

Iminodiacetic Acid-Containing Polymer Brushes Grafted onto Silica Gel for Preconcentration and Determination of Copper(II) in Environmental Samples

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ABSTRACT: Silica gel has been modified by silylation with 3-mercaptopropyltrimethoxysilane followed by graft polymerization of dimethylacrylamide and (*N,N*-bis-carboxymethyl)-amino-3-allylglycerol-*co*-dimethylacrylamide, synthesized via the reaction of allyl glycidyl ether with iminodiacetic acid. The sorbent, poly(AGE/IDA-*co*-DMAA)-grafted silica gel, has been characterized by FTIR, elemental analysis, thermogravimetric analysis (TGA), FT-Raman, and scanning electron microscopy and studied for the preconcentration and determination of trace amounts of Cu(II) ion in environmental water samples. The optimum pH value for quantitative sorption of Cu(II) in batch mode was 5.5 and desorption was achieved, using 0.5 mol L⁻¹ nitric acid. The sorption capacity of functionalized sorbent is 32.3 mg g⁻¹. The chelating sorbent was reused for 15 sorption–desorption cycles without any significant change in sorption capacity. The profile of copper uptake

by the sorbent reflected good accessibility of the chelating sites in the poly(AGE/IDA-*co*-DMAA)-grafted silica gel. Scatchard analysis demonstrated homogeneous nature of binding sites. The equilibrium adsorption data of Cu(II) on modified sorbent were analyzed by Langmuir, Freundlich, Temkin, and Redlich–Peterson models. Based on equilibrium adsorption data, the Langmuir, Freundlich, and Temkin constants were determined as 0.0665, 4.26, and 8.34, respectively, at pH 5.5 and 20°C. Adsorption isotherms were analyzed at different temperatures to obtain free energy, enthalpy, and entropy of adsorption. The method was applied for Cu(II) determination in sea water samples. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: solid-phase extraction; polymer grafting; copper; isotherm study; preconcentration

INTRODUCTION

The critical concentration of Cu(II) in drinking water lies between 6 and 10 ng L⁻¹. Daily requirement of Cu(II) for human consumption is 2–2.5 mg, which is assimilated by bowels. Over consumption of Cu(II) could cause nausea, gastritis, diarrhea, muscle cramp, and muscle tremble. The direct determination of trace elements in real samples is difficult. The main restrictions come from the complexity of the matrix and the extremely low concentrations of analytes in those samples, which are often below the detection limits of available techniques.^{1,2} Thus, highly sensitive and selective techniques are required. Although the sensitive and accurate determination of trace elements by some instrumental techniques including inductively coupled plasma mass spectrometry, graphite furnace atomic absorption spectrometry is possible, flame atomic absorption spectrometry,^{3,4} is preferred for

trace element determination due to low costs and simplicity. However, the determinations of trace elements by flame atomic absorption spectrometry at levels below µg L⁻¹ are not possible. Thus, the preconcentration procedures are needed.^{5–7} There are many methods of preconcentration and separation such as liquid–liquid extraction,⁸ ion exchange methods,⁹ coprecipitation,¹⁰ membrane filter techniques,^{11,12} and cloud point extraction.^{13,14}

Surface modification of solid substrates by grafting polymer chains is a useful method for the production of materials with specific surface and structural properties.¹⁵ Grafted polymers offer unique opportunities to tailor and manipulate interfacial properties while retaining the basic mechanical strength and geometry of the supporting solid substrate. Surface-grafted water-soluble polymers, which are of interest in this work, have been investigated for use as chromatographic support resins.^{16–18}

In this context, the performance of a novel support for Cu(II) adsorption is evaluated. The support was produced by free-radical graft co-polymerization of *N,N*-dimethylacrylamide (DMAA) and a functional monomer containing metal chelating group, 1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol (allyl glycidyl

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ether/iminodiacetic acid AGE/IDA) onto a silica surface that has been modified with (3-mercaptopropyl)trimethoxy silane (MPTMS). The interaction between the metal ions and the chelating agent in the polymer should be reversible character for sorption and desorption phenomena. The tree-dentate ligand can sorb the metal ions not too loose to release it in sorption phenomena and not too tight to not release it in the desorption phenomena. For the purpose of demonstration of the principle, affinity binding of the metal upon the modified support is investigated with batch-wise method. However, for better characterization of the support, isotherm and kinetic studies are carried out.

EXPERIMENTAL

Instruments

Flame atomic absorption spectrometer (FAAS) Varian, (Palo Alto, CA) AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L min⁻¹, respectively) and inductive couple plasma-atomic emission spectroscopy (ICP-AES), Varian, model Vista were used for measuring concentration of metal ions. Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FTIR-410, Jasco, Easton, MD). Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Thermogravimetric analysis (TGA) was carried out on TGA-50H (Shimadzu Corporation, Kyoto, Japan). The scanning electron microscopy (SEM) micrographs were obtained on a SEM-PHILIPS XL30 scanning electron microscope.

Reagents and solutions

3-Mercaptopropyltrimethoxysilane, DMAA, and aluminum oxide were from Aldrich (Steinheim, Germany). DMAA (3 mL) was purified by flash chromatography on a column (2.5 × 0.9 cm) containing 1.6 g aluminum to remove impurities inhibiting polymerization. 2, 2'-Azobis (2-methylpropionitrile) was purchased from Acros (NJ). Allyl glycidyl ether was purchased from Fluka Chemica (Buchs, Switzerland). Anhydrous 1,4-dioxane, silica gel 60 for column chromatography (0.2–0.5 mm), IDA, NaOH, HCl, H₂SO₄, HNO₃, NaOH, K₂SO₄, NaCl, CH₃COOH, CH₃COONa, NaH₂PO₄, Na₂HPO₄, Pb(NO₃)₂, FeSO₄·7H₂O, CuSO₄·5H₂O, Co(NO₃)₂·6H₂O, Ni SO₄·6H₂O, Zn SO₄·7H₂O, Hg(NO₃)₂, Al(NO₃)₃, Ag (NO₃), Mg(NO₃)₂, Ca(NO₃)₂, Ba(NO₃)₂, and C₂H₅OH were products of Merck (Darmstadt, Germany). All the reagents were of analytical grade and used without any further purification.

The stock solution (1000 mg L⁻¹) of Cu(II) was prepared by dissolving appropriate amounts of Cu

(NO₃)₂ in deionized water. To adjust the pH of the solution, 10 mL of 0.1M acetic acid–acetate buffer (pH 3–6.5) or 0.01M phosphate buffer (pH 6.5–9) were used wherever suitable.

Synthesis of poly(AGE/IDA-co-DMAA)-grafted silica gel

Synthesis of the functional monomer 1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol-co-dimethylacrylamide (AGE/IDA)

Before the reaction of IDA with AGE, the IDA was neutralized with a KOH solution to keep carboxylic acid from reacting with the epoxy ring of AGE. Dipotassium salt of IDA solution (1M, 50 mL) was added slowly to AGE at a 1 : 1 molar ratio. The mixture was kept at 65°C for 1 h under powerful stirring. When the reaction was finished, the oil–water mixture changed to a transparent water phase. The yellowish liquid monomer was purified by pouring into acetone and dissolving in distilled water repeatedly. The identity of obtained product was 1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol-co-dimethylacrylamide. Structure of AGE-IDA was confirmed by IR and ¹H-NMR and ¹³C-NMR spectra. IR (NaCl, cm⁻¹) 3360 (OH), 1615 (C=C), 1395 (CH₂) and 1085 (C–O).

¹H-NMR (300 MHz, CDCl₃) δ: 1.59 (1 H, OH), 3.25–4.17 (5H {2H d, 1H tt, 2H d}, CH₂–O–CH₂–CH), 5.03–6.18 (9H {4H s, 2H d, 1H tt, 2H d}, N(CH₂)₂, CH₂=CH).

¹³C-NMR (300 MHz, D₂O) δ: 49.55 (CH₂–OH), 58.10 (O–CH₂), 58.16 (CH₂–N), 65.80 (CH₂–O), 72.03 (N–CH₂), 72.58 (N–CH₂), 118.90 (CH₂), 134.27 (CH), 171.96 (COO), and 173.59 (COO).

Polymer grafting

A two-step method was used: The first step was modification of silica with MPTMS and the next step is grafting the DMAA-AGE/IDA copolymer on the modified silica.

Modification of silica with (3-mercaptopropyl) trimethoxy silane

Details of the preparation and characterization of the poly[1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol-co-dimethylacrylamide] are reported in the previous work.¹⁹ Before the silylation reaction, the silica particles were cleaned with a 1M HCl; this was followed by immersion in water (for hydrolysis of the surface siloxanes) and subsequent filtration. The slurry was then vacuum-filtered and washed with deionized water until the filtrate pH was no longer acidic. The washed silica was dried for 3 h at 150°C and kept at this temperature until the start of the reaction. At this point, 10 g hydroxylated silica

particles were silylated by an anhydrous solution of 5% of MPTMS in 1,4-dioxane. The silylation reaction was carried out in the boiling solution for 24 h. Then, the silica particles were washed several times with 1,4-dioxane and dried under vacuum in a desiccator over dry calcium chloride.

Graft polymerization

The free-radical graft copolymerization of DMAA and AGE/IDA onto MPTMS-modified silica particles was carried out in a temperature-controlled reactor with vigorous stirring under a nitrogen atmosphere. Silica particles, modified with MPTMS, were placed into the degassed polymerization mixture (20 mL ethanol, 450 mg AGE/IDA, 2.07 mL DMAA, and 53.7 mg 2,2'-azobis (2-methyl-propionitrile) for 6 h at 75°C. The grafted silica sample was filtered immediately, and washed with 100 mL of ethanol, water and again ethanol, and dried under vacuum in a desiccator over dry calcium chloride. It was found that triple washing of grafted silica with ethanol and water was sufficient for removing any homopolymer that may have adsorbed. The methodology used to synthesize poly(AGE/IDA-co-DMAA)-grafted silica gel is summarized in Figure 1(a). The grafted silica gel was characterized by FTIR, elemental analysis, TGA, FT-Raman, and SEM.

Batch method of Cu(II) adsorption

A sample solution (100 mL) containing 0.5 $\mu\text{g mL}^{-1}$ Cu(II) was taken in a glass stoppered bottle and pH was adjusted to the required value. The 0.05 g of poly(AGE/IDA-co-DMAA)-grafted silica gel was added to the bottle and the mixture was shaken for certain time. The sorbent was filtered and sorbed metal ion was eluted with 0.5M nitric acid (10 mL). The concentration of the metal ion in the elute was determined by FAAS.

Isotherm studies

Isotherm studies were carried out by adding a fixed amount of sorbent (0.05 g) to a series of beakers filled with 50 mL Cu(II) solutions (10–100 $\mu\text{g mL}^{-1}$). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm for 4 h at 20, 30, and 40°C, respectively, and pH 5.5 (adjusted by adding 0.01M acetate buffer). The beakers were then removed from the shaker, and the final concentration of Cu(II) in the solution was measured. The amount of Cu(II) bound at equilibrium q_e (mg g^{-1}) by poly(AGE/IDA-co-DMAA)-grafted silica gel was calculated from the following equation:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of Cu(II) at initial and equilibrium, respectively, V (L) is the volume of the solution and W (g) is the mass of the adsorbent used.

RESULT AND DISCUSSION

Characterization of poly(AGE/IDA-co-DMAA)-grafted silica gel

IR spectrum

IR (NaCl, cm^{-1}) 3456 (OH), 1640 (C=O), 2930 bending (CH_2), 1026 (C—O), 1404 stretching (CH_2), 1400 stretching (CH_3), and 710 stretching (C—S). The spectrum indicates covalent grafting of poly(AGE/IDA-co-DMAA) to silica via termination of chains at sulfur atom.

Elemental analysis

The instruction used in this study is reported in ThermoFinnigan elemental analyzer manual. Elements of C, H, and N in the sample and standards in a column containing oxidant at 900°C were converted to CO_2 , H_2O , and N_2 , respectively. They were separated in a GC column containing molecular sieve and detected by a thermal conductivity detector (TCD). The percentages of C, H, and N in the sample were ascertained after drawing the calibration curve for standards and data processing for the sample.

The elemental analysis for poly(AGE/IDA-co-DMAA)-grafted silica gel (found: C, 10.38; H, 3.18; N: 1.62%, calculated for $(\text{SiO}_2)_{22} (\text{C}_5\text{H}_9 \text{ON})_n (\text{C}_{10}\text{H}_{17}\text{O}_6\text{N})_m$ on condition that $m = n = 1$: C, 10.81; H, 1.50; N, 1.68%) show that on an average 1 DMAA or AGE/IDA molecule is present in each 22 repeated units of the polymer.

Thermal analysis

TGA of the silica gel shows two-step weight loss during heating to 600°C. The weight loss up to 150°C was due to the water loss. The weight loss when heating above 200°C remained rather constant. Poly(AGE/IDA-co-DMAA)-grafted silica gel showed a completely different thermal behavior. The weight loss up to 100°C was due to the water molecules in the grafted silica and the weight loss at 200–600°C was due to the decomposition of chemically immobilized polymer (Fig. 2).

Raman spectroscopy

Raman spectrum of poly(AGE/IDA-co-DMAA)-grafted silica gel (cm^{-1}): 3316.18 (OH and C—N), 2932.39 bending (CH_2), 1642.32 (COO), and 1455.52 stretching (CH_2).

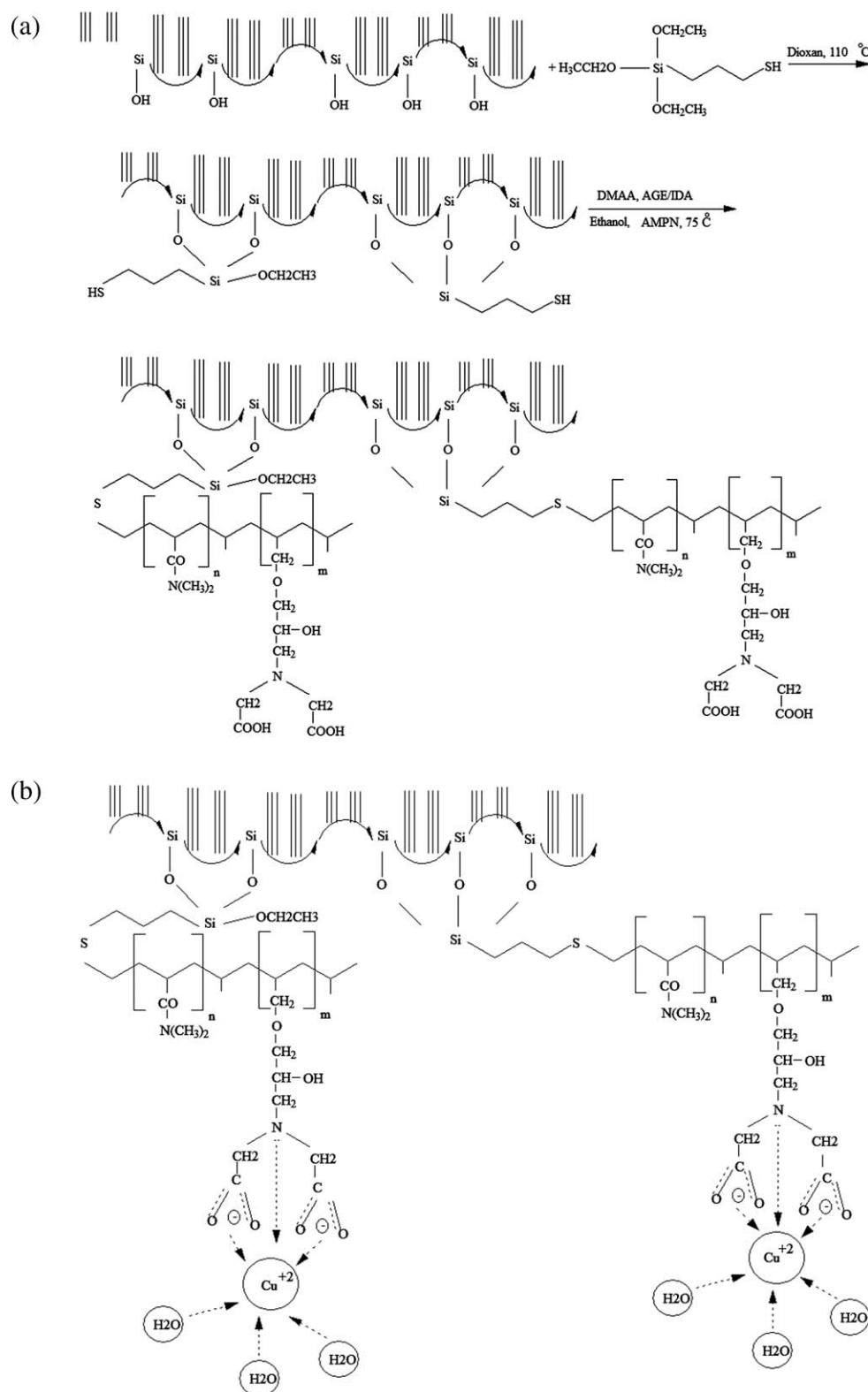


Figure 1 (a) Schematic presentation of the production of poly(AGE/IDA-co-DMAA)-grafted silica gel, (b) complex formation of Cu(II) with iminodiacetate residues of the polymer.

Raman spectrum of poly(AGE/IDA-co-DMAA)-grafted silica gel loaded Cu(II) (cm^{-1}): 3329.3 (OH and C–N), 2931.72 bending (CH_2), 1624.41 (COO), and 1450.91 stretching (CH_2).

The band observed in the poly(AGE/IDA-co-DMAA)-grafted silica gel at 3316.18 and 1642.32 cm^{-1} can be assigned to (OH/C–N) and (COO) shift to 3329.30 and 1624.41 cm^{-1} poly(AGE/IDA-co-

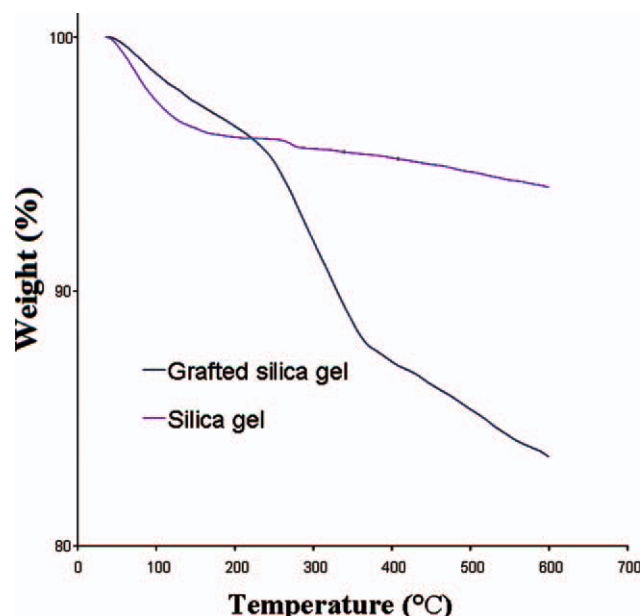


Figure 2 TGA of silica gel and poly(AGE/IDA-co-DMAA)-grafted silica gel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DMAA)-grafted silica gel-Cu⁺², respectively. These results demonstrate that the amidic and acidic groups on the grafted polymer interact with Cu⁺² and confirm the formation of poly(AGE/IDA-co-DMAA)-grafted silica gel-Cu⁺² complexes [see Fig. 1(b)].

Scanning electron microscopy

SEM was used to examine the external surface of the silica gel before and after modification. The surface of ungrafted silica gel has a smooth and highly homogeneous appearance [Fig. 3(a)]. The surface of poly(AGE/IDA-co-DMAA)-grafted is more coarse and grooved [Fig. 3(b)] in comparison with the plain grafted silica gel surface. The porosity of silica seems to be unchanged by grafting.

Metal sorption

The metal sorption by grafted silica at different pH values was determined using batch equilibration technique. The optimum pH range for the sorption of the metal ion is shown in Figure 4. The maximum recovery was 95.4% at pH 5.5.

The equilibrium sorption capacity increased with increasing Cu(II) concentration and was only slightly dependent on temperature in the range 20–40°C (Fig. 5) of sorbent after 15 cycles of its equilibration with Cu(II), changes less than 10% after 15 cycles of equilibration with Cu(II) regeneration with 0.5M HNO₃. The sorption capacity of the sorbent stored for more than 6 month under ambient conditions has been found to be practically unchanged.

The profile of copper uptake on this sorbent reflects good accessibility of the chelating sites in the poly(AGE/IDA-co-DMAA)-grafted silica gel (Fig. 6). Equilibrium sorption was achieved within less than 10 min.

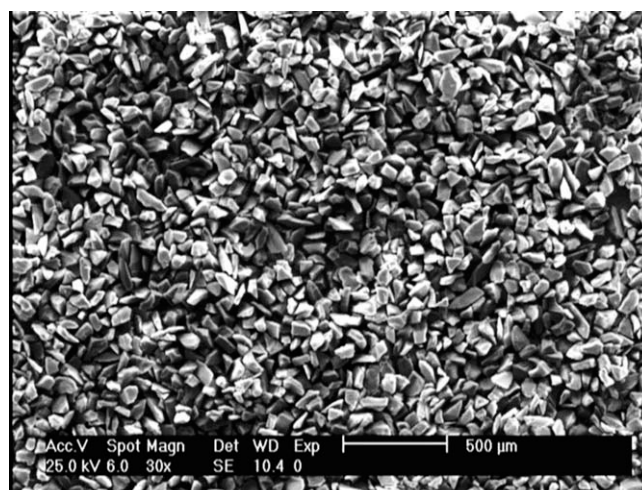
Adsorption isotherms

The Langmuir equation was given in the following form²⁰:

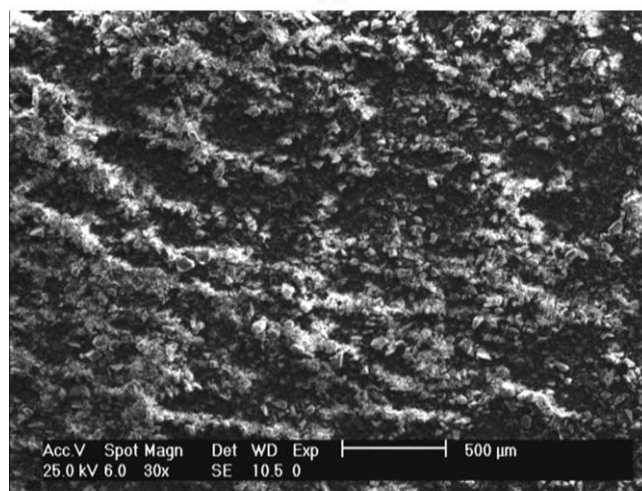
$$q_e = q_{\max} \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad (2)$$

where q_{\max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g⁻¹) and K_L is the Langmuir constant (L mg⁻¹). Equation (2) can be rearranged to a linear form:

$$C_e/q_e = (1/q_{\max} \cdot K_L) + (C_e/q_{\max}) \quad (3)$$



(a)



(b)

Figure 3 SEM photograph of silica gel (a) and poly(AGE/IDA-co-DMAA)-grafted silica gel (b).

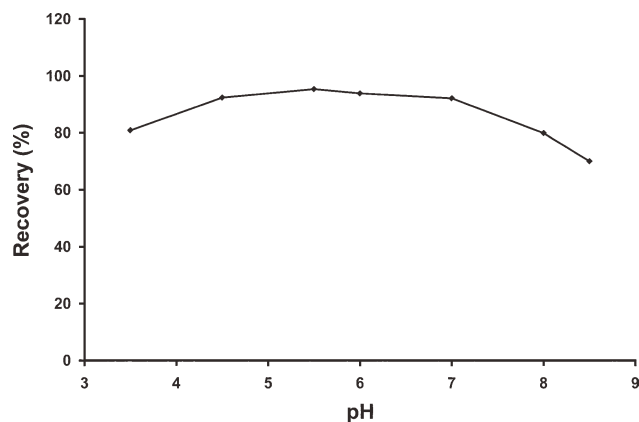


Figure 4 Effect of pH on the sorption of Cu(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel.

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Fig. 7).

Fitting the experimental data into Langmuir isotherm model indicates the homogeneous nature of binding sites of poly(AGE/IDA-co-DMAA)-grafted silica. Langmuir parameters calculated from eq. (3) are listed in Table I.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L , defined as²¹:

$$R_L = 1/(1 + K_L \cdot C_0) \quad (4)$$

Table I shows that the values of R_L (0.131–0.194) are in the range of 0–1 indicating the favorable uptake of the Cu(II) (Table II).

The Freundlich equation is an empirical equation describing heterogeneous systems, using the heterogeneity factor $1/n$. Hence, the empirical equation can be written as²²:

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

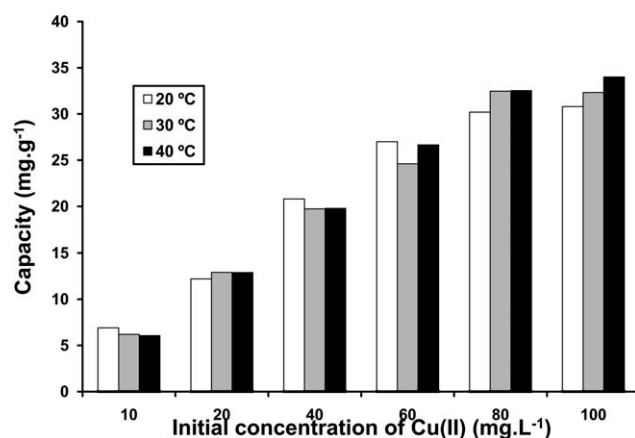


Figure 5 Effect of initial concentration of the Cu(II) and temperature on sorption capacity.

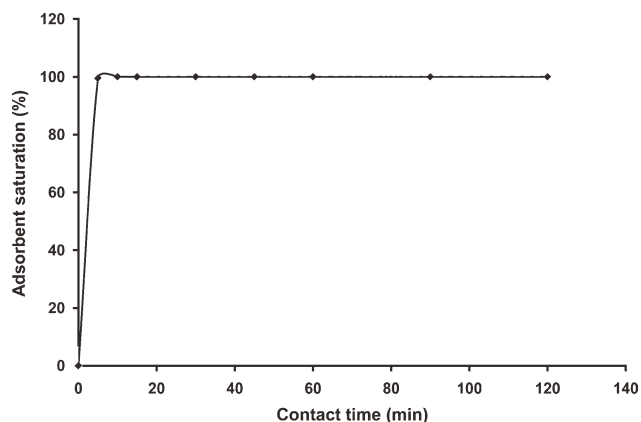


Figure 6 Kinetics of Cu(II) sorption on poly(AGE/IDA-co-DMAA)-grafted silica gel.

where K_F is the Freundlich constant (mg g^{-1}) (L mg^{-1}) and $1/n$ is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the eq. (5):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (6)$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ (Fig. 8) allows K_F and $1/n$ to be determined. The Freundlich equation predicts that the Cu(II) concentration on the adsorbent will increase as long as there is an increase in the Cu(II) concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (7)$$

and can be linearized:

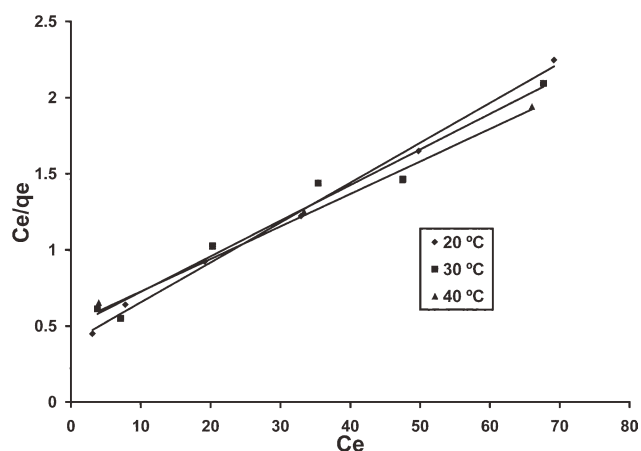


Figure 7 Langmuir isotherm for Cu(II) sorption on poly(AGE/IDA-co-DMAA)-grafted silica gel at different temperatures.

TABLE I
Isotherm Parameters

Langmuir isotherm model				
Temperature	q_{\max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R_L	R^2
20°C	38.2	0.0665	0.131	0.9963
30°C	42.7	0.0478	0.173	0.9708
40°C	47.0	0.0415	0.194	0.9796
Freundlich isotherm model				
Temperature	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	n		R^2
20°C	4.26	1.996		0.9370
30°C	3.57	1.816		0.9509
40°C	3.30	1.708		0.9535
Temkin isotherm model				
Temperature	A (L g ⁻¹)	B (J mol ⁻¹)	b (J mol ⁻¹)	R^2
20°C	0.666	8.34	292	0.9855
30°C	0.513	9.19	274	0.9675
40°C	0.461	9.96	261	0.9826
Redlich–Peterson isotherm model				
G	B (dm ³ mg ⁻¹) ^g	A (dm ³ g ⁻¹)		R^2
1.02	0.045	2.1		0.9394

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where $B = RT/b$ and b is the Temkin constant related to heat of sorption (J mol⁻¹). A is the Temkin isotherm constant (L g⁻¹), R the gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K). Therefore, plotting q_e versus $\ln C_e$ (Fig. 9) enables one to determine the constants A and B . Temkin parameters calculated from eqs. (7) and (8) are listed in Table I.

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm is characterized by a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (9)$$

It has three isotherm constants, namely, A , B , and g ($0 < g < 1$), which characterize the isotherm. The limiting behavior can be summarized as follows: where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \quad (10)$$

i.e., the Langmuir form results.

TABLE II
The R_L Parameter Indicating the Binding Type

Value of R_L	Binding type
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

where constants A and B are much greater than unity²³:

$$q_e = \frac{A}{BC_e^{g-1}} \quad (11)$$

i.e., the Freundlich form results. where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \quad (12)$$

i.e., the Henry's Law form results.

Equation (9) can be converted to a linear form by taking logarithms:

$$\ln\left(\frac{AC_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \quad (13)$$

Three isotherm constants, A , B , and g can be evaluated from the linear plot represented by eq. (13)

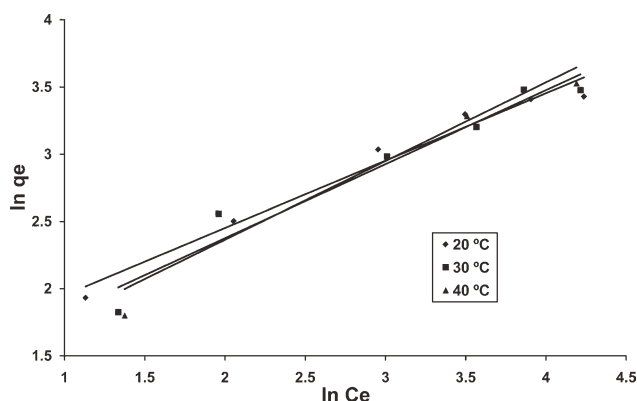


Figure 8 Freundlich isotherm for Cu(II) sorption on poly(AGE/IDA-co-DMAA)-grafted silica gel at different temperatures.

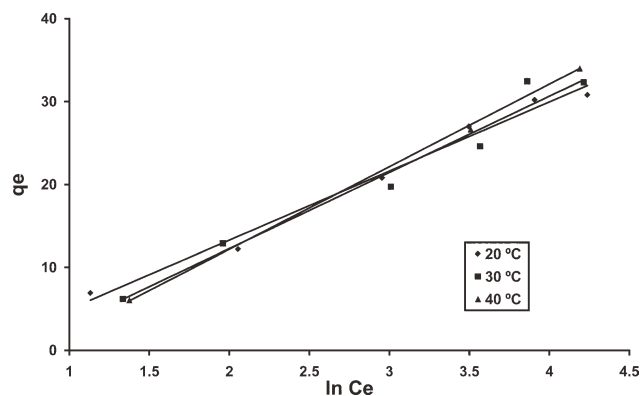


Figure 9 Temkin isotherm for Cu(II) sorption on poly(AGE/IDA-co-DMAA)-grafted silica gel at different temperatures.

using computer best-fit procedure maximizing the coefficient of determination, R^2 , for a series of values of A for linear regression of $\ln(Ce)$ on $\ln[A(Ce/qe)-1]$ and to obtain the best value of A which yields a maximum “optimized” value of R^2 using the solver add-in (Microsoft Excel). The results are presented in Table I.

The coefficient of determination for Langmuir model is higher than for the other models. The g values of Freundlich model are close to unity, indicating that the experimental isotherms are approaching the Langmuir form and rather than the Freundlich form of the isotherm. Thus, Langmuir isotherm is a best-fit for the equilibrium data for adsorption of Cu(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel.

Thermodynamic studies

The thermodynamic parameters such as standard free energy of adsorption (ΔG_a^0), enthalpy of adsorption (ΔH_a^0), and entropy of adsorption (ΔS_a^0) were determined by using the following equations:

$$\Delta G_a^0 = -RT \ln K_L \quad (14)$$

$$\ln K_L = \frac{\Delta S_a^0}{R} - \frac{\Delta H_a^0}{RT} \quad (15)$$

where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant, T (K) the absolute temperature, and K_L (L mg^{-1}) is the

TABLE III
Thermodynamic Parameters of Cu(II) Adsorption on Poly(AGE/IDA-co-DMAA)-Grafted Silica Gel

Temperature (°C)	Thermodynamic parameters		
	ΔG_a^0 (kJ mol ⁻¹)	ΔH_a^0 (kJ mol ⁻¹)	ΔS_a^0 (J mol ⁻¹ K ⁻¹)
20	-0.184	-29.5	-122
30	-0.110		
40	-0.091		

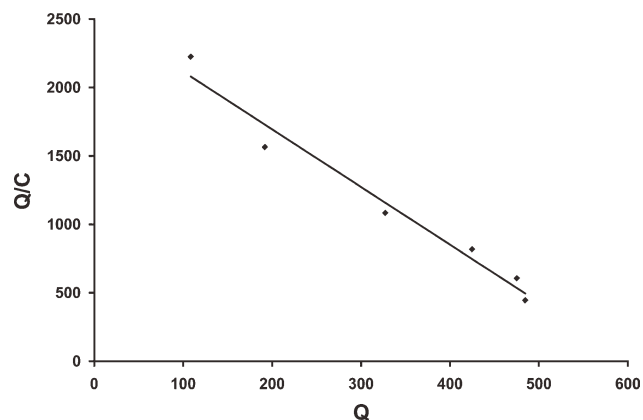


Figure 10 Scatchard plots for Cu(II) sorption onto poly(AGE/IDA-co-DMAA)-grafted silica gel at 20°C.

Langmuir thermodynamic constant. By plotting a graph of $\ln K_L$ versus $1/T$ (figure not shown), the values ΔH_a^0 and ΔS_a^0 can be estimated from the slopes and intercepts. The negative values of ΔG_a^0 and ΔH_a^0 in Table III indicated that the Cu(II) adsorption process is spontaneous and exothermic.

Scatchard analysis

Scatchard analysis was employed to further analyze the binding isotherms, which is an approximate model commonly used in solid phase extraction (SPE) characterization. The Scatchard equation can be expressed as, $Q/C = (Q_{\max} - Q)/K_d$, where C ($\mu\text{mol mL}^{-1}$) is the equilibrium Cu(II) concentration; Q ($\mu\text{mol g}^{-1}$) is the equilibrium adsorption amount at each concentration; Q_{\max} ($\mu\text{mol g}^{-1}$) is the maximum adsorption amount; and K_d ($\mu\text{mol mL}^{-1}$) is the equilibrium dissociation constant at binding sites. Figure 10 shows the Scatchard plots of Cu(II) binding to the

TABLE IV
Effect of Other Ions on Sorption Cu(II) by Poly(AGE/IDA-co-DMAA)-Grafted Silica Gel

Interfering	A	L (%)	E (%)	D
-	7.00	0.00	35.0	0.538
Hg (II)	7.00	0.00	35.0	0.538
Ni (II)	7.00	0.00	35.0	0.538
Ba (II)	7.00	0.00	35.0	0.538
Zn (II)	6.40	8.57	32.0	0.470
Ag (I)	6.90	1.42	34.5	0.527
Co (II)	7.00	0.00	35.0	0.538
K (I)	7.00	0.00	35.0	0.538
Na (I)	7.00	0.00	35.0	0.538
Al (III)	6.60	5.71	33.0	0.492
Mg (II)	7.00	0.00	35.0	0.538
Pb (II)	6.98	0.28	34.9	0.536
Sm (III)	7.00	0.00	35.0	0.538
Mixed above ions	6.50	7.14	32.5	0.481

A : Amount of adsorbed Cu(II) (mg L^{-1}), L : Loss adsorption (%), E : extraction percentage (%), and D : distribution ratio.

TABLE V
Recovery, Preconcentration Factor, and Capacities of the Sorbents Described in the Literature

Sorbent used	R	P	C	D	T	Ref.
2,2-bipyridyl and erythrosine	94–98	50	–	10.3	FAAS	24
Manganese dioxide	96–105	80	–	5	FAAS	25
Cerium(IV) hydroxide	95	–	–	1.8	FAAS	26
Erbium hydroxide	95	25	–	0.11	FAAS	27
Indium hydroxide	94–103	–	–	0.6	FAAS	28
Modified silica gel with aminothioamidoanthraquinone	105	–	–	1	FAAS	29
Gallic acid-modified silica gel	98.6	200	15.38	0.65	FAAS	30
Benzothiazole-based chelating	74	20	–	18	FAAS	31
Chromosorb-102	95	–	–	0.44	FAAS	32
Metal alkoxide glass immobilized 8-quinolinol	99	–	–	0.05	ICP/MS	33
Activated carbon	101	–	–	0.02	CPI-MIP-AES 34	
Diaion SP-850 resin	95	–	–	0.47	FAAS	35
5-Formyl-3-(1V-carboxyphenylazo) salicylic acid-bonded silica gel	98	–	–	0.07–14	FAAS	36
Poly(AGE/IDA-co-DMAA)- grafted silica gel (Our sorbent)	95.4	10	32.32	3.7	FAAS	–

R: recovery(%), P: preconcentration factor, C: capacity (mg g⁻¹), D: detection limit (µg L⁻¹), T: technique.

ICP/MS: inductively coupled plasma mass spectrometry

CPI-MIP-AES: continuous powder introduction microwave-induced plasma atomic emission spectrometry

sorbent. It is clear that the Scatchard plot for the sorbent is a single straight line. The linear regression equation was $Q/C = -4.212Q + 2537.4$ ($R^2 = 0.9702$), suggesting that the homogeneous recognition sites for Cu(II) were formed. From the slope ($-4.212 (1/K_d)$) and intercept ($2537.4 (Q_{max}/K_d)$), K_d and Q_{max} for the affinity binding sites were calculated as $0.2374 \mu\text{mol mL}^{-1}$ and $602.4 \mu\text{mol g}^{-1}$, respectively.

Effect of foreign ions

In order to evaluate the selectivity of the preconcentration system, the effect of some metal ions (20 mg L^{-1}) on the sorption behavior of Cu(II) ion (20 mg L^{-1}) was investigated. The extraction percentage ($E\%$) and the distribution ratio (D) were calculated from the following equations:

$$Q = (C_0 - C_e)V/W \quad (16)$$

$$E = (C_0 - C_e)/C_0 \quad (17)$$

$$D = Q/C_e \quad (18)$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e are initial and equilibrium concentration of Cu(II) ($\mu\text{g mL}^{-1}$), W is the mass of the sorbent (g), V is the volume of metal ion solution (L), E (%) is the extraction percentage, and D is the distribution ratio (mL g^{-1}). The most effective ions affecting adsorption of Cu(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel are Zn(II) and Al(III) (Table IV). The effects of other tested foreign ions at given concentrations is negligible. The efficient adsorption of Cu(II) on the poly(AGE/IDA-co-

DMAA)-grafted silica gel even in the presence of tested ions shows that the Cu(II) can be determined quantitatively in the environmental samples. Comparison with the methods of Cu(II) preconcentration described in the literature indicates that the developed method is characterized by a very high sorption capacity (Table V).

Determination of Cu(II) in an environmental sample

Poly(AGE/IDA-co-DMAA)-grafted silica gel was used to preconcentrate and determine Cu(II) ions in water from the Persian Gulf (Boshehr, Nuclear Power Plant, Iran) using FAAS. Since no Cu(II) was detected in the water sample, 100 mL water sample was spiked with 0.02 and 0.04 mg of Cu(II) before subjecting it to the developed procedure. The results (Table VI) demonstrate the applicability of the procedure for copper determination in samples with high recovery (>91%).

TABLE VI
Cu(II) Determination in The Persian Gulf water

	Sample (I)	Sample (II)
Found (without spiking of Cu(II))	N.D.	N.D.
Spiked Cu(II) ($\mu\text{g mL}^{-1}$)	0.2	0.4
Found Cu(II), after preconcentration ($\mu\text{g mL}^{-1}$)	1.83	3.70
Preconcentration factor	10	10
Recovery (%)	91.5	92.5
Standard deviation	0.091	0.180
Relative standard deviation (%) ^a	4.95	4.86

^a Calculated for three determinations.

TABLE VII
Cu(II) in Water Samples Stored in Contact with Copper

Temperature (°C)	Time (min)	Preconcentration factor	Cu(II) ($\mu\text{g L}^{-1}$) ^a
50	60	10	31 ± 8
100	20	10	56 ± 7
100	30	10	59 ± 8
100	60	10	123 ± 6

^a Calculated for three determinations.

In many countries copper dishes, utensils, and vessels are used to cook and store food. The copper is released into the food and supply the daily copper which is needed for the body. In this investigation, one liter of deionized water was poured in copper dishes in different times and temperatures and amount of copper ion in the water was determined by the developed procedure (Table VII).

Analytical performance of the proposed system

Seven replicate determinations of 0.6 mg L^{-1} Cu(II) solutions gave a relative standard deviation of 3.1%. The limit of detection corresponding to three times the blank standard deviation was found to be $4 \mu\text{g L}^{-1}$. The limit of quantification corresponding to ten times the blank standard deviation was found to be $12 \mu\text{g L}^{-1}$. The regression equation (after preconcentration) was $A = 0.0510C_{\text{Cu}} + 3 \times 10^{-4}$ ($R^2 = 0.9999$), and the conventional regression equation was $A = 0.0235C_{\text{Cu}} + 1 \times 10^{-4}$ ($R^2 = 0.9986$). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 2.2. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10.

CONCLUSION

A method for the free-radical graft polymerization of DMAA-AGE/IDA on to silica has been developed resulting in the sorbent having good potential for enrichment of trace amount of Cu(II) from large sample volumes. The sorbent has also an advantage of fast Cu(II) capture, high adsorption capacity, good reusability, and high chemical stability. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 38.2, 42.7, and 47.0 (mg g^{-1}) at 20, 30, and 40°C, respectively. The R_L values showed that the poly(AGE/IDA-co-DMAA)-grafted silica gel was favorable for the adsorption of Cu(II). Preconcentration using the developed sorbent in combination with flame atomic absorption spectrometry was successfully applied for the determination of trace Cu(II) ions in sea water and potable water stored in contact with copper.

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