Synthesis, Characterization, and Application of Amberlite XAD-2- Salicylic Acid- Iminodiacetic Acid for Lead Removal from Human Plasma and Environmental Samples

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ABSTRACT: A new chelating resin is prepared by coupling Amberlite XAD-2 with salicylic acid (SAL) through an azo spacer. Then the polymer support was coupled with iminodiacetic acid (IDA). The resulting sorbent has been characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) and studied for the preconcentration and determination of trace Pb (II) ion from human biological fluid and environmental water samples. The optimum pH value for sorption of the metal ion was 5. The sorption capacity of functionalized resin is 67 mg g^{-1}. The chelating sorbent can be reused for 20 cycles of sorption–desorption without any significant change in sorption capacity. A recovery of 95% was obtained for the metal ion with 0.5M nitric acid as eluting agent. The profile of lead uptake on this sorbent reflects good accessibility of the chelating sites in the Amberlite XAD-2-SAL/IDA. Scatchard analysis revealed that the homogeneous binding sites were formed in the polymers. The equilibrium adsorption data of Pb (II) on modified resin were analyzed by Langmuir, Freundlich, Temkin, and Redlich-Peterson models. Based on equilibrium adsorption data the Langmuir, Freundlich, and Temkin constants were determined 0.428, 20.99, and 7 × 10^{-12} at pH 5 and 20°C. The method was successfully applied for determination of lead ions in human plasma and sea water sample. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1127–1136, 2011

Key words: solid phase extraction; Amberlite XAD-2; lead; human plasma; isotherm study; preconcentration

INTRODUCTION

Recently, heavy metals pollution in natural water has been receiving tremendous attention. The toxic heavy metals such as Pb, Cd, and Hg are significant elements in human body and are capable of causing ecological risk to aquatic organisms. The toxic heavy metals could also gradually accumulate in human body through food chain and cause damage to human health.[1] Lead accumulates in the skeleton, especially in bone marrow. It is a neurotoxin and causes behavioral abnormalities, retarding intelligence, and mental development. It interferes in the metabolism of calcium and vitamin D and affects hemoglobin formation and causes anemia.[2] In view of the above facts, accurate determination of heavy metals has become increasing necessary to solve the problems connected with environmental water pollution.

However, the direct determination of these elements in real samples is a difficult task. 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. 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 its cheap cost and simplicity. However, the determinations of elements at μg 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 achievement of low detection limits.[5,6] There are many methods of preconcentration and separation such as liquid–liquid extraction,[7] ion exchange techniques,[8] coprecipitation,[9,10] membrane filter techniques,[11] cloud point extraction.[12,13]

Amberlite XAD-2, a polystyrene sorbent has only 4% crosslinking and is reasonably porous. XAD resins as the copolymer backbone for the immobilization of chelating ligands have physical superiorities

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such as porosity, uniform pore size distribution, high surface area, durability, and chemical stability toward acids, bases, and oxidizing agents.

Recently, Amberlite XAD-2 functionalized with chelating ligands has shown good capacity. It therefore was thought worthwhile to immobilize two different chelating ligands on this polymeric support sequentially via two-step procedure. The purpose of present study is to indicate the feasibility of using Amberlite XAD-2- SAL/IDA as a solid-phase extractant for preconcentration of trace lead in biological fluid and environmental water samples. Trace lead can be retained on the surface of Amberlite XAD-2-SAL/IDA and then desorbed with 0.5M nitric acid prior to determination by FAAS. This proposed novel method has advantages of good accuracy and precision, high recovery and preconcentration factor.

EXPERIMENTAL

Instruments

Flame atomic absorption spectrometer of the Varian, AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L min^{-1}, respectively) was 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, Easton, MD) by the potassium bromide pellet method. 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).

Reagents and solutions

SnCl$_2$, HCl, H$_2$SO$_4$, HNO$_3$, NaNO$_2$, NaOH, Cr (NO$_3$)$_3$, Cu (NO$_3$)$_2$, Hg (NO$_3$)$_2$, Cd (NO$_3$)$_2$, Zn (NO$_3$)$_2$, Ba (NO$_3$)$_2$, Ag NO$_3$, K NO$_3$, Al (NO$_3$)$_3$, NaCl, CH3COOH, 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, Ni SO$_4$.6H$_2$O, Zn SO$_4$.7H$_2$O, iminodiacetice acid (IDA), ethanol, ethylenediaminetetraacetic acid (EDTA), thionyl chloride, salicylic acid, CH$_3$COCH$_3$, C$_2$H$_5$OH, Sn powder and brilliant green were products of Merck (Darmstadt, Germany). Amberlite XAD-2resin (surface area 745 m^2 g^{-1}, pore diameter 5 nm, and bead size 20–60 meshes) was obtained from serva (Heidelberg, NY).

All the solutions were prepared in deionized water using analytical grade reagents.

The stock solution (1000 mg L^{-1}) of Pb (II), were prepared by dissolving appropriate amounts of Pb (NO$_3$)$_2$, 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 resin

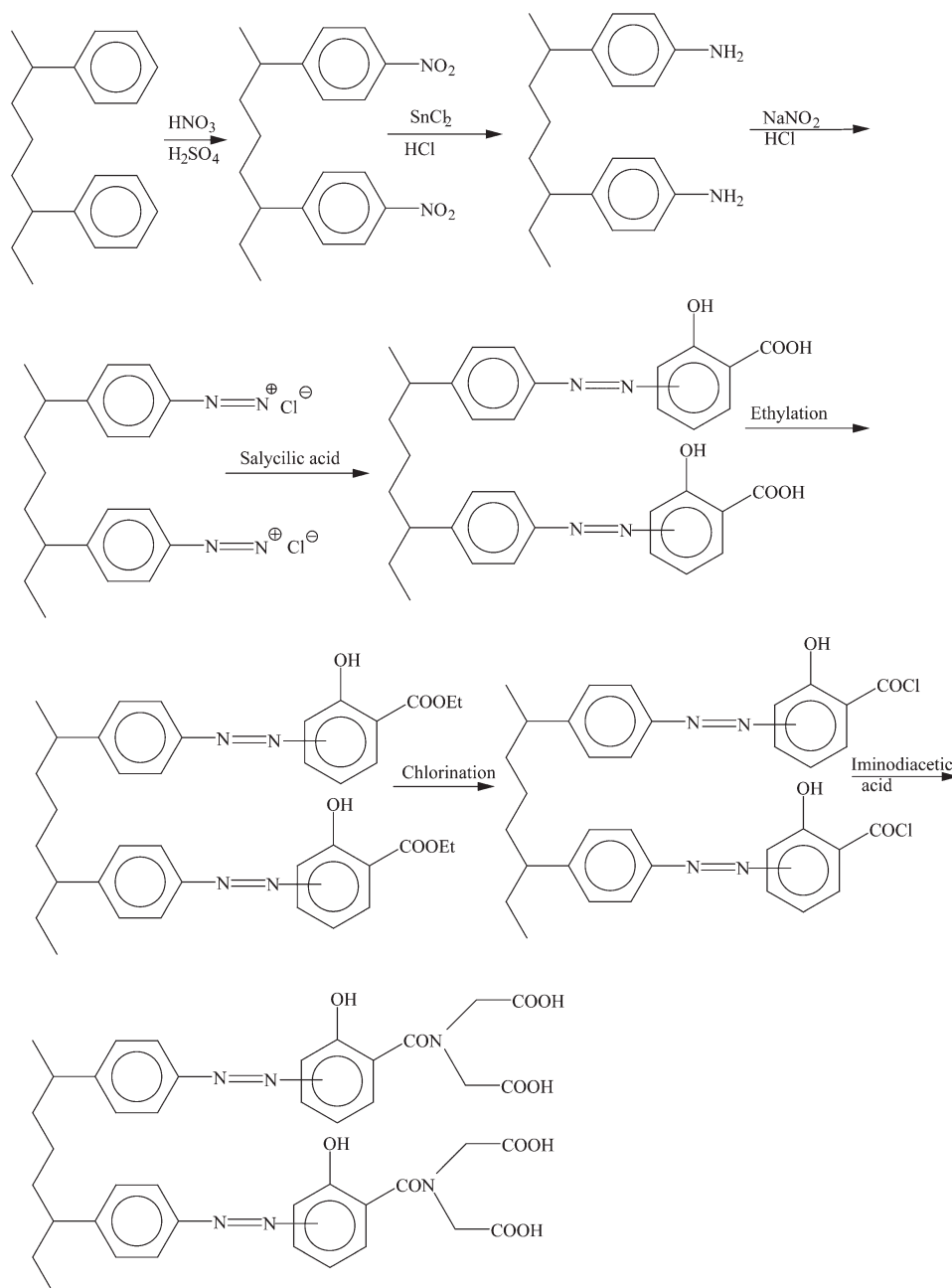### Synthesis of Amberlite XAD-2-[salicylic acid] (Amberlite XAD-2- SAL)

Amberlite XAD-2 bead (5 g) were treated with 10 cm^3 of concentrated HNO$_3$ and 25 cm^3 of concentrated H$_2$SO$_4$ and the mixture was stirred at 60°C for 1 h in an oil bath. Then the reaction mixture was poured into an ice water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid and treated with a reducing mixture of 40 g of SnCl$_2$, 45 cm^3 of concentrated HCl, and 50 cm^3 of ethanol. The mixture was refluxed for 12 h at 90°C. The solid precipitate was filtered and washed with water and 2 mol dm^{-3} NaOH which released amino resin (R-NH$_2$) from (RNH$_3$)$_2$ SnCl$_6$ (R = resin matrix).The amino was first washed with 2 mol dm^{-3} HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice-water mixture (350 cm^3) and treated with 1 mol dm^{-3} HCl and 1 mol dm^{-3} NaNO$_2$ (added in small aliquots of 1 cm^3) until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was filtered, washed with ice-cold water and reacted with salicylic acid (2.5 g in 300 cm^3 of glacial acetic acid and 150 cm^3 of acetone) at 0–3°C for 24 h. The resulting brown-colored beads were filtered and washed with water. The methodology used to synthesize modified XAD-2 resin is summarized in Figure 1.

Synthesis of XAD-2-[ethyl salicylate]

The brown-colored beads from previous section were refluxed with a mixture of dried ethanol (15 mL) and sulfuric acid (5 mL) for 10 h.

Synthesis of XAD-2-[salicyl-iminoiddiacetic acid] (Amberlite XAD-2- SAL/IDA)

A mixture of XAD-2-[ethyl salicylate] and thionyl chloride (10 mL) was gently refluxed for 2 days to precipitate XAD-2[salicyl chloride] in light needles form. The thionyl chloride was distilled off at reduced pressure and the acid chloride was separated via liquid phase extraction and treated with a mixture of iminodiacetic acid (0.01 mol) and NaOH solution (1M) upon cooling. The reaction mixture was stirred in room temperature for 5 h. The product was neutralized with HCl (%10) and washed with water before using as resin. Immobilization was taken via N=N linker and the resulting macromolecular chelator was characterized by IR, elemental

**Figure 1** Schematic presentation of synthesis of Amberlite XAD-2-SAL/IDA.

analyses, and TGA. The resin was dried at 60°C and placed in a desiccator.

Batch method

A sample solution (100 mL) containing (0.5 μg mL^{-1}) of Pb (II) was taken in a glass stopper bottle, and the pH was adjusted to optimum value. The 0.05 g of Amberlite XAD-2-SAL/IDA was added to the bottle and the mixture was shaken for optimum time. The resin was filtered and sorbed metal ion was eluted with 0.5M nitric acid (10 mL). The concentration of the metal ion in the eluant was determined by FAAS.

Isotherm studies

Isotherm studies were carried out by adding a fixed amount of adsorbent (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 placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (4 h) at 20, 30, and 40°C and optimum pH (5). pH adjustments have been done using 0.01M 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
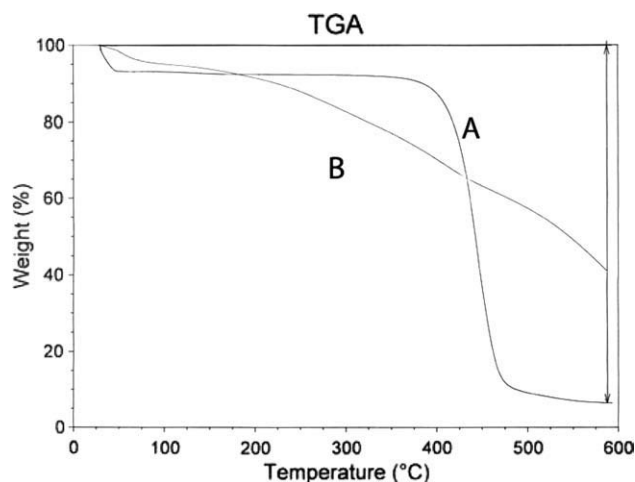
Figure 2 Thermogravimetric analysis of Amberlite XAD-2 (A) and Amberlite XAD-2-SAL/IDA (B).

equilibrium q_e (mg g^{-1}) on Amberlite XAD-2-SAL/IDA was calculated from the following equation:

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

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

RESULTS AND DISCUSSION

Characterization of the resin

IR spectrum

IR spectrum of salicylic acid loaded Amberlite XAD-2 (cm^{-1}): 3433 (OH), 1526 aromatic (C=C), 1607 (N=N), 1701 (C=O), 1209 (C—O), 3027 aromatic (C=H), and 2927 aliphatic (C—H).

   IR spectrum of synthesis of XAD-2-[ethyl salicylate] (cm^{-1}): 3392 (OH), 1620 (N=N), 1715 (C=O), 1092, 1349 (C—O), and 2924 aliphatic (C—H).

   IR spectrum of synthesis of XAD-2-[salicyl-iminoiddiacetic acid] (cm^{-1}): 3443 (OH), 1624 (N=N), 1701 (C=O), 1625 amidic (C=O), 1037 phenolic (C—O), and 2926 aliphatic (C—H).

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 ascer-

tained after drawing the calibration curve for standards and data processing for the sample.

   The elemental analysis for Amberlite XAD-2-SAL (found: C, 69.25; H, 6.15; N: 6.78%, calculated for $(C_8H_7)_2$ C_7H_5 N_2 O_3: C, 74.39; H, 5.12; N, 7.54%) show that on an average one salicylic acid molecule is present in each two repeated unit of the polymer.

   The elemental analysis for Amberlite XAD-2-SAL/IDA (found: C, 59.48; H, 6.25; N: 6.86%, calculated for $[(C_8H_7)_2 (C_7H_4 N_2 O_2)]_1 (C_4 H_6 N O_4)_1$: C, 62.18; H, 4.41; N, 8.06%) show that on an average one iminodiacetic acid molecule is present in each repeated unit of the Amberlite XAD-2-SAL.

Thermal analysis

TGA of the Amberlite XAD-2 shows two-step weight loss up to 600°C. The weight loss up to 100°C was due to the water molecules in the polymer. The major weight loss after 400°C is due to decomposition of the polymer. Amberlite XAD-2-SAL/IDA shows completely different thermal behavior. The weight loss up to 100°C was due to the water molecules in the polymer and the weight loss 200–600 was due to the dissociation of chemically immobilized moiety and the polymeric matrix (Fig. 2).

Scanning electron microscopy

The surface morphology and internal structure of polymer beads are investigated by the scanning electron micrographs which were given in Figure 3. As clearly seen here, Amberlite XAD-2-SAL/IDA is comprised of heterogeneous small particles. The size of the large pores between the clusters in Figure 3 is about 1 μm. These macropores reduce diffusional mass transfer resistance and facilitate convective mass transport because of their spacious internal surface area.

Metal sorption as a function of pH

The degree metal sorption at different pH values was determined by batch equilibration technique. A set of solutions (the volume of each 100 mL) containing 0.5 μg mL^{-1} of Pb (II) was taken. Their pH values were adjusted between the ranges 3–9 with 0.01M acetate and/or phosphate buffer solutions. The 0.05 g of Amberlite XAD-2-SAL/IDA was added to each solution and the mixture was shaken for 4 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Pb (II) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from Amberlite XAD-2-SAL/IDA with 0.5M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Figure 4. The maximum recovery was 95% at pH 5.
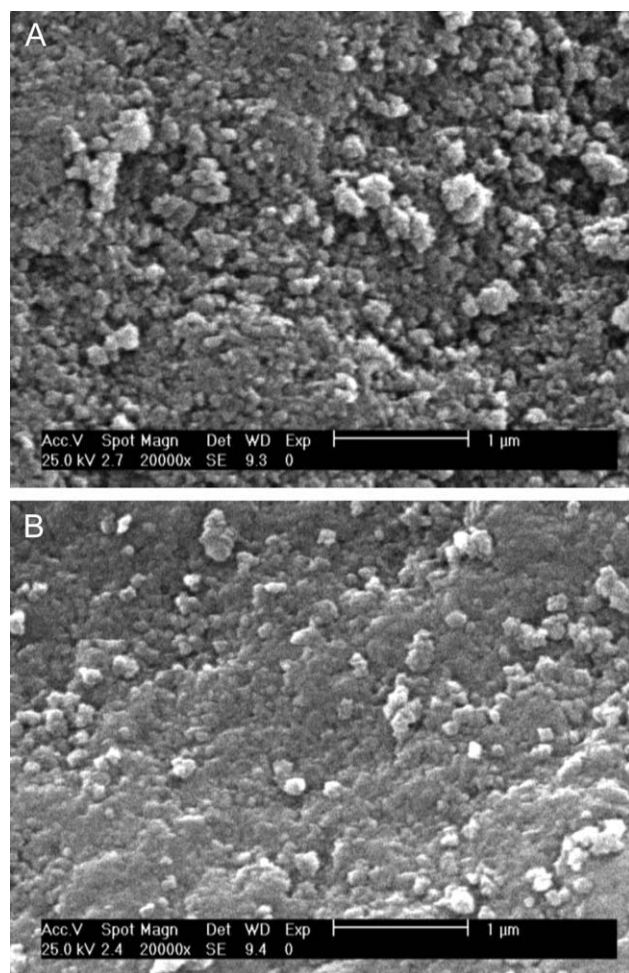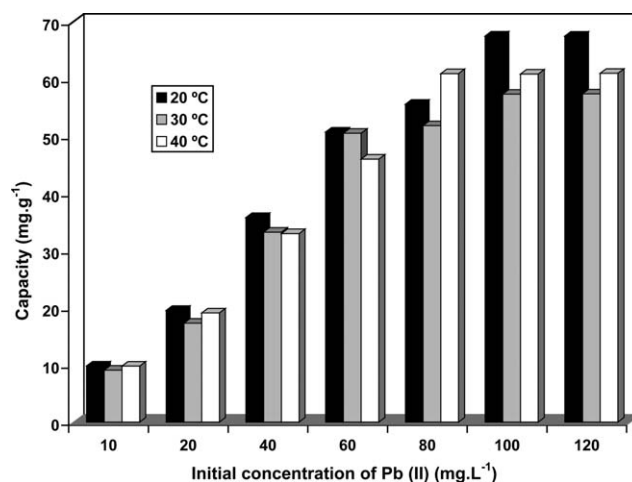
Figure 3 SEM photograph of Amberlite XAD-2 (A) and Amberlite XAD-2-SAL/IDA (B).

Total sorption capacity

At this point, 0.05 g of Amberlite XAD-2-SAL/IDA was stirred for 4 h with 50 mL solution containing10–120 μg mL^{-1} of Pb (II) at optimum pH and 20, 30, and 40°C. The metal ion concentration in the
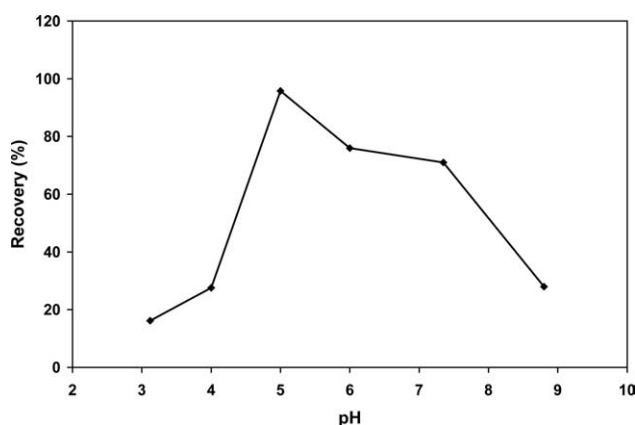
Figure 4 Effect of pH sorption of Pb (II) onto Amberlite XAD-2-SAL/IDA.

Figure 5 Effect of initial concentration of the Pb in the solution and temperature on sorption capacity of Pb (II) onto Amberlite XAD-2-SAL/IDA.

supernatant liquid was estimated by FAAS. The sorption capacity of the sorbent for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The saturated adsorption capacity of the resin was shown in Figure 5. This Figure indicates the effect of initial concentration of the Pb (II) in the solution and temperature on sorption capacity of Pb (II) by Amberlite XAD-2-SAL/IDA. The adsorption capacity in initial concentration of 100 μg mL^{-1} of Pb (II) at optimum pH and 20°C was obtained 67 mg g^{-1}.

Stability and reusability of the sorbent

The Pb (II) was sorbed and desorbed on 1 g of the Amberlite XAD-2-SAL/IDA several times. It was found that sorption capacity of resin after 20 cycles of its equilibration with Pb (II), changes less than 10%. Therefore, repeated use of the resin is feasible. The resin cartridge after loaded with samples can be readily regenerated with 0.5M HNO$_3$. The sorption capacity of the resin stored for more than 6 month under ambient conditions has been found to be practically unchanged.

Optimization of sorption time of lead ions

Amberlite XAD-2-SAL/IDA (0.05 g) was shaken with 50 mL of solution containing 80 μg mL^{-1} of Pb (II) for different length of time (5, 15, 30, 45, 60, and 90 min) under optimum pH. After filtration of the sorbent, the concentration of lead ions in solution was determined with FAAS using the recommended batch method. The sorption as a function of contact time for all the metal ions is shown in Figure 6. Less than 5-min shaking was required for 98% sorption.
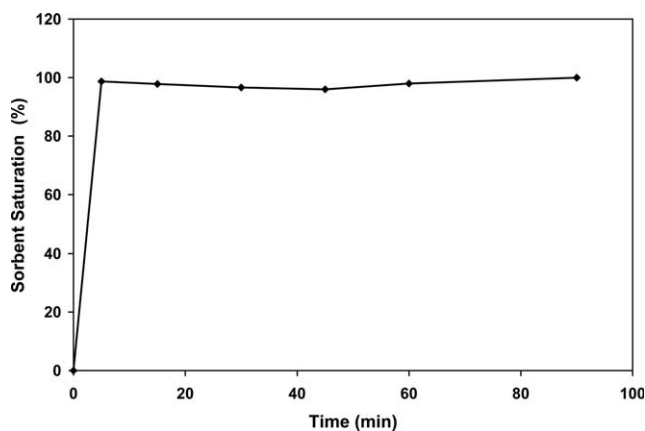
Figure 6 Kinetics of lead sorption on Amberlite XAD-2-SAL/IDA.

The profile of lead uptake on this sorbent reflects good accessibility of the chelating sites in the Amberlite XAD-2-SAL/IDA.

Adsorption isotherms

The Langmuir equation was given in the following form:[14]

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

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}). The eq. (2) can be rearranged to a linear form:

$$C_e/q_e - (1/q_{max}.K_L) + (C_e/q_{max}) \qquad (3)$$

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).

Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of Amberlite XAD-2-SAL/IDA surface. 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 as:[15]

$$R_L = 1/(1 + K_L.C_0) \qquad (4)$$

Table I shows the values of R_L (0.023–0.054) were in the range of 0–1 at optimum pH which confirms the favorable uptake of the Pb (II) (Table II).

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity

factor $1/n$. Hence, the empirical equation can be written as:[16]

$$q_e = K_F.C_e^{1/n} \qquad (5)$$

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

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

Therefore, 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 Freundlich equation predicts that the Pb (II) concentration on the adsorbent will increase as long as there is an increased in the Pb (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:

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

and can be linearized:

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

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.
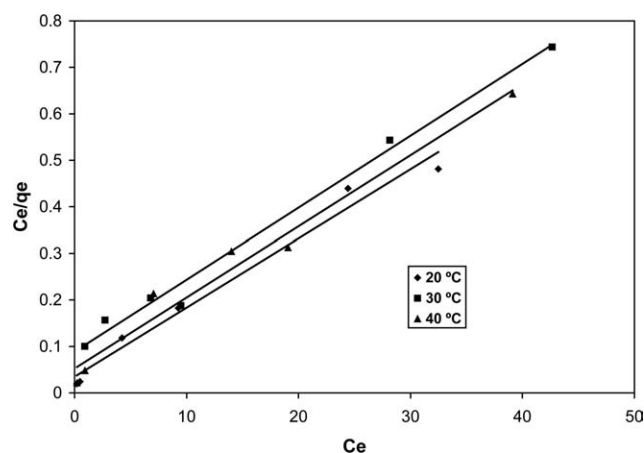
Figure 7 Langmuir isotherm for Pb (II) adsorption onto Amberlite XAD-2-SAL/IDA at different temperatures.

TABLE I
Isotherm Parameters Obtained by Using Linear Method

Temperature	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
Langmuir isotherm model				
20	67.11	0.428	0.023	0.9795
30	64.52	0.175	0.054	0.9897
40	65.36	0.291	0.033	0.9731

Temperature	K_F (mg g^{-1}) (L mg^{-1})1/n		n	R^2
Frendlich isotherm model				
20	20.99		2.91	0.9625
30	11.28		2.05	0.9021
40	18.04		2.79	0.9789

Temperature	A (L g^{-1})	B (J mol^{-1})	b (J mol^{-1})	R^2
Temkin isotherm model				
20	7×10^{-12}	0.0935	26,053	0.9698
30	8×10^{-10}	0.0689	36,562	0.9175
40	1×10^{-9}	0.0896	29,043	0.9182

g	B (dm^3 mg^{-1})^g	A (dm^3 g^{-1})	R^2
Redlich–Peterson isotherm model			
1.01	0.994	60	0.9961

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich-Peterson isotherm has 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.
Where constants A and B are much greater than unity[17]

$$q_e = \frac{AC_e}{1 + BC_e} \quad (11)$$

i.e., the Freundlich form results.

TABLE II
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

Where $g = 0$

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

i.e., the Henry's Law form results.
Equation (9) can be converted to a linear form by taking logarithms:

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

Three isotherm constants, A, B, and g can be evaluated from the linear plot represented by eq. (13) using a trial and error procedure, which is applicable to computer operation. It was developed to
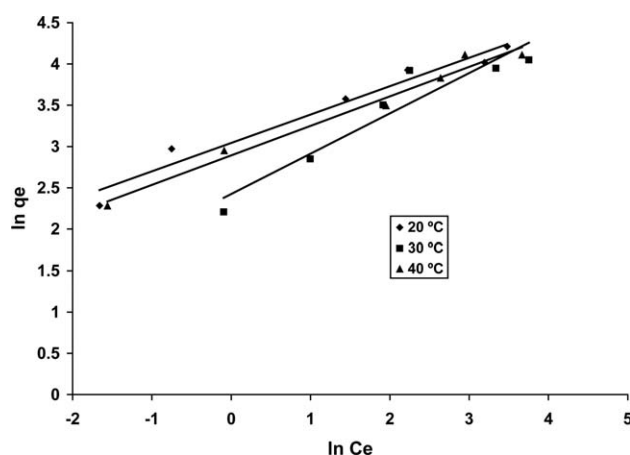

Figure 8 Freundlich isotherm for Pb (II) adsorption onto Amberlite XAD-2-SAL/IDA at different temperatures.
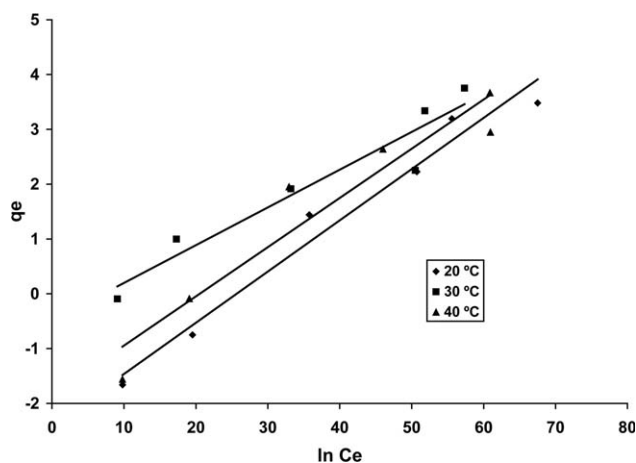
Figure 9 Temkin isotherm for Pb (II) adsorption onto Amberlite XAD-2-SAL/IDA at different temperatures.

determine the isotherm parameters by optimization routine to maximize the coefficient of determination, R^2, for a series of values of A for the linear regression of $\ln(C_e)$ on $\ln[A(C_e/q_e) - 1]$ and to obtain the best value of A which yields a maximum "optimized" value of R^2 using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

The Redlich-Peterson isotherm constants, A, B, and g as well as the coefficient of determination, R^2, for the sorption of Pb(II) on to Amberlite XAD-2-SAL/IDA using the linear regression is shown in Table I. It was observed that the coefficient of determination of Langmuir is higher than the other isotherms. It can be seen that the values of g were close to unity, which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. The result shows that the Langmuir isotherm best-fit the equilibrium data for adsorption of Pb (II) on Amberlite XAD-2-SAL/IDA.
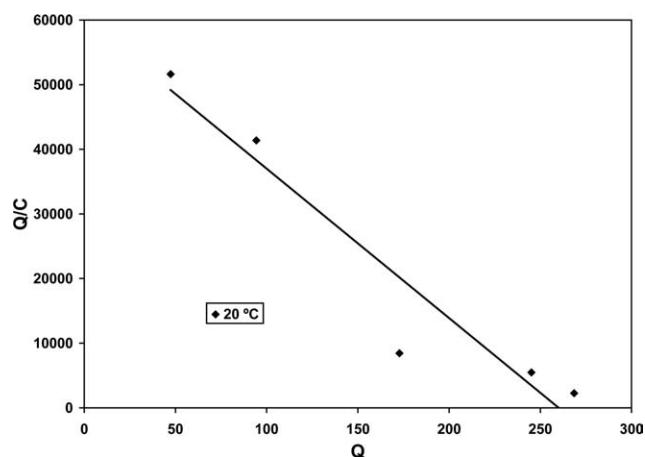
Figure 10 Scatchard plots of Pb (II) adsorption onto Amberlite XAD-2-SAL/IDA at 20°C.

TABLE III
Effect of Other Ions on Sorption

Interfering ions	Amount of adsorbed Pb(II) (mg L^{-1})	Loss adsorption (%)
–	10	0
Cr (II)	9.66	3.4
Ni (II)	9.84	1.6
Co (II)	9.69	3.1
Fe (II)	9.99	0.08
Hg (II)	9.90	1
Cd (II)	9.81	1.9
Zn (II)	9.74	2.6
Ba (II)	9.99	0.04
Ag (I)	9.98	0.13
Cu (II)	9.85	1.5
K (I)	9.99	0.1
Al (III)	10	0
Mixed above ions	9.14	8.6

Scatchard analysis

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 adsorption amount; and K_d (μmol mL^{-1}) is the equilibrium dissociation constant at binding sites. Figure 10 shows the Scatchard plots of the binding of lead to the resin. It is clear that the Scatchard plot for resin is a single straight line. The linear regression equation was $Q/C = -231.14Q + 60127$ ($R^2 = 0.9168$), suggesting that the homogeneous recognition sites for lead were formed in the SPE resin. From the slope [-231.14 ($1/K_d$)] and intercept [$60,127$ (Q_{max}/K_d)], K_d and Q_{max} for the affinity binding sites were calculated to be 0.0043 μmol mL^{-1} and 260.1 μmol g^{-1}, respectively.

Effect of foreign ions

To evaluate the selectivity of the preconcentration system, the effect of some metal ions (10 mg L^{-1}) on the sorption behavior of Pb (II) ion (concentration 10 mg L^{-1}) was investigated. The result was shown in Table III. This Table indicates that the most effective ions on adsorption of Pb (II) on Amberlite XAD-2-SAL/IDA are Co (II), Ni (II), and Zn (II). The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Pb (II) on the Amberlite XAD-2-SAL/IDA in presence of all mentioned ions (with each ion having the concentration of 10 mg L^{-1}) shows that the Pb (II) can be determined quantitatively in the environmental samples.

TABLE IV
Comparison of Recovery, Preconcentration, and Capacities with Some Literatures

Resin used	Recovery (%)	Preconcentration factor	Capacity (mg g^{-1})	Ref.
Amberlite XAD-2 functionalized with o-aminophenol	91	40	3.32	18
Microcrystalline triphenylmethane loaded with quinolin-8-olate	98	100	–	19
Gallic acid-modified silica gel	96	25	12.63	20
Cellulose modified with triethylenetetramine	–	–	192.3	21
Sugarcane bagasse chemically modified with succinic anhydride	–	–	83.3	22
Chitosan modified ordered mesoporous silica	95	–	22.9	1
Macroporous epoxy resin-based polymer monolithic matrix	97	10	106.8	23
Thioureasulfonamide resin	97	20	0.5	24
Dibenzyldithiocarbamate chelates on Dowex Optipore V-493	96	4–8	8.6	25
Amberlite XAD-2 with chromotropic acid	97	4–10	186.3	26
Amberlite XAD-2 with pyrocatechol	94	4–10	104.7	26
Amberlite XAD-2 with thiosalicylic acid	93	4–10	89.3	26
Amberlite XAD-7 with xylenol orange	91	4–10	16.9	26
Amberlite XAD-2-SAL/IDA (Our resin)	95	10	67	–

Comparison with other methods

Comparative information from a number of studies on preconcentration of Pb (II) by various methods for the figure of merits is given in Table IV. This new developed method has been successfully applied to the analysis of trace lead ions in natural water sample.

Application of method

Amberlite XAD-2-SAL/IDA was used to preconcentrate and determine Pb (II) ions in The Persian Gulf (Boshehr, Nuclear Power Plant, Iran). The pH of water sample was adjusted to the optimum pH. Solid phase extraction with Amberlite XAD-2-SAL/IDA coupled with FAAS was applied to determination of Pb (II) in water sample. After no detection Pb (II) in the water, 100 mL water sample was spiked with 0.02, 0.04, and 0.06 mg of Pb (II) before subjecting it to the recommended procedure. The results are shown in Table V. These results demonstrate the applicability of the procedure for Pb determination in samples with high recovery (>98%).

Determination of Pb (II) in plasma

Adsorption of Pb (II) ions on the Amberlite XAD-2-SAL/IDA from human serum was also studied in batch-wise. Human blood was collected from thoroughly controlled voluntary blood donors. Each unit was separately controlled and found negative for HBS antigen and HIV I, II, and hepatitis C antibodies. No preservatives were added to the samples.

Human blood was collected into EDTA containing vacutainers and red blood cells were separated from 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 detection Pb (II) 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 volume of human serum containing 0.4 μg mL^{-1} of Pb (II) ions were treated with 0.1 g of Amberlite XAD-2-SAL/IDA at room temperature and magnetically stirred at a speed of 600 rpm. After the desired treatment periods, the sorbent was taken out and sorbed metal ion was eluted with 0.5*M* nitric acid (10 mL). The concentration of the metal ion in the eluant was determined by FAAS. The experiments were performed in replicates of three. The results are shown in Table

TABLE V
Results Obtained for Pb (II) Determination in Plasma and Water Sample of (I), (II), and (III)

	Plasma	(I)	(II)	(III)
Found (without spiking of Pb (II)	N.D.	N.D.	N.D.	N.D.
Added Pb (II) (μg mL^{-1})	0.4	0.2	0.4	0.6
Found Pb (II), after preconcentration (μg mL^{-1})	0.74	2.04	3.98	5.88
Preconcentration factor	2.5	10	10	10
Recovery (%)	74.4	100	99	98
Standard deviation	0.016	0.086	0.094	0.10
Relative standard deviation (%)[a]	2.2	3.2	2.4	1.8

[a] For three determinations.

V and indicate the suitability of the present sorbent for the preconcentration of lead from plasma samples. The similarity of results obtained by mentioned methods indicate that the reliability of the lead content data presented in Table V is reasonable.

CONCLUSIONS

A new chelating resin is prepared by coupling Amberlite XAD-2 with salicylic acid and then iminodiacetic acid. The synthesis of the resin is simple and economical. 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. The sorption of the investigated metal ions increases by increasing the contact time. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 67.11, 64.52 and 65.36 (mg g^{-1}) at 20, 30, and 40°C, respectively. The R_L values showed that the Amberlite XAD-2-SAL/IDA was favorable for the adsorption of Pb (II). Preconcentration by this resin combined with FAAS and ICP-AES can be applied to the determination of trace lead (II) ions in water and the mineral reference sample with satisfactory results.

References

1. Chen, D.; Hu, B.; Huang, C. Talanta 2009, 78, 491.
2. Memon, S. Q.; Hasany, S. M.; Bhanger, M. I.; Khuhawar, M. Y. J Colloid Interface Sci 2005, 291, 84.
3. Cesur, H.; Aksu, C. Anal Sci 2006, 22, 727.
4. Ghaedi, M.; Ahmadi, F.; Karimi, H.; Gharaghani, S. J Korean Chem Soc 2006, 50, 23.
5. Ahmad Panahi, H.; Sid Kalal, H.; Moniri, E.; Nikpour Nezhati, M.; Taheri Menderjani, M.; Ranjbar Kelahrodi, S.; Mahmoudi, F. Microchem J 2009, 93, 49.
6. Prabhakaran, D.; Subramanian, M. S. Talanta 2003, 61, 423.
7. Saito, K.; Taninaka, I.; Yamamoto, Y.; Murakami, S.; Muromatsu, A.; Talanta 2000, 51, 913.
8. Alguacil, F. J.; Adeva, P.; Alonso, M. Gold Bull 2005, 38, 9.
9. Prasad, K.; Gopikrishna, P.; Kala, R.; Rao, T. P.; Naidu, G. R. K. Talanta 2006, 69, 938.
10. Kagaya, S.; Sagisaka, T.; Miwa, S.; Morioka, K.; Hasegawa, K. Bull Chem Soc Jpn 2006, 79, 717.
11. Karatepe, A. U.; Soylak, M.; Elci, L. Anal Lett 2002, 35, 1561.
12. Sombra, L.; Luconi, M.; Silva, M. F.; Olsina, R. A.; Fernandez, L. Analyst 2001, 126, 1172.
13. Zhang, Y.; Luo, W. H.; Li, H. Spectrosc Spect Anal 2005, 25, 576.
14. Langmuir, L. J Am Chem Soc 1918, 40, 1361.
15. Hall, K. L.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. Ind Eng Chem Fundam 1966, 5, 212.
16. Frendlich, H. M. A. J Phys Chem 1906, 57, 385.
17. Ho, Y.; Augustine, E. Biochem Eng J 2006, 30, 117.
18. Kumar, M.; Rathore, D. P. S.; Singh, A. K. Talanta 2000, 51, 1187.
19. Hu, L.; Gang Ren, Z. Chin Chem Lett 2009, 20, 334.
20. Xie, F.; Lin, X.; Wu, X.; Xie, Z. Talanta 2008, 74, 836.
21. Vinícius, L.; Gurgel, A.; Frédéric Gil, L. Carbohydr Polym 2009, 77, 142.
22. Vinícius, L.; Gurgel, A.; Pereira de Freitas, R; Frédéric Gil, L. Carbohydr Polym 2008, 74, 922.
23. Wang, S.; Zhang, R. Anal Chim Acta 2006, 575, 166.
24. Filiz Senkal, B.; Ince, M.; Yavuz, E.; Yaman, M. Talanta 2007, 72, 962.
25. Melek, E.; Tuzen, M.; Soylak, M. Anal Chim Acta 2006, 578, 213.
26. Tewari, P. K.; Singh, A. K. Talanta 2002, 56, 735.