	1.09
5	60.72	90.2	0.99
6	59.06	87.8	0.89
7	54.16	80.5	0.95
8	53.82	80.0	0.94

pacity is more significant than the dynamic capacity. The breakthrough capacity was calculated with the assumption that the breakthrough occurred at $C_e/C_i = 0.01$. It was 60.2 mg.g⁻¹ of dry functionalized silica gel and very close to static adsorption capacity as a result of fast kinetic of adsorption.^{38,39}

CONCLUSION

In this research, a new adsorbent for selective adsorp-



Fig. 5. Variation of adsorption capacity of the ion-imprinted sorbent within eight adsorption/desorption cycles.



Fig. 6. Breakthrough curve of the Cu(II)-imprinted silica gel (Cu(II) conc. 20 mg.L⁻¹, adsorbate 0.5 g, flow rate 0.1 mL.min⁻¹).

tion of Cu²⁺ was developed by synthesis of Cu(II)-imprinted salen-functionalized silica gel through surface imprinting technique. The adsorption process was kinetically fast, promising the removal and pre-concentration of Cu²⁺ by solid phase extraction method. The high selectivity of the adsorbent in the presence of Zn^{2+} and Ni²⁺ allowed the separation of Cu²⁺ from real samples. The synthesized Cu(II)-imprinted silica gel of this work showed higher selectivity, capacity and faster kinetic compared to the adsorbent reported by the other workers.⁴⁰⁻⁴⁷ Moreover the reusability and stability of this sorbent was satisfactory. Therefore it can be concluded that the prepared adsorbent can be used an desirable solid-phase extraction sorbent for on-line pre-concentration/separation of trace Cu²⁺ in complicated matrix samples. Moreover the Cu(II)-imprinted silica gel sorbent were used successfully for real samples analysis.

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