Grafting of poly[1-(N,N-*bis*-carboxymethyl)amino-3-allylglycerol-*co*-dimethylacrylamide] copolymer onto siliceous support for preconcentration and determination of lead (II) in human plasma and environmental samples

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ABSTRACT

A method is reported for surface grafting of polymer containing a functional monomer for metal chelating, poly[1-(N,N-*bis*-carboxymethyl)amino-3-allylglycerol-*co*-dimethylacrylamide] (poly(AGE/IDA-*co*-DMAA) onto silica modified by silylation with 3-mercaptopropyltrimethoxysilane. Monomer 1-(N,N-*bis*-carboxymethyl)amino-3-allylglycerol (AGE/IDA) was synthesized by reaction of allyl glycidyl ether with iminodiacetic acid. The resulting sorbent has been characterized using FT-IR, elemental analysis, thermogravimetric analysis (TGA), FT-Raman and scanning electron microscopy (SEM) and evaluated for the preconcentration and determination of trace Pb(II) in human biological fluid and environmental water samples. The optimum pH value for sorption of the metal ion was 5.5. The sorption capacity of functionalized resin was $15.06\,\mathrm{mg\,g^{-1}}$. The chelating sorbent can be reused for 15 cycles of sorption–desorption without any significant change in sorption capacity. A recovery of 96.2% was obtained for the metal ion with 0.5 M nitric acid as eluting agent. The profile of lead uptake by the sorbent reflects good accessibility of the chelating sites in the poly(AGE/IDA-*co*-DMAA)-grafted silica gel. Scatchard analysis revealed that the homogeneous binding sites were formed in the polymers. The equilibrium adsorption data of Pb(II) by modified resin were analyzed by Langmuir, Freundlich, Temkin and Redlich–Peterson models. On the basis of equilibrium adsorption data the Langmuir, Freundlich and Temkin constants were determined as 0.70, 1.35 and 2.7, respectively at pH 5.5 and $20\,^{\circ}\mathrm{C}$. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption.

1. Introduction

Recently, heavy metals pollution in natural water has received increasing attention. The toxic heavy metals could gradually accumulate in human body through the food chain and cause damage to human health. Lead accumulates in the skeleton, especially in bone marrow. It is a neurotoxin and causes behavioural abnormalities, retarding intelligence and mental development, interfering with the metabolism of calcium and vitamin D and affecting hemoglobin formation that results in anaemia. Toxic heavy metals such as Pb, Cd, Hg are causing ecological risk to aquatic organism [1,2]. Thus, accurate determination of heavy metals has become increasingly necessary to study the problems connected with environmental water pollution.

However, the direct determination of these elements in real samples is difficult. The main restrictions come from the complexity of the matrix and the extremely low concentrations of analytes in the samples, with concentrations often below the detection limit of available techniques. Thus, highly sensitive and selective techniques are required. Although the assay of trace elements by instrumental techniques like inductively coupled plasma mass spectrometry and graphite furnace atomic absorption spectrometry is possible, flame atomic absorption spectrometry [3,4] is preferred owing to their cost efficiency and simplicity. However, the determinations of elements at $\mu\mathrm{g\,L^{-1}}$ concentration level by flame atomic absorption spectrometry are not possible. To solve this problem, preconcentration–separation procedures have been proposed. Preconcentration is a very important issue for the achievement of low detection limits [5–7]. There are many methods of preconcentration and separation such as liquid–liquid extraction [8] ion exchange techniques [9], coprecipitation [10,11], membrane filter techniques [12], cloud point extraction [13,14].

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Surface modification by grafting polymer chains to solid substrates is a useful method for the creation of materials which possess specific surface and structural properties and could be used for preconcentration of trace metals. Polymer grafting is a process of attaching living polymer chains to reactive sites on polymers or other surfaces [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. Applications of polymer-grafted substrates include filler-polymer control in polymer composites [16], producing adsorbents for liquid and gas chromatography [17–19], development of biocompatible surfaces [20], making suspensions with high colloid stability [21,22], and modifying inorganic membranes [23,24]. In particular, surface-grafted water-soluble polymers, which are used in this work, have been investigated as chromatographic resins [25–28].

In this work, 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 (AGE/IDA) onto silica surface modified with (3-mercaptopropyl)trimethoxy silane (MPTMS) is reported. The purpose of the present study is to indicate the feasibility of using poly(AGE/IDA-co-DMAA)-grafted silica gel as a solid-phase extractant for preconcentration of Pb(II) in biological fluid and environmental water samples. Trace lead can be retained on the surface of poly(AGE/IDA-co-DMAA)-grafted silica gel and then desorbed with 0.5 M nitric acid prior to determination by FAAS.

2. Experimental

2.1. Instruments

Flame atomic absorption spectrometer Varian (Palo Alto, CA, USA) 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 concentration measurements of metal ions. The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland). Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Thermogravimetric analysis (TGA) was carried out by using a TGA-50H (Shimadzu Corporation, Kyoto, Japan). The SEM micrographs were obtained on a SEM-PHILIPS XL30 scanning electron microscopy.

2.2. Reagents and solutions

N,N-Dimethylacrylamide (DMAA), 3-mercaptopropyltrimethoxysilane, and aluminum oxide were from Aldrich (Steinheim, Germany). 2,2′-Azobis (2-methylpropionittrile) was purchased from Acros (New Jersey, USA). 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), iminodiacetic acid, NaOH, HCl, H$_2$SO$_4$, HNO$_3$, NaOH, K$_2$SO$_4$, NaCl, CH$_3$COOH, CH$_3$COONa, NaH$_2$PO$_4$, Na$_2$HPO$_4$, Pb(NO$_3$)$_2$, FeSO$_4$·7H$_2$O, CuSO$_4$·5H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, NiSO$_4$·6H$_2$O, ZnSO$_4$·7H$_2$O, Hg(NO$_3$)$_2$, Al(NO$_3$)$_3$, AgNO$_3$, Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Ba(NO$_3$)$_2$, ethylenediaminetetraacetic acid (EDTA) and C$_2$H$_5$OH 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 Pb(II), was prepared by dissolving appropriate amounts of Pb(NO$_3$)$_2$, in deionized water. To adjust the pH of the solution, 10 mL of 0.1 M acetic acid–acetate buffer (pH 3–6.5) or 0.01 M phosphate buffer (pH 6.5–9) were used wherever suitable.

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

2.3.1. 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 (1 M, 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. The identity of the product 1-(N,N-bis-carboxymethyl)amino-3-allylglycerol-co-dimethylacrylamide was confirmed as the monomer by IR, ^{1}H NMR and ^{13}C NMR.

IR (NaCl, cm^{-1}) 3360 (OH), 1615 (C=C), 1395 (CH$_2$) and 1085 (C–O).

^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.59 (1 H, OH), 3.25–4.17 (5H{2H d, 1H t.t, 2H d}, CH$_2$-O-CH$_2$-CH), 5.03–6.18 (9H {4H s, 2H d, 1H t.t, 2H d}, N(CH$_2$)$_2$, CH$_2$=CH).

^{13}C NMR (300 MHZ, D$_2$O) δ: 49.55 (CH$_2$-OH), 58.10 (O-CH$_2$), 58.16 (CH$_2$-N), 65.80 (CH$_2$-O), 72.03 (N-CH$_2$), 72.58 (N-CH$_2$), 118.90 (CH$_2$), 134.27 (CH), 171.96 (COO) and 173.59 (COO).

2.3.2. Polymer grafting

Two popular methods for graft polymerization onto inorganic oxide supports are free-radical polymerization [19,29] and anionically initiated polymerization [30]. Free-radical graft polymerization onto silica requires modification of the surface by bonding reactive sites, either initiator or reactive functional groups, to the silica. The surface modification can be achieved, for example, with organosilanes [31]. A two-step method was used: The first step was modification of silica with (3-mercaptopropyl) trimethoxy silane (MPTMS) and the next step was grafting the DMAA-AGE/IDA copolymer on the modified silica by mercaptopropyl.

2.3.3. Modification of silica with (3-mercaptopropyl) trimethoxy silane

Before the silylation reaction, the silica particles were cleaned with 1 M HCl; this was followed by immersion in water (for hydrolysis of 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 reaction was carried out in boiling solution for 24 h. The silica particles were washed several times with 1,4-dioxane and dried under vacuum in a desiccator over dry calcium chloride.

2.3.4. Flash chromatography

A column (2.5 cm × 0.9 cm) containing 1.6 g aluminum oxide was used for removing the impurities from 3 mL N,N-dimethylacrylamide (DMAA). These impurities play an inhibiting role in polymerization reaction. This amount of DMAA was applied to the column dropwise and drained by gravity.

2.3.5. Graft polymerization

The free radical graft copolymerization of AGE/IDA and DMAA-onto MPTMS-modified silica particles was carried out in a temperature-controlled reactor with vigorous stirring under a
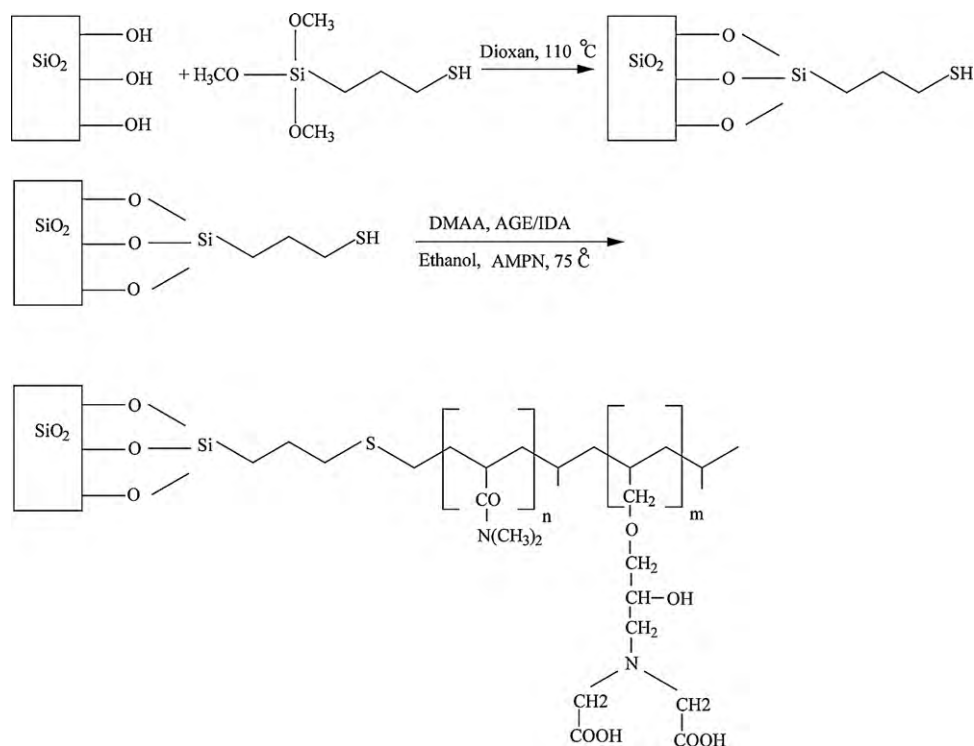
Fig. 1. Schematic presentation of synthesis and grafting process of poly(AGE/IDA-co-DMAA)-grafted silica gel.

nitrogen atmosphere. The nitrogen atmosphere was necessary to exclude oxygen, which promotes the formation of acetaldehyde, a known chain transfer agent [31]. 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 (2methyl-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 the 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 Fig. 1. The grafted silica gel was characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA), FT-Raman and scanning electron microscopy (SEM).

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).

Elemental analysis was carried out according 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 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 DMAA-AGE/IDA-grafted silica gel (found: C, 10.38; H, 3.18; N, 1.62%, calculated for $(SiO_2)_{22}$ $(C_5H_9ON)_n$ $(C_{10}H_{17}O_6N)_m$ on the condition that $m = n = 1$: C, 10.81; H, 1.50; N, 1.68%) show that on an average one DMAA or AGE/IDA molecule is present in each of the 22 repeated units of the polymer.

2.4. Batch method of Pb(II) adsorption

A set of solutions (the volume of each being 100 mL) containing 0.5 µg mL^{-1} of Pb(II) was taken. Their pH values were adjusted between the range 3 and 9 with 0.01 M acetate and/or phosphate buffer solutions. 0.05 g of poly(AGE/IDA-co-DMAA)-grafted silica gel was added to each solution and the mixture was shaken for 4 h. The sorbent was filtered and the adsorbed metal ions were eluted with 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluate was determined by FAAS.

2.5. 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 diluted solutions of Pb(II) (10–100 µg mL^{-1}). The beakers were then sealed and
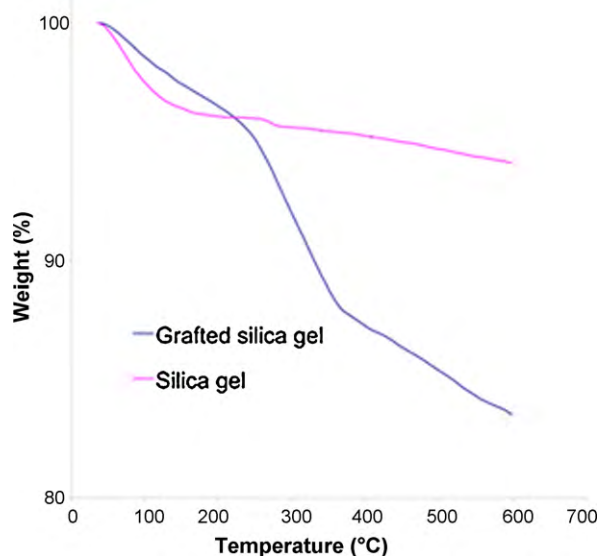

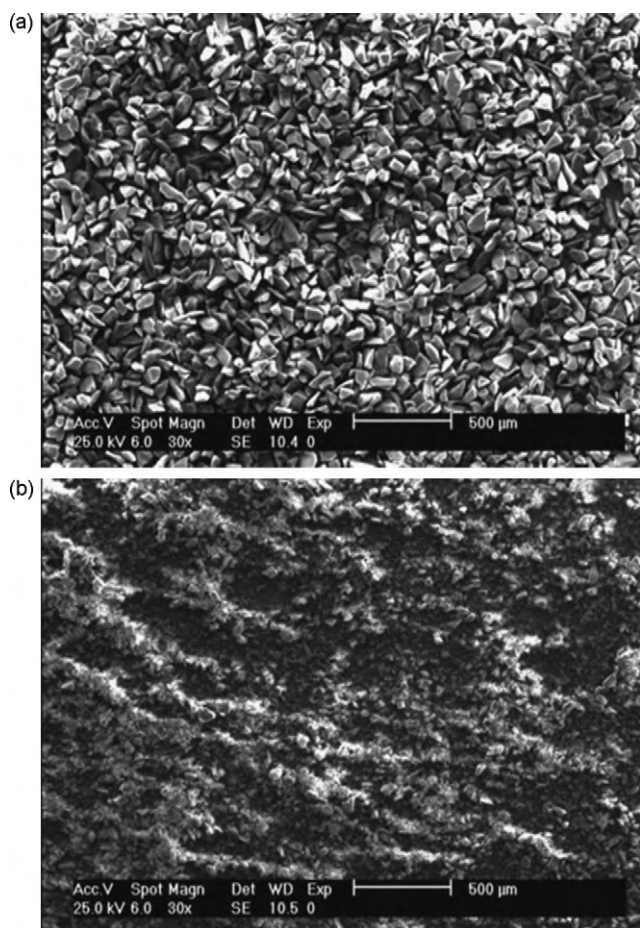**Fig. 2.** Thermogravimetric analysis of silica gel and poly(AGE/IDA-co-DMAA)-grafted silica gel.

(a)

(b)

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

Fig. 4. Effect of pH sorption of Pb(II) onto poly(AGE/IDA-*co*-DMAA)-grafted silica gel.

placed in a water bath shaker for 4 h at pH 5.5 and 20, 30 and 40 °C respectively. pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Pb(II) in the solution was measured by FAAS. The amount of Pb(II) at equilibrium q_e (mg g^{-1}) on poly(AGE/IDA-*co*-DMAA)-grafted silica gel was calculated from the following equation:

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

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

3. Result and discussion

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

The grafted silica gel was characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA), FT-Raman and scanning electron microscopy (SEM). FT-IR confirmed the presence of carbonyl and C–S groups at the surface of the grafted material.

The TGA of unmodified silica gel showed that a weight loss up to 150 °C was due to the desorption of water molecules from the surface and after 200 °C the weight 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
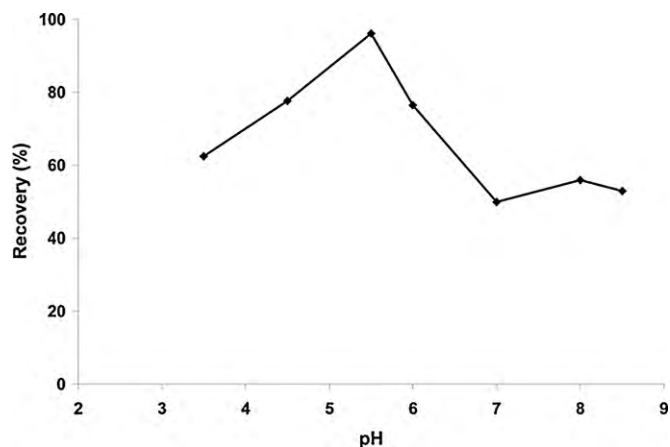
the water molecules in the grafted silica and the weight loss at 200-600 °C was due to the decomposition and desorption of chemically immobilized polymeric matrix (Fig. 2).

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$_2$).

Raman spectrum of poly(AGE/IDA-*co*-DMAA)-grafted silica gel loaded Pb(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*-DMAA)-grafted silica gel-Pb^{2+} respectively. These results demonstrate the amidic and acidic groups on the grafted polymer interact with Pb^{2+} and confirm the formation of poly(AGE/IDA-*co*-DMAA)-grafted silica gel-Pb^{2+} complexes. FT-IR, elemental analysis, thermogravimetric analysis (TGA), and FT-Raman spectroscopy consistently confirmed the structure of the grafted polymer as presented in Fig. 1.

Scanning electron microscopy (SEM) was used to examine the external surface of the silica gel before and after modification. The SEM images are presented in Fig. 3. The surface of ungrafted silica gel has a smooth and highly homogeneous appearance. As shown in Fig. 3a and b, since poly(AGE/IDA-*co*-DMAA)-grafted silica gel has been grafted with polymer chains containing DMAA and AGE/IDA, its surface is more coarse and grooved in comparison with the plain
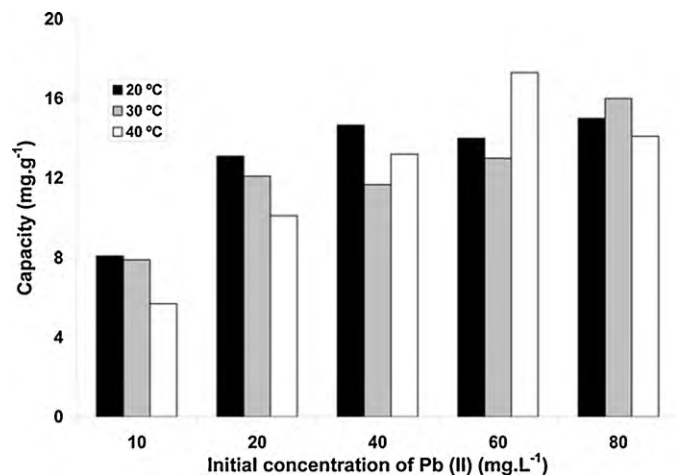

Fig. 5. Effect of initial concentration of the Pb(II) and temperature on sorption capacity.
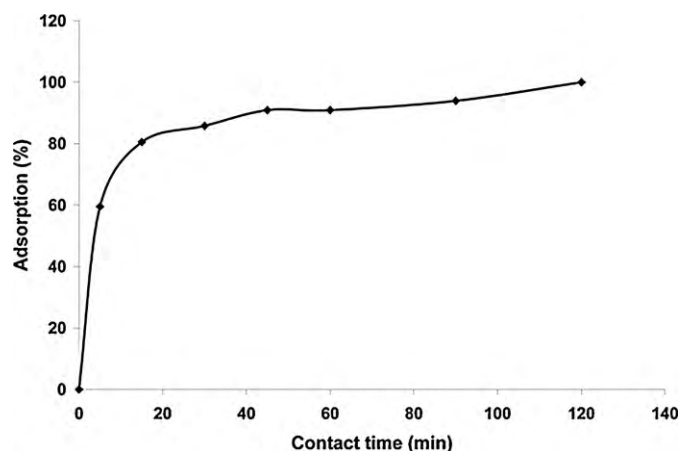
Fig. 6. Kinetics of lead sorption on poly(AGE/IDA-*co*-DMAA)-grafted silica gel.

silica gel surface. The pore sizes as judged by SEM for both silica and grafted silica seem to be similar.

3.2. Pb(II) adsorption

The pH dependence for Pb(II) sorption is shown in Fig. 4 with the maximum recovery of 96% achieved at pH 5.5. The binding capacity of poly(AGE/IDA-*co*-DMAA)-grafted silica gel at optimum pH increased up to about 15 mg g^{-1} with increasing initial Pb(II) concentration (Fig. 5). The sorption as a function of contact time for all the metal ions is presented in Fig. 6. Less than 15 min shaking was required for 80% sorption reflecting good accessibility of the chelating sites in the poly(AGE/IDA-*co*-DMAA)-grafted silica gel. The sorbent was readily regenerated with 0.5 M HNO$_3$ and used repeatedly with sorption capacity after 15 cycles changing less than 10%. The sorption capacity of the resin stored for more than 6 months under ambient conditions was unchanged.

3.3. Adsorption isotherms

Fitting experimental data to the linearized form of Langmuir isotherm $C_e/q_e = (1/q_{max}K_L) + (C_e/q_{max})$ [32], 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}), indicates the homogeneous nature of poly(AGE/IDA-*co*-DMAA)-grafted surface (Fig. 7). Langmuir parameters calculated from mentioned Equation are listed in Table 1.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as [33]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{2}$$

Table 1 shows that the values of R_L (0.018–0.067) are in the range of 0–1 at optimum pH which confirms the favorable uptake of the Pb(II) (Table 2).

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$ with empirical equation written as [34]:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F is the Freundlich constant (mg g^{-1}) (L mg^{-1})$^{1/n}$ and $1/n$ is the heterogeneity factor. A plot of $\ln q_e$ versus $\ln C_e$ (Fig. 8) enables the constant K_F and exponent $1/n$ to be determined.

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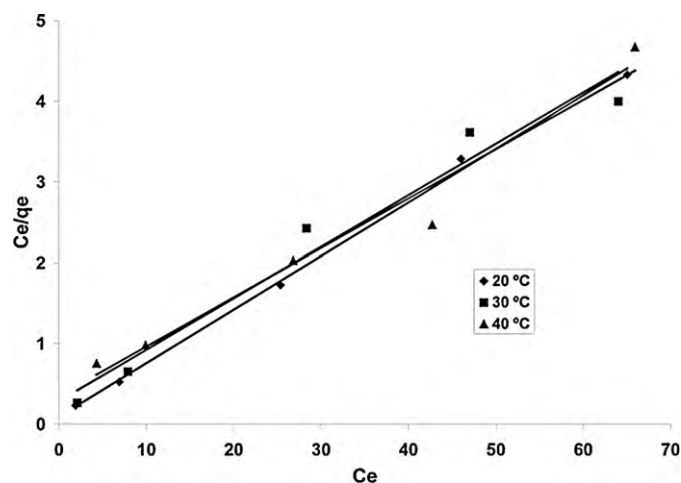

Fig. 7. Langmuir isotherm for Pb(II) adsorption onto poly(AGE/IDA-*co*-DMAA)-grafted silica gel at different temperatures.

Table 1
Isotherm parameters obtained by using linear method.

Langmuir isotherm model				
Temperature	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
20 °C	15.06	0.700	0.018	0.9978
30 °C	15.70	0.221	0.054	0.9650
40 °C	16.34	0.174	0.067	0.9641

Frendlich isotherm model			
Temperature	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	n	R^2
20 °C	1.35	3.34	0.9505
30 °C	5.07	3.37	0.9159
40 °C	3.59	2.76	0.9249

Temkin isotherm model			
Temperature	A (L g^{-1})	B (J mol^{-1})	b (J mol^{-1})	R^2
20 °C	2.73	3.6284	671.7	0.9784
30 °C	2.21	3.5032	719.45	0.9634
40 °C	1.30	3.4272	759.67	0.9462

Redlich–Peterson isotherm model			
g	B (dm^3 mg^{-1})^g	A (dm^3 g^{-1})	R^2
1.01	0.559	9	0.9996

$$q_e = \frac{RT}{b}\ln(AC_e) \tag{4}$$

and can be linearized:

$$q_e = B\ln A + B\ln C_e \tag{5}$$

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 the constants A

Table 2
The parameter R_L indicated the shape of isotherm.

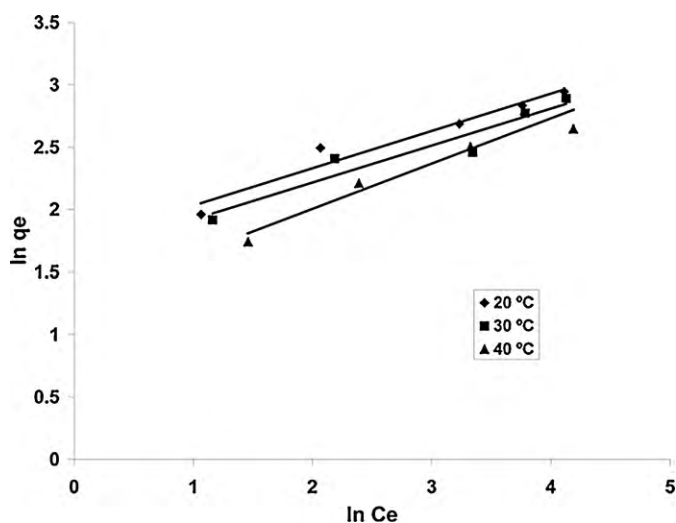| Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
R_L 0	Irreversible

Fig. 8. Freundlich isotherm for Pb(II) adsorption onto poly(AGE/IDA-co-DMAA)-grafted silica gel at different temperatures.

and B. Temkin parameters calculated from Eqs. (4) and (5) are listed in Table 1.

The Redlich–Peterson isotherm contains three parameters and incorporates the features of both the Langmuir (at $g = 1$) and the Freundlich (at $g = 0$) isotherms [35]:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{6}$$

Three isotherm constants, A, B, and g can be evaluated from the linear form (7)

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \tag{7}$$

using best fitting computer calculations (Table 1). The g values were close to unity, indicating that the isotherms are approaching the Langmuir form rather than Freundlich isotherm.

Scatchard analysis was employed to further analyze the binding isotherms, which is an approximate model commonly used in SPE characterization. The Scatchard equation can be expressed as $Q/C = (Q_{max} - Q)/K_d$, where C (μmol mL^{-1}) is the equilibrium concentration of lead, Q (μmol g^{-1}) is the equilibrium adsorption amount at each concentration, Q_{max} (μmol g^{-1}) is the maximum

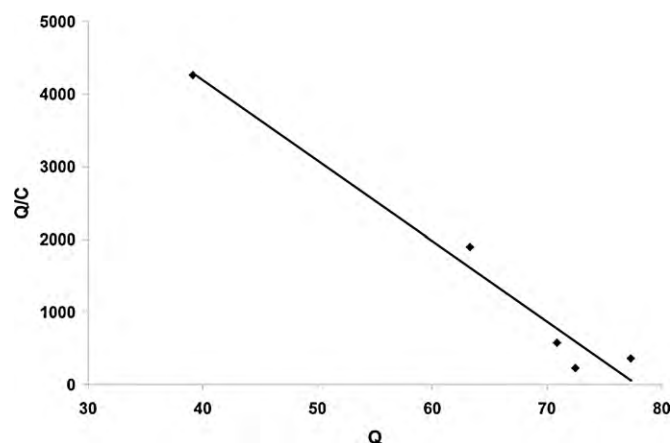Fig. 9. Temkin isotherm for Pb(II) adsorption onto DMAA-AGE/IDA-grafted silica gel at different temperatures.

Fig. 10. Scatchard plots of Pb(II) adsorption onto poly(AGE/IDA-co-DMAA)-grafted silica gel at 20 °C.

adsorption amount and K_d (μmol mL^{-1}) is the equilibrium dissociation constant at binding sites. Fig. 10 shows the Scatchard plots of the binding of lead to the sorbent. It is clear that the Scatchard plot for sorbent is a single straight line with linear regression equation $Q/C = -110.74Q + 8622.1$ ($R^2 = 0.9701$), suggesting that the homogeneous recognition sites for lead were formed in the sorbent. The calculated K_d and Q_{max} were 0.0090 μmol mL^{-1} and 77.86 μmol g^{-1}, respectively.

3.4. Thermodynamic studies

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

$$\Delta G_a^\circ = -RT \ln K_L \tag{8}$$

$$\ln K_L = \frac{\Delta S_a^\circ}{R} - \frac{\Delta H_a^\circ}{RT} \tag{9}$$

where R (8.314 J mol^{-1} K^{-1}) is the gas constant, T (K) the absolute temperature and K_L (L mg^{-1}) is the Langmuir thermodynamic constant. By plotting a graph of $\ln K_L$ versus $1/T$ (figure not shown) the values ΔH_a° and ΔS_a° can be estimated from the slopes and intercepts. The negative values of ΔG_a° and ΔH_a° in Table 3 indicate that the Pb(II) adsorption process is spontaneous and exothermic. The positive value of ΔS° suggests that increased randomness at the solid/solution interface occurs in the internal structure of the adsorption of Pb(II) onto poly(AGE/IDA-co-DMAA)-grafted silica gel.

3.5. 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 Pb(II) ion (20 mg L^{-1}) was investigated. The extraction percentage ($E\%$) and the distribution ratio (D) were calculated from

Table 3
Thermodynamic parameters of Pb(II) adsorption on poly(AGE/IDA-co-DMAA).

Temperature (°C)	Thermodynamic parameters		
	ΔG_a° (kJ mol^{-1})	ΔH_a° (kJ mol^{-1})	ΔS_a° (J mol^{-1} K^{-1})
20	−1.27	−2.1037	11.5
30	−1.39		
40	−1.50		
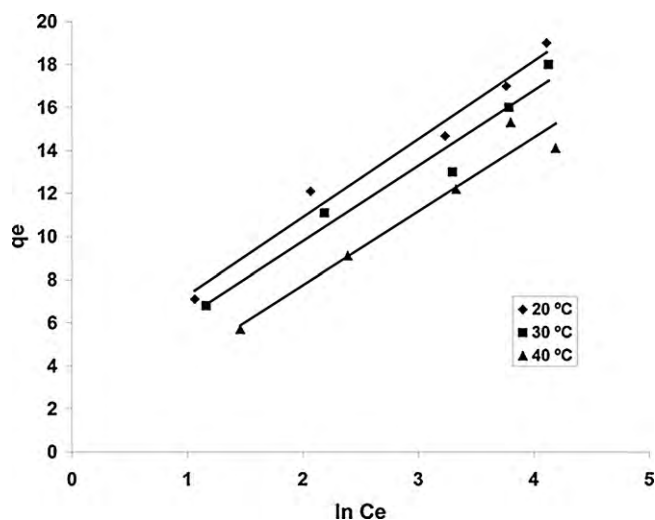
Table 4
Effect of other ions on sorption.

Interfering ion	A	L (%)	E (%)	D
–	12.62	0	63.1	1.71
Ca(II)	12	4.9	60	1.5
Hg(II)	11.10	12	55.5	1.25
Ni(II)	12.62	0	63.1	1.71
Ba(II)	12.15	3.7	60.7	1.55
Zn(II)	11.15	11.6	55.7	1.26
Fe(II)	11.3	11.8	55.65	1.25
Cu(II)	12.62	0	63.1	1.71
Ag(I)	11.0	12.8	55	1.22
Co(II)	11.98	5.1	59.9	1.49
Na(I)	12.62	0	63.1	1.71
K(I)	12.60	0.2	63.0	1.70
Al(III)	11.2	11.3	56.0	1.27
Mg(II)	11.97	5.2	59.8	1.49
Mixed above ions	9.63	23.7	48.15	0.93

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

the following equations:

$$Q = (C_0 - C_e)\frac{V}{W} \quad (10)$$

$$E = \frac{C_0 - C_e}{C_0} \quad (11)$$

$$D = \frac{Q}{C_e} \quad (12)$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e represent the initial and equilibrium concentration of Pb(II) (µg mL^{-1}), W is the mass 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 result was shown in Table 4. This table indicates the most effective ions on adsorption of Pb(II) on poly(AGE/IDA-co-DMAA)-grafted silica gel are Ag(I), Zn(II), Al(III), Hg(II) and Fe(II). The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Pb(II) on the poly(AGE/IDA-co-DMAA)-grafted silica gel in presence of all mentioned ions (with

each ion having the concentration of 20 mg L^{-1}) shows that the Pb(II) can be determined quantitatively in the environmental samples.

3.6. Application of method

Comparative information from the studies on Pb(II) preconcentration by various methods is presented in Table 5. The sorption capacity and recovery of the developed adsorbent is superior in comparison to all the matrices shown in Table 5.

Poly(AGE/IDA-co-DMAA)-grafted silica gel was used to preconcentrate and determine Pb(II) ions in water from Anzali marsh, Gilan state, Iran. The pH of water sample was adjusted to the optimum pH. Solid phase extraction with poly(AGE/IDA-co-DMAA)-grafted silica gel coupled with FAAS was applied to determine of the Pb(II) in water sample. Since no Pb(II) was detected in the water sample, 100 mL water sample was spiked with 0.02 and 0.04 mg of Pb(II) before subjecting it to the recommended procedure. The results shown in Table 6 demonstrate the applicability of the procedure for lead determination with high recovery (>94%). Well water (Pishva, Varamin, Iran) also was examined to preconcentrate and determine Pb(II) ions with proposed method. Table 6 shows that the method can be successfully applied for determination of lead ions in environmental water sample.

Adsorption of Pb(II) ions on the poly(AGE/IDA-co-DMAA)-grafted silica gel from human serum was studied in a batch-wise mode. Human blood was collected from thoroughly controlled voluntary blood donors. Each blood-containing unit was separately controlled and found negative for HBS antigen and HIV I, II and hepatitis C antibodies. No preservatives were added to the blood samples. Human blood was collected into EDTA containing vacutainers and red blood cells were separated from the plasma by centrifugation at 4000 × g for 30 min at room temperature, then filtered (3 µm Sartorius filter) and frozen at −20 °C. Before use, the plasma was thawed for 1 h at 37 °C. After no Pb(II) was detected in the plasma, 25 mL plasma was spiked with 0.01 mg of Pb(II) before subjecting it to the recommended procedure. Then 25 mL of human

Table 5
Comparison of recovery, preconcentration and capacities with some literatures.

Resin used	Recovery (%)	Preconcentration factor	Capacity (mg g^{-1})	Reference
Amberlite XAD-2 functionalized with o-aminophenol	91	40	3.32	[36]
Microcrystalline triphenylmethane loaded with quinolin-8-olate	98	100	–	[37]
Gallic acid-modified silica gel	96	25	12.6	[38]
Cellulose modified with triethylenetetramine	–	–	192	[39]
Sugarcane bagasse chemically modified with succinic anhydride	–	–	83.3	[40]
Chitosan modified ordered mesoporous silica	95	–	22.9	[1]
Macroporous epoxy resin-based polymer monolithic matrix	97	10	107	[41]
Thioureasulfonamide resin	97	20	0.5	[42]
Dibenzyldithiocarbamate chelates on Dowex Optipore V-493	96	4-8	8.6	[43]
Amberlite XAD-2 with chromotropic acid	97	4-10	186	[44]
Amberlite XAD-2 with pyrocatechol	94	4-10	105	[44]
Amberlite XAD-2 with thiosalicylic acid	93	4-10	89.3	[44]
Amberlite XAD-7 with xylenol orange	91	4-10	16.9	[44]
DMAA-AGE/IDA-grafted silica gel (Our resin)	96	10	15.1	–

Table 6
Results obtained for Pb(II) determination in plasma, sea water sample of (I) and (II) and well water sample (III) and (IV).

	plasma	(I)	(II)	(III)	(IV)
Found (without spiking of Pb(II)) (µg mL^{-1})	N.D.	N.D.	N.D.	0.06	0.06
Added Pb(II) (µg mL^{-1})	0.4	0.2	0.4	–	0.1
Found Pb(II), after preconcentration (µg mL^{-1})	0.97	1.94	3.79	0.57	1.54
Preconcentration factor	2.5	10	10	10	10
Recovery (%)	97	97	94	95	96
Standard deviation	0.046	0.093	0.150	0.028	0.071
Relative standard deviation (%)[a]	4.7	4.8	4.0	4.9	4.5

[a] For three determinations.

serum containing $0.4\,\mu g\,mL^{-1}$ of Pb(II) ions was treated with 0.1 g of poly(AGE/IDA-*co*-DMAA)-grafted silica gel at room temperature and magnetically stirred at a speed of 600 rpm. After the desired treatment periods, the sorbent was taken out and adsorbed metal ion was eluted with 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluate was determined by FAAS. The experiments were performed in replicates of three. The results are shown in Table 6 and indicate the suitability of the present sorbent for the preconcentration of lead from plasma samples. The similarity of results obtained by mentioned methods indicates that the reliability of the lead content data presented in Table 6 is reasonable.

3.7. Analytical performance of the proposed system

Seven replicate determinations of $0.6\,mg\,L^{-1}$ lead solutions gave a relative standard deviation of 3.8%. The limit of detection corresponding to three times the blank standard deviation was found to be $3.5\,\mu g\,L^{-1}$. The limit of quantification corresponding to ten times the blank standard deviation was found to be $11.7\,\mu g\,L^{-1}$. The regression equation (after preconcentration) was $A = 0.0139 C_{Pb} + 5 \times 10^{-4}$ ($R^2 = 0.9981$), and the conventional regression equation was $A = 0.0041 C_{Pb} + 9 \times 10^{-6}$ ($R^2 = 0.9980$). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 3.4. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10.

4. Conclusion

A method for the free-radical graft polymerization of AGE/IDA and DMAA-onto silica was described. The resin has a good potential for enrichment of trace amount of Pb(II) from large sample volumes. The resins also present the advantage of high adsorption capacity, good reusability and high chemical stability. On the basis of Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 15.0, 15.7 and 16.3 ($mg\,g^{-1}$) at 20, 30, and $40\,°C$, respectively. Preconcentration by this resin combined with FAAS can be applied to the determination of traces of Pb(II) ions in human plasma and the environmental water samples.

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