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Removal of cobalt from human serum and environmental samples by adsorption using Amberlite XAD-2–salicylic acid–iminodiacetic acid

Homayon Ahmad Panahi[a,*], Hayedeh Bagheri Sadeghi[a], Nasim Farahmandnejad[a], Ali Rezaii Badr[b], Elham Moniri[c]

[a]*Department of Chemistry, Islamic Azad University, Central Tehran Branch, Tehran, Iran*
Email: h.ahmadpanahi@iauctb.ac.ir
[b]*Department of Chemistry, Islamic Azad University, Shahr Rey Branch, Tehran, Iran*
[c]*Department of Chemistry, Islamic Azad University, Varamin (Pishva) Branch, Varamin, Iran*

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ABSTRACT

A new chelating resin was 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, and scanning electron microscopy, and studied for the preconcentration and determination of trace Co(II) ion from human biological fluid and environmental water samples. The optimum pH value for sorption of the metal ion was 7.5. The sorption capacity of functionalized resin was 87.4 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 95.3% was obtained for the metal ion with 0.5 M nitric acid as the eluting agent. The profile of cobalt 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 Co(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 to be 2.265, 56.82, and 148.56 at pH 7.5 and 25°C, respectively. The method was applied for cobalt ion determination from human plasma and sea water sample.

Keywords: Solid-phase extraction; Amberlite XAD-2; Cobalt determination; Isotherm study; Environmental samples

1. Introduction

Cobalt is known to be an essential element at trace level in human beings, animals, and plants for metabolic processes. Cobalt helps to repair the myelin sheath, pernicious anemia, and building of red blood cells. More attention has been focused on the toxicity of cobalt in large concentrations, since it has been found that cobalt can cause vasodilation, flushing, and cardiomyopathy in human beings and animals. It was reported that cobalt-mediated free radical generation contributes to interfere with DNA repair processes [1–3]. The International Agency for Research on Cancer (IARC) has classified this metal as possibly carcinogenic to human beings [4].

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*Corresponding author.

Except occupational sources, the main sources of cobalt are foods and beverages. World Health Organization (WHO) recommends that 0.005–0.010 mg of cobalt might be the daily optimal intake for adults [5]. Therefore, the determination of Co in water, food, and environmental samples is important in the fields of environmental analysis and medicine.

Due to the allowable low levels of cobalt in food and beverages, and its very low concentrations in natural waters as described above, reliable and sensitive analytical methods are required for determination of this metal. Preconcentration techniques in connection with the analytical methods such as electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS) are reported by a number of authors [6–8]. Because of the disadvantages such as the interferences from matrix components, the necessity of operational expertise, and relatively higher costs of other methods [9,10], the use of preconcentration techniques in the determination of Co by flame atomic absorption spectrometry (FAAS) can still be of importance. Among preconcentration techniques, solid-phase extraction (SPE) is widely used due to its simplicity, high concentration factor, and more environmentally friendly reagents used [11,12].

The purpose of the present study is to indicate the feasibility of using Amberlite XAD-2–SAL/IDA as a solid-phase extractant for preconcentration of trace cobalt in biological fluid and environmental water samples. Trace cobalt can be retained on the surface of Amberlite XAD-2–SAL/IDA and then desorbed with 0.5 M nitric acid prior to determination by FAAS. This proposed novel method has advantages of good accuracy and precision, high recovery, and preconcentration factor.

2. Experimental

2.1. Instruments

Flame atomic absorption spectrometer of the 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 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) 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 Corporation, Kyoto, Japan).

2.2. Reagents and solutions

Tin(II) chloride, hydrochloric acid, sulfuric acid, nitric acid, sodium nitrite, sodium hydroxide, chrome(III) nitrate, copper(II) nitrate, mercury(II) nitrate, cadmium(II) nitrate, zinc nitrate, barium nitrate, silver nitrate, potassium nitrate, aluminum nitrate, sodium chloride, sodium acetate, acetic acid, sodiumdihydrogen phosphate, disodiumhydrogen phosphate, lead(II) nitrate, ferrous sulfate, copper(II) sulfate, cobalt(II) nitrate, nickel sulfate, iminodiacetic acid (IDA), ethanol, ethylenediaminetetraacetic acid (EDTA), thionyl chloride, salicylic acid (SAL), CH_3COCH_3, C_2H_5OH, Sn powder, and brilliant green were products of Merck (Darmstadt, Germany). Amberlite XAD-2resin (surface area 745 m^2/g, pore diameter 5 nm, and bead size 20–60 meshes) was obtained from Serva (Heidelberg, New York).

All the reagents were of analytical grade and used without any further purification.

The stock solution (1,000 mg L^{-1}) of Co(II) was prepared by dissolving appropriate amounts of Co $(NO_3)_2$, in deionized water. The 0.1 M acetic acid–acetate buffer (pH 3–6.5) and 0.01 M phosphate buffer (pH 6.5–9) were used to adjust the pH of the solutions, wherever suitable.

2.3. Synthesis of sorbent

2.3.1. Synthesis of Amberlite XAD-2–[SAL]

Amberlite XAD-2 beads (5 g) were treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4, and the mixture was stirred at 60°C for 1 h on 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 mL of concentrated HCl, and 50 mL of ethanol. The mixture was refluxed for 12 h at 90°C. The solid precipitate was filtered and washed with water and 2 mol L^{-1} NaOH which released amino resin (R-NH_2) from $(RNH_3)_2$ $SnCl_6$ (R = resin matrix). The amino resin was first washed with 2 mol L^{-1} HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice–water mixture (350 mL) and treated with 1 mol L^{-1} HCl and 1 mol L^{-1} $NaNO_2$ (added in small aliquots of 1 mL) 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 SAL (2.5 g in 300 mL of glacial acetic acid and 150 mL 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 Fig. 1.

2.3.2. 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.

2.3.3. Synthesis of 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 IDA (0.01 mol) and NaOH solution (1 M) upon cooling. The reaction mixture was stirred at 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 analysis and TGA. The resin was dried at 60˚C and placed in a desiccator.

2.4. Sorption/desorption procedure

A sample solution (100 mL) containing (0.5 μg mL^{-1}) of Co(II) was taken in a glass-stoppered bottle, and the pH was adjusted to 7.5. 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 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluant was determined by FAAS.

2.5. 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 Co(II) (40–100 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 25˚C and optimum pH (7.5). pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Co(II) in the solution was measured by FAAS. The amount of Co(II) at equilibrium q_e (mg/g) on Amberlite XAD-2–SAL/IDA was calculated from the following equation:

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

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

3. Result and discussion

3.1. Characterization of the resin

3.1.1. IR spectrum

IR spectrum of synthesis of SAL loaded Amberlite XAD-2 (cm^{-1}): 3,433 (OH), 1,526 aromatic (C=C), 1,607 (N=N), 1,701 (C=O), 1,209 (C–O), 3,027 aromatic (C–H), and 2,927 aliphatic (C–H).

IR spectrum of synthesis of XAD-2-[ethyl salicylate] (cm^{-1}): 3,392 (OH), 1,620 (N=N), 1,715 (C=O), 1,092, 1,349 (C–O), and 2,924 aliphatic (C–H).

IR spectrum of synthesis of XAD-2-[SAL/IDA] (cm^{-1}): 3,443 (OH), 1,624 (N=N), 1,701 (C=O), 1,625 amidic (C=O), 1,037 phenolic (C–O), and 2,926 aliphatic (C–H).

3.1.2. Elemental analysis

The instruction used in this study is reported in Thermo-Finnigan 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. The above mentioned elements 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 Amberlite XAD-2–SAL (found: C, 69.25; H, 6.15; N: 6.78%, calculated for $(C_8H_7)_2$ C_7H_5 N_2O_3: C, 74.39; H, 5.12; N, 7.54%) shows that on an average, one SAL molecule is present in each two repeated units of the polymer.

The elemental analysis for Amberlite XAD-2–SAL/IDA (found: C, 59.48; H, 6.25; N: 6.86%, calculated for $[(C_8H_7)_2\ (C_7H_4N_2O_2)]_1\ (C_4H_6NO_4)_1$: C, 62.18; H, 4.41; N, 8.06%) shows that on an average, one IDA molecule is present in each repeated unit of the Amberlite XAD-2–SAL.

3.1.3. Thermogravimetric analysis

TGA of the Amberlite XAD-2 shows a two-step weight loss up to 600˚C. The weight loss up to 100˚C

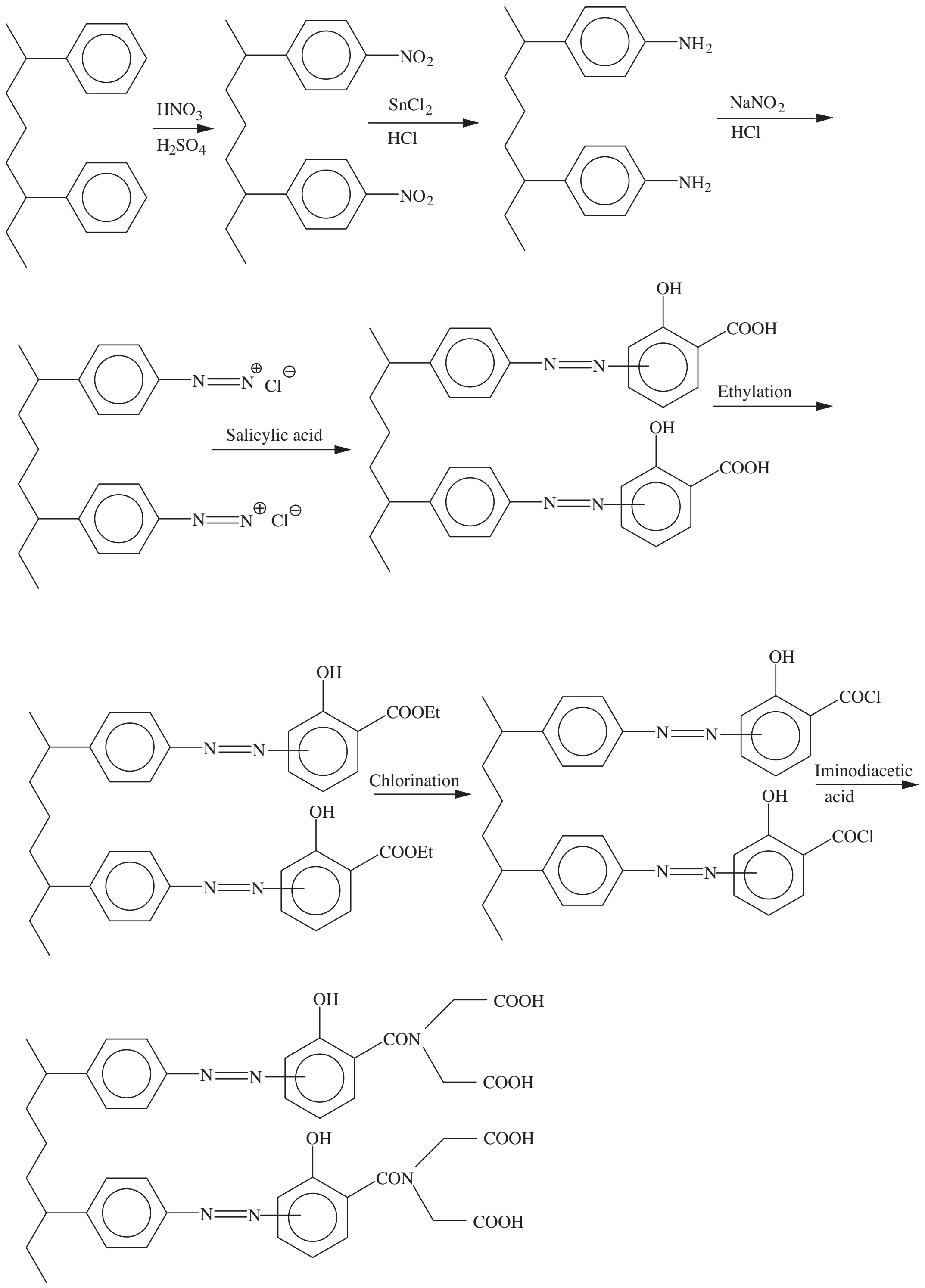

Fig. 1. The methodology of synthesize of Amberlite XAD-2–SAL/IDA.

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 a 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).

3.1.4. Scanning electron microscopy (SEM)

The surface morphology and internal structure of polymer beads are investigated by the scanning electron micrographs which are given in Fig. 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 Fig. 3 is about 1 μm. It is these macropores that would reduce diffusional mass transfer resistance and facilitate convective mass transport because of their spacious internal surface area.

3.2. Metal sorption as a function of pH

The degree of metal ionsorption at different pH values was determined by the batch equilibration technique. A set of solutions (the volume of each 100 mL) containing 0.5 μg mL^{-1} of Co(II) was taken. Their pH values were adjusted between the ranges 3 and 9 with 0.01 M 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 Co(II) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from Amberlite XAD-2–SAL/IDA with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Fig. 4. The maximum recovery is 95.3% at pH 7.5.

3.3. Total sorption capacity

At this point, 0.05 g of Amberlite XAD-2–SAL/IDA was stirred for 4 h with 50 mL solution containing 10–100 μg mL^{-1} of Co(II) at pH 7.5 and 25°C. The metal ion concentration in the 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 is shown in Fig. 5. This figure indicates the effect of initial concentration of the Co(II) in the solution and temperature on the sorption capacity of Co(II) by Amberlite XAD-2–SAL/IDA. The capacity increases with increasing initial concentration of the Co(II) in the solution and reaches a constant value after 100 μg mL^{-1} concentration of Co(II) (87.4 mg g^{-1}).

3.4. Stability and reusability of the sorbent

The Co(II) was sorbed and desorbed on 1 g of the Amberlite XAD-2–SAL/IDA several times. It was

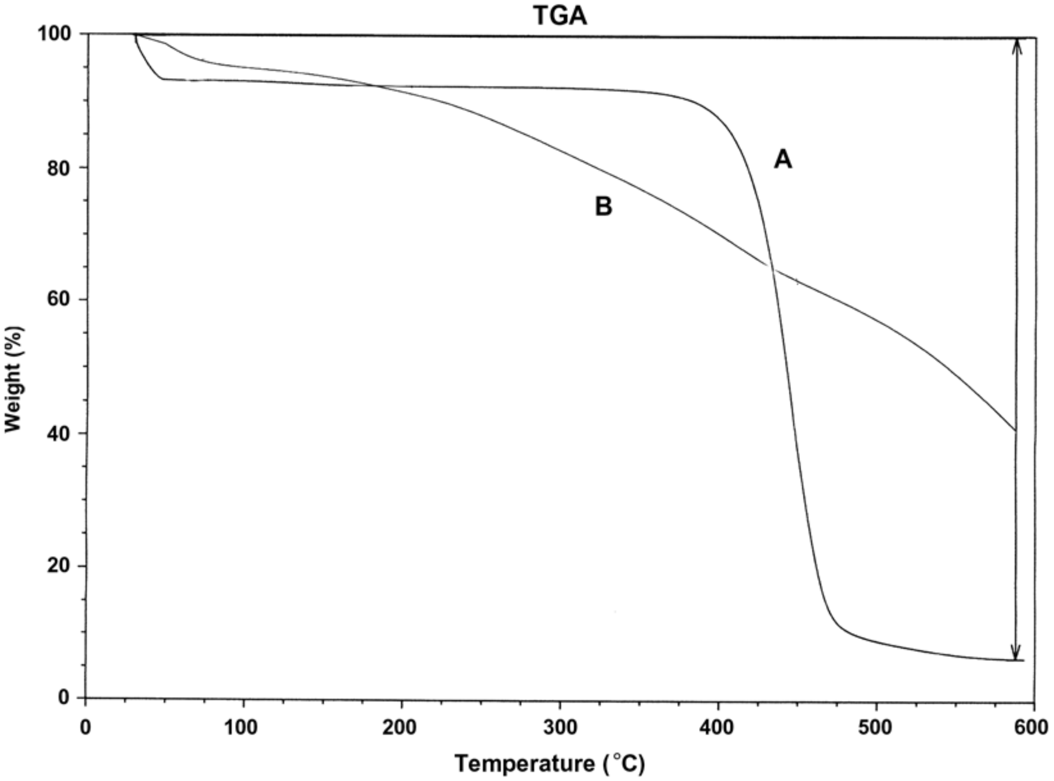

Fig. 2. TGA of Amberlite XAD-2 (A) and Amberlite XAD-2–SAL/IDA (B).

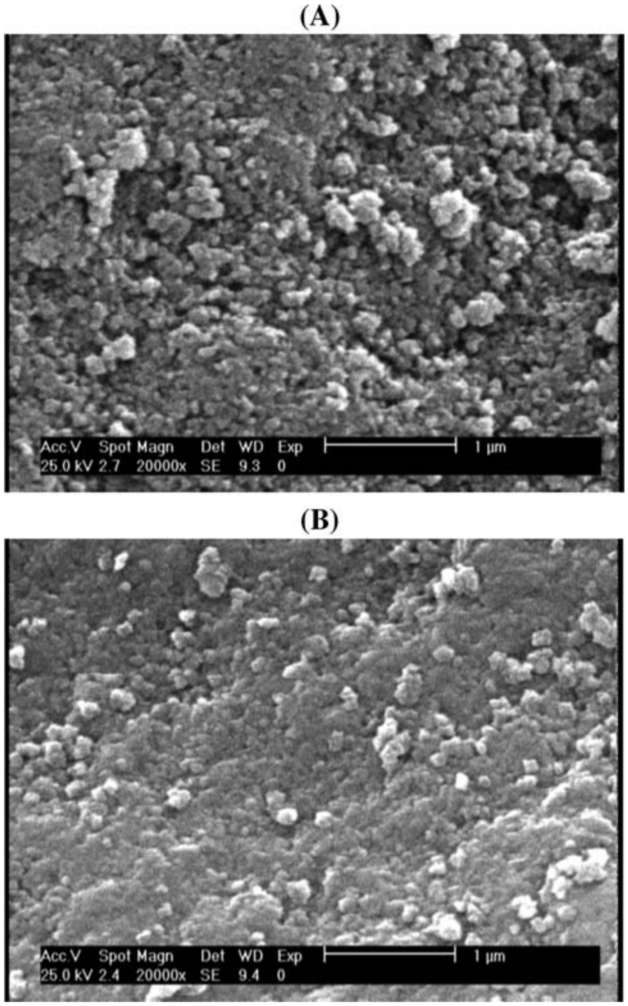

Fig. 3. SEM photograph of Amberlite XAD-2 (A) and Amberlite XAD-2–SAL/IDA (B).

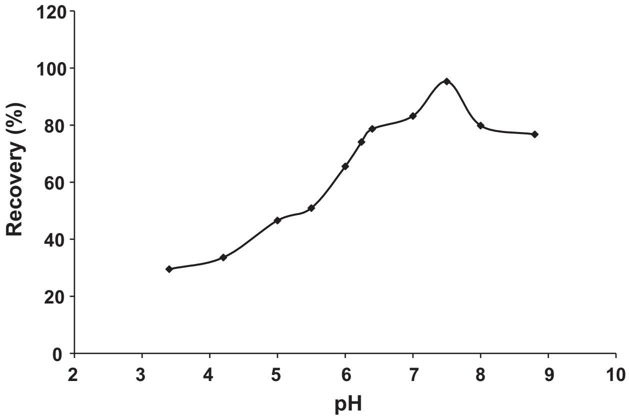

Fig. 4. Effect of pH on the sorption of Co(II) onto Amberlite XAD-2–SAL/IDA.

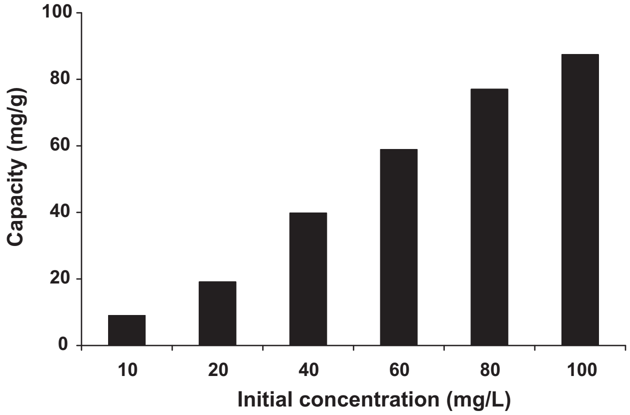

Fig. 5. Effect of initial concentration of the Co in the solution and temperature on capacity sorption of Co(II) onto Amberlite XAD-2–SAL/IDA.

found that the sorption capacity of the resin after 20 cycles of its equilibration with Co(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 0.5 M HNO_3. The sorption capacity of the resin stored for more than 6 months under ambient conditions has been found to be practically unchanged.

3.5. Optimization of sorption time of cobalt ions

Amberlite XAD-2–SAL/IDA (0.05 g) was shaken with 50 mL of solution containing 80 $\mu g\,mL^{-1}$ of Co(II) for different lengths of time (5, 15, 30, 45, 60, 90, and 120 min) under optimum pH (7.5). After filtration of the sorbent, the concentration of cobalt 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 Fig. 6. Less than 15 min shaking was required for 94% sorption. The profile of cobalt uptake on this sorbent reflects good accessibility of the chelating sites in the Amberlite XAD-2–SAL/IDA.

3.6. Adsorption isotherms

The Langmuir equation was given in the following form [13]:

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

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

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

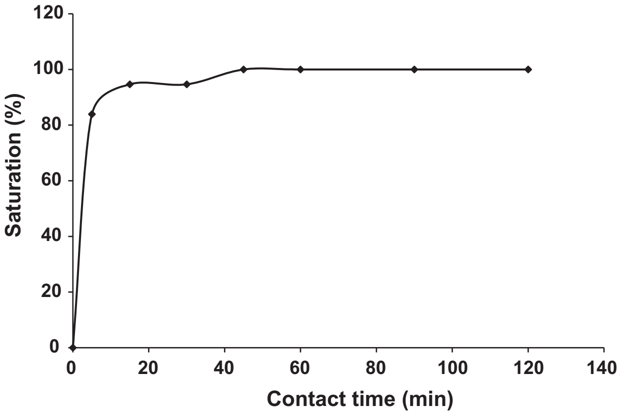

Fig. 6. Kinetics of cobalt sorption on Amberlite XAD-2–SAL/IDA.

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

Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of the Amberlite XAD-2–SAL/IDA surface. Langmuir parameters calculated from Eq. (3) 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 [14]:

$$R_L = 1/(1 + K_L \times C_0) \tag{4}$$

Table 1 shows the value of R_L (0.0044) is in the range of 0–1 at optimum pH, which confirms the favorable uptake of Co(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 [15]:

$$q_e = K_F \times C_e^{1/n} \tag{5}$$

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

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{6}$$

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

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

and can be linearized:

$$q_e = B \ln A + B \ln C_e \tag{8}$$

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

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:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{9}$$

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:

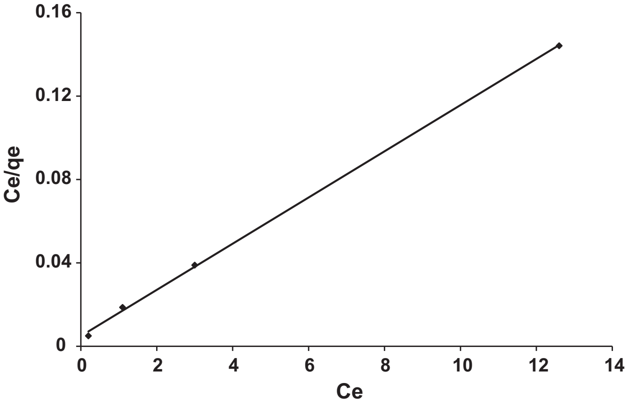

Fig. 7. Langmuir isotherm for Co(II) adsorption onto Amberlite XAD-2–SAL/IDA at 25°C.

Table 1
Isotherm parameters obtained by using the linear method

Temperature	$q_{\max}$ (mg/g)	K_L (L/mg)	R_L	R^2
Langmuir isotherm model				
25	90.09	2.265	0.0044	0.9994
Freundlich isotherm model				
Temperature		K_F (mg/g) (L/mg)$^{1/n}$	n	R^2
25		56.82	5.11	0.9,610
Temkin isotherm model				
Temperature	A (L/g)	B (J/mol)	b (J/mol)	R^2
25	148.56	11.893	211.92	0.9,787
Redlich–Peterson isotherm model				
g		B (dm^3/mg)g	A (dm^3/g)	R^2
1.1		0.888	260	0.9,910

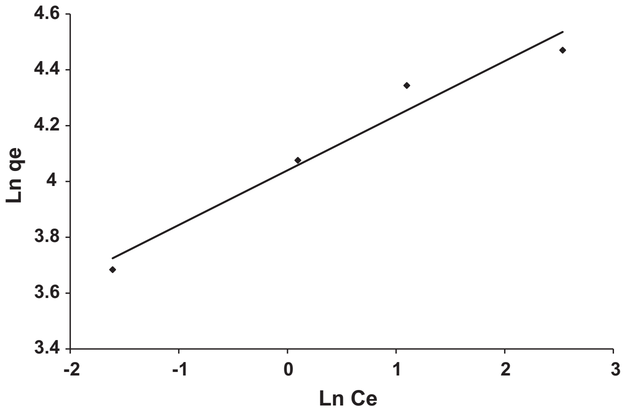

Fig. 8. Freundlich isotherm for Co(II) adsorption onto Amberlite XAD-2–SAL/IDA at 25°C.

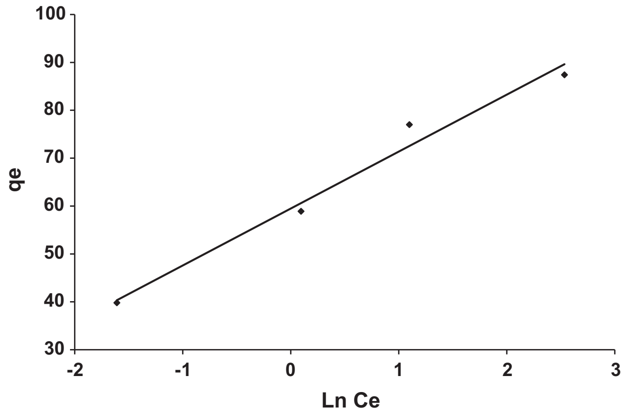

Fig. 9. Temkin isotherm for Co(II) adsorption onto Amberlite XAD-2–SAL/IDA at 25°C.

Where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \tag{10}$$

i.e. the Langmuir form results.

Where constants A and B are much greater than unity [16]

$$q_e = \frac{A}{BC_e^{g-1}} \tag{11}$$

i.e. the Freundlich form results.

Where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \tag{12}$$

i.e. Henry's Law form results.

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

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

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 determine the isotherm parameters by the 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 Co(II) on to Amberlite XAD-2–SAL/IDA using the linear regression are shown in Table 1. 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 Co(II) on Amberlite XAD-2–SAL/IDA.

3.7. 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 cobalt; 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. The linear regression Scatchard equation was $Q/C = -111.58Q + 170{,}799$ ($R^2 = 0.9904$), suggesting that the homogeneous recognition sites for cobalt were formed in the SPE resin. From the slope ($-111.58\,(1/K_d)$) and intercept ($170{,}799\,(Q_{\max}/K_d)$), K_d and $Q_{\max}$ for the affinity binding sites were calculated to be 0.0090 μmol mL^{-1} and 1,530 μmol g^{-1}, respectively.

3.8. Effect of foreign ions

In order to evaluate the selectivity of the preconcentration system, the effect of some metal ions (10 mg L^{-1}) on the sorption behavior of Co(II) ion (concentration 10 mg L^{-1}) was investigated. The extraction percentage (E %) and the distribution ratio (D) were calculated from the following equations:

$$Q = (C_0 - C_e)V/W \tag{14}$$

$$E = (C_0 - C_e)/C_0 \tag{15}$$

$$D = Q/C_e \tag{16}$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e represent the initial and equilibrium concentrations of Co(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 is shown in Table 2. This Table indicates that the most effective ions on adsorption of Co(II) on Amberlite XAD-2–SAL/IDA are Cu(II), Pb(II), Fe(II), and Ni(II). The effect of other mentioned foreign ions at given concentrations is negligible. The adsorption of Co(II) on the Amberlite XAD-2–SAL/IDA in the presence of all mentioned ions (with each ion having the concentration of 10 mg L^{-1}) shows that Co(II) can be determined quantitatively in the environmental samples.

Table 2
Effect of other ions on sorption

Interfering ions	*A*	*L* (%)	*E* (%)	*D*
Ni(II)	7.15	0	71.5	1.25
Fe(II)	6.70	6.3	67	1.01
Hg(II)	7.15	0	71.5	1.25
Zn(II)	6.80	4.9	68	1.06
Ba(II)	7.15	0	71.5	1.25
Ag(I)	6.87	3.9	68.6	1.09
Cu(II)	6.5	9	65	0.93
K(I)	7.15	0	71.5	1.25
Ca(II)	6.8	4.5	68	1.06
Mg(II)	7.0	2.1	70	1.17
Pb(II)	6.7	6.3	67	1.02
Mixed above ion	6.4	10.5	64	0.89

Note: *A*: amount of adsorbed Co(II) (mg L^{-1}) ions, *L*: loss adsorption (%), *E*: extraction percentage (%), and *D*: distribution ratio.

Table 3
Comparison of recovery, preconcentration, and capacities with some literature

Resin used	*R*	*P*	*C*	Ref.
m-PhenylendiamineAmberlite XAD-4	98	10	–	[10]
Silica gels modified with triphenylphosphonium	–	–	1.47	[17]
Bis(2,4,4-trimethylpentyl) monothiophosphinic acid	–	–	1.58	[18]
Amberlite XAD-7 impregnated with xylenol orange	98	100	2.6	[19]
Quinalizarin anchored on Amberlite XAD-2	91–99	25	93	[20]
Pyrogallol immobilized Amberlite XAD-2	96	4	4.10	[21]
2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino} benzoic acid immobilized Amberlite XAD-16	98.2	167	13.02	[22]
Pyrocatechol-modified Amberlite XAD-2 resin	97	10	12.9	[23]
Dithiocarbomate onto C18-SPE column	98.8	10	–	[24]
Amberlite XAD-2 functionalized with o-aminophenol	96	100	3.29	[25]
Cellulose-pyrocatechol	98.2	10	9.43	[26]
Amberlite XAD-2–SAL/IDA (Our resin)	95.3	10	87.4	_

Note: *R*: recovery (%), *P*: preconcentration factor, *C*: capacity (mg g^{-1}), Ref.: Reference.

3.9. Comparison with other methods

Comparative information from a number of studies on preconcentration of Co(II) by various methods for the figure of merits is given in Table 3. The sorption capacity of the present sorbent is superior in comparison to all the matrices shown in Table 3. This newly developed method has been successfully applied to the analysis of trace cobalt ions in a natural water sample.

3.10. Application of method

Amberlite XAD-2–SAL/IDA was used to preconcentrate and determine Co(II) ions in the Persian Gulf (Bushehr Nuclear Power Plant, Iran). The pH of water sample was adjusted to the optimum pH (7.5). SPE with Amberlite XAD-2–SAL/IDA coupled with FAAS was applied to determination of the Co(II) in a water sample. Since no Co(II) was detected in the water sample, 100 mL water sample was spiked with 0.02, 0.04, and 0.06 mg of Co(II) before subjecting it to the recommended procedure. The results are shown in Table 4. These results demonstrate the applicability of the procedure for Co determination in samples with high recovery (>90%).

3.11. Determination of Co(II) in plasma

Adsorption of Co(II) ions on the Amberlite XAD-2–SAL/IDA from human serum was also studied in batchwise. Human blood was collected from thoroughly controlled voluntary blood donors. Each unit was separately controlled and found negative to be 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 4,000 × *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 of Co(II) in the plasma, 25 mL plasma was spiked with 0.01 mg of Co(II) before subjecting it to the recommended procedure. Then 25 mL volume of human serum containing 0.4 μg mL^{-1} of Co(II) ions was 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 the 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 triplicate. The results are shown in Table 4 and indicate the suitability of the present sorbent for the preconcentration of cobalt from plasma samples. The similarity of results obtained by mentioned methods indicates that the reliability of the cobalt content data presented in Table 4 is reasonable.

3.12. Analytical performance of the proposed system

Seven replicate determinations of 0.6 mg L^{-1} cobalt solutions gave a relative standard deviation of 4.1%. The limit of detection corresponding to three times the standard deviation blank was found to be 13 μg L^{-1}. The limit of quantification corresponding to ten times the blank standard deviation was found to be 43 μg L^{-1}. The regression equation (after preconcentration) was $A = 0.014C_{\mathrm{Co}} + 0.0023$ ($R^2 = 0.9997$), and the conventional regression equation was

Table 4
Results obtained for Co(II) determination in plasma and water sample of (I), (II), and (III)

	Plasma	(I)	(II)	(III)
Sample (without spiking of Co(II))	ND	ND	ND	ND
Added Co(II) ($\mu g\,mL^{-1}$)	0.4	0.2	0.4	0.6
Found Co(II), after preconcentration ($\mu g\,mL^{-1}$)	0.87	1.81	3.69	5.57
Preconcentration factor	2.5	10	10	10
Recovery (%)	87	90.5	92.2	92.8
Standard deviation	0.051	0.066	0.143	0.226
Relative standard deviation (%)[a]	5.86	3.65	3.88	4.06

[a] For three determinations.

$A = 0.004C_{Co} + 0.0031$ ($R^2 = 0.9961$). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 3.5. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluant volume (10 mL), was 10.

4. Conclusion

A new chelating resin is prepared by coupling Amberlite XAD-2 with SAL and then IDA. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Co(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 90.09 ($mg\,g^{-1}$) at 25°C. The R_L values showed that the Amberlite XAD-2–SAL/IDA was favorable for the adsorption of Co(II). Preconcentration by this resin combined with FAAS and ICP-AES can be applied to the determination of trace cobalt(II) ions in water and the mineral reference sample with satisfactory results.

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