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Uptake of lead(II) from water sample by 2-allyl-phenol-functionalized amberlite XAD-4: isotherm and thermodynamic study

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ABSTRACT

A new polymeric sorbent is prepared by coupling Amberlite XAD-4 with phenol through an azo spacer, then modified by allyl bromide and characterized using FTIR, elemental analysis, and thermogravimetric analysis 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 is 80 mg g^{-1}. The modified sorbent can be reused for 20 cycles of sorption–desorption without any significant change in sorption capacity. A recovery of 89–95% was obtained for the metal ion with 0.5 mol L^{-1} nitric acid as eluting agent. The profile of lead uptake by this sorbent reflects good accessibility of the active sites in the Amberlite XAD-4-[2-(allyl-phenol)]. 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 to be 1.60, 44.00, and 51.83 at pH 5.5 and 20°C, respectively. The method was applied for lead ions determination from human plasma and sea water sample.

Keywords: Solid phase extraction; Amberlite XAD-4; Preconcentration; Lead; Isotherm study; Thermodynamic study

1. Introduction

Recently, heavy metals pollution in natural water has received increasing tremendous attention. The toxic heavy metals such as Pb, Cd, and Hg are insignificant elements in human body and are capable of causing ecological risk to aquatic organisms. The toxic heavy metals could gradually accumulate in human body through the food chain and cause dam-

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age to human health [1]. Lead accumulates in the skeleton, especially in bone marrow. It is a neurotoxin and causes behavioral abnormalities and 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 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 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 like 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 $\mu g\,L^{-1}$ 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 elements with 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], and cloud point extraction [12,13].

The purpose of present study is to indicate the feasibility of using Amberlite XAD-4-[2-(allyl-phenol)] as a solid-phase extractant for preconcentration of trace lead in biological fluids and environmental water samples. Trace lead can be retained on the surface of Amberlite XAD-4-[2-(allyl-phenol)] and then desorbed with 0.5 mol L^{-1} nitric acid prior to determination by flame atomic absorption spectroscopy (FAAS). This proposed novel method has advantages of good accuracy and precision, high recovery, and preconcentration factor. Polar adsorption sites on the sorbent arise from surface oxygen (OH groups) that interacts strongly with polar compounds like heavy metals. Moreover, the combination of OH groups beside π electrons on the polymeric sorbent for capturing the heavy metal ions was more successful than two vicinal OH groups [14].

2. Experimental

2.1. 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) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES), Varian, model Vista were used for concentration measurement 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).

2.2. Reagents and solutions

$SnCl_2$, HCl, H_2SO_4, HNO_3, $NaNO_2$, NaOH, KI, NaCl, CH3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4, $Pb(NO_3)_2$, $FeSO_4{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $NiSO_4{\cdot}6H_2O$, $ZnSO_4{\cdot}7H_2O$, CH_3COCH_3, C_2H_5OH, phenol, Sn powder, and allyl bromide were products of Merck (Darmstadt, Germany). Amberlite XAD-4 resin (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 solutions were prepared in deionized water using analytical grade reagents.

The stock solution ($1{,}000\,mg\,L^{-1}$) of Pb(II) was prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ in deionized water. 10 mL, 0.1 mol L^{-1} acetic acid—acetate buffer (pH 3–6.5), 0.01 mol L^{-1} phosphate buffer (pH 6.5–9) were used to adjust the pH of the solutions, wherever suitable.

2.3. Synthesis of Amberlite XAD-4-[2-(allyl-phenol)]

Amberlite XAD-4 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℃ 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 mL of concentrated HCl, and 50 mL of ethanol. The mixture was refluxed for 12 h at 90℃. 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 aliquits 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 phenol (0.03 mol) in sufficient amount of 10% NaOH solution. The reaction mixture was stirred at 0–5°C for 24 h. The colored beads of [Amberlite XAD-4-(phenol)] were filtered, washed with water, and dried in air. After that, phenol immobilized Amberlite XAD-4 (3 g) was treated with allyl bromide (0.03 mol), potassium carbonate (0.03 mol), and 20 mL of acetone in reflux condition for 10 h. As previous step, the resulting new resin Amberlite XAD-4-[2-(allyl-phenol)] was filtered and washed with water and dried in air. The methodology used to synthesize modified XAD-4 resin is summarized in Fig. 1.

2.4. Batch method

A set of solutions (the volume of each 100 mL) containing 0.5 μg mL^{-1} of Pb(II) was taken, and the pH was adjusted to optimum value (5.5). The 0.05 g of Amberlite XAD-4-[2-(allyl-phenol)] was added to the beakers and the mixture was shaken for optimum time (20 min). The resin was filtered and sorbed metal ion was eluted with 0.5 mol L^{-1} 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 Pb(II) (10–100 μg mL^{-1}). The beakers were then sealed and placed in a water bath shaker for 4 h at pH 5.5 and at 20, 30, and 40°C, respectively. pH adjustments have been done using 0.01 mol L^{-1} acetate buffer. The beak-

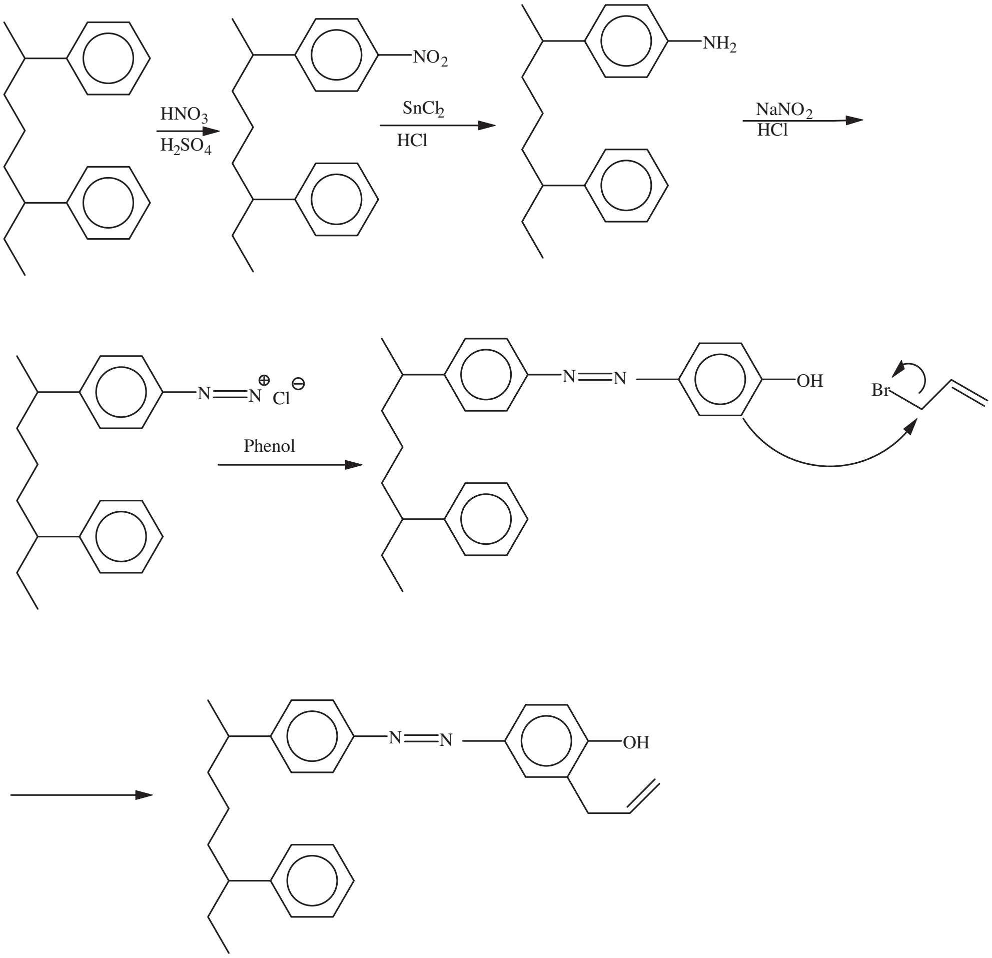


Fig. 1. The methodology of synthesis of Amberlite XAD-4-[2-(allyl-phenol)].

ers 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) on Amberlite XAD-4-[2-(allyl-phenol)] was calculated from the following equation:

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

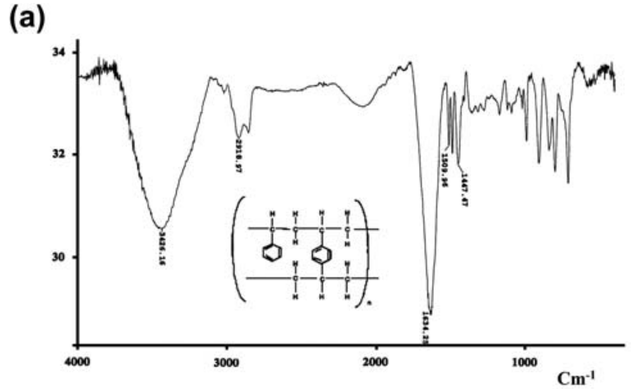
where C_0 and C_e ($\mathrm{mg\,L^{-1}}$) are the liquid phase concentrations of Pb(II) at initial and equilibrium, respectively, V (L) the volume of the solution, and W (g) is the mass of adsorbent used.

3. Result and discussion

3.1. Characterization of resin

3.1.1. IR spectrum

The IR spectrum of 2-allyl-phenol loaded Amberlite XAD-4 (Fig. 2) is compared with that of free Amberlite XAD-4. There are seven additional bands at (920 and 994), 1,362, 1,420, 1,603, 1721, and 3,433 $\mathrm{cm^{-1}}$ which appear to originate due to contribution of vinyl group, C–N, CH_2 (bending), N=N, C=O, and OH vibrations, respectively.



Amberlite-XAD-4

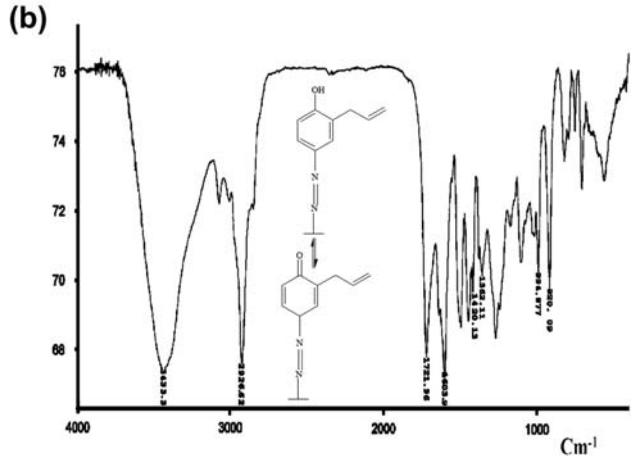


Fig. 2. The IR spectrum of (a) Amberlite XAD-4 and (b) Amberlite XAD-4-[2-(allyl-phenol)].

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℃ 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. 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-4-[2-(allyl-phenol)] (found: C, 73.38; H, 7.04; N, 4.97%; calculated for $(C_8H_8)_2\,C_9N_2H_8O(H_2O)_1$: C, 77.31; H, 6.73; N, 7.25%) show that on an average, one 2-(allyl-phenol) molecule is present in each two repeated units of the polymer. The variation between values of C, H, and N is found and calculated one is due to cross-linking agent, divinyl benzene, in the polymer backbone which is not considered in calculation.

3.1.3. Thermal analysis

TGA of the Amberlite XAD-2 shows one-step weight loss up to 600℃ in nitrogen atmosphere. The polymeric sorbent is stable up to 400℃. The major weight loss after 400℃ is due to decomposition of the polymer. Amberlite XAD-4-[2-(allyl-phenol)] shows completely different thermal behavior. The modified sorbent is stable up to 300℃. The weight loss up to 100℃ was due to the water molecules in the polymer and the weight loss 300–600 was due to the dissocia-

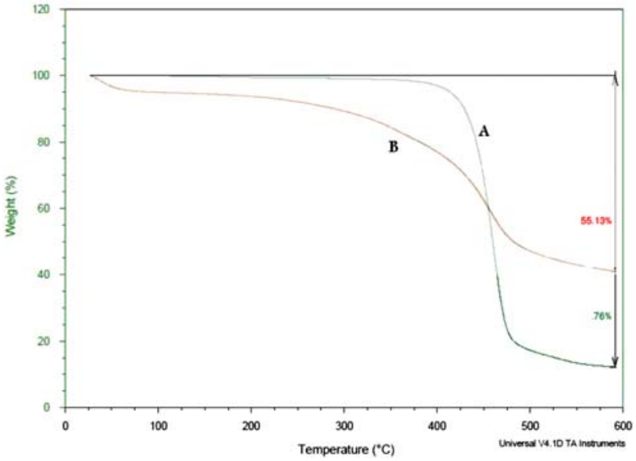


Fig. 3. Thermogravimetric analysis of Amberlite XAD-4 (A) and Amberlite XAD-4-[2-(allyl-phenol)] (B).

tion of chemically immobilized moiety and the polymeric matrix (Fig. 3).

3.2. 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 0.01 M acetate and/or phosphate buffer solutions. The 0.05 g of Amberlite XAD-4-[2-(allyl-phenol)] 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-4-[2-(allyl-phenol)] 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 was 100% at pH 5.5. At acidic pH values, pH < 5.5, immobilized ligand cannot act as agent adsorbing cationic forms of Pb(II) in solution, because the unbounded electron pair in O was blocked by hydrogen ions. At pH above 7, the recovery was decreased because in presence of OH^-, precipitation of Pb(II) hydroxide is formed.

3.3. Total sorption capacity

At this point, 0.05 g of Amberlite XAD-4-[2-(allyl-phenol)]was stirred for 4 h. with 50 mL solution containing 10–100 μg mL^{-1} of Pb(II) at optimum pH and 20, 30, and 40℃. 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 was shown in Fig. 5. This Figure indicates the effect of initial concentration of the Pb(II) in the solution and temperature on capacity sorption of Pb (II) by Amberlite XAD-4-[2-(allyl-phenol)]. The capacity increased with increasing initial concentration of the Pb(II) in the solution and reaches a constant value after 100 μg mL^{-1} concentration of Pb (II) (80.4 mg g^{-1}).

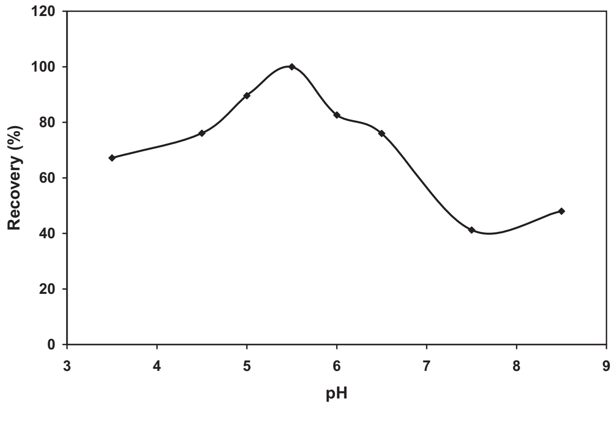


Fig. 4. Effect of pH sorption of Pb(II), onto Amberlite XAD-4-[2-(allyl-phenol)].

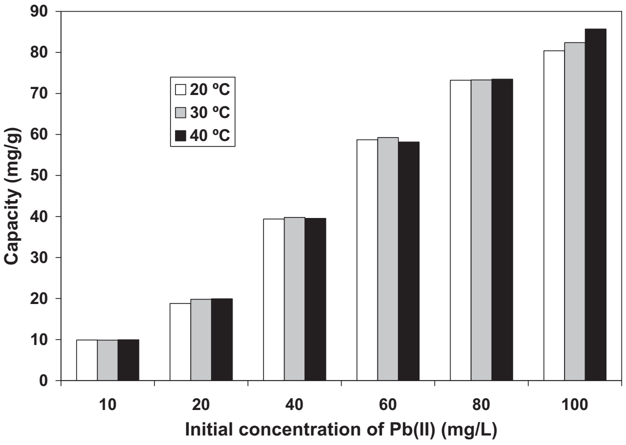


Fig. 5. Effect of initial concentration of the Pb in the solution and temperature on capacity sorption of Pb(II) onto Amberlite XAD-4-[2-(allyl-phenol)].

3.4. Stability and reusability of the sorbent

The Pb(II) was sorbed and desorbed on 1 g of the Amberlite XAD-4-[2-(allyl-phenol)] several times. It was found that sorption capacity of resin after 10 cycles of its equilibration with Pb(II) changes less than 10%. Therefore, repeated use of the resin is feasible. The resin cartridge after loading with samples can be readily regenerated with 0.5 mol L^{-1} HNO_3. The sorption capacity of the resin stored for more than six months under ambient conditions has been found to be practically unchanged.

3.5. Optimization of sorption time of lead ions

Amberlite XAD-4-[2-(allyl-phenol)] (0.05 g) was shaken with 50 mL of solution containing 80 μg mL^{-1} of Pb(II) for different length of time (10, 15, 30, 45, 60, 90, and 120 min) under optimum pH (5.5). After filtration of the sorbent, the concentration of lead ions in solution was determined with FAAS using the recommended batch method. Less than 10 min shaking was required for 95% sorption. The profile of lead uptake on this sorbent reflects good accessibility of the active sites in the Amberlite XAD-4-[2-(allyl-phenol)].

3.6. Adsorption isotherms

The Langmuir equation was given in the following form [15]:

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

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:

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

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e vs. C_e (Fig. 6).

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of Amberlite XAD-4-[2-(allyl-phenol)] surface. Langmuir parameters calculated from Equation (3) are listed in Table 1.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L, defined as [16]:

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

Table 1 shows the values of R_L (0.0048–0.0057) were 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 [17]:

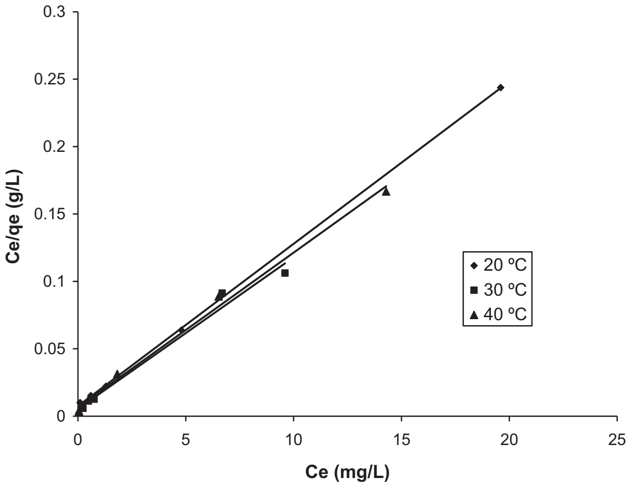


Fig. 6. Langmuir isotherm for Pb(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at optimum pH.

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

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

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

Therefore, a plot of In q_e vs. ln C_e (Fig. 7) 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 [18]:

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

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 heat of sorption (J/mol). A is the Temki isotherm constant $(\mathrm{L\,g^{-1}})$, R the gas constant (8.314 J/mol K), and T is the absolute temperature (K). Therefore plotting q_e vs. $\ln C_e$ (Fig. 8) enables 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 [19]:

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

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

where $g = 1$

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

Table 1
Isotherm parameters obtained by using linear methods

Langmuir isotherm model

Temperature (℃)	$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
20	83.33	1.60	0.0062	0.9999
30	84.49	2.09	0.0048	0.9791
40	86.95	1.74	0.0057	0.9948

Frendlich isotherm model

Temperature (℃)	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	n	R^2
20	44.00	2.17	0.9632
30	44.04	2.77	0.9482
40	44.93	2.96	0.9651

Temkin isotherm model

Temperature (℃)	A (L g^{-1})	B (J mol^{-1})	b (J mol^{-1})	R^2
20	51.83	12.53	194.4	0.9608
30	18.84	16.13	156.17	0.9824
40	95.84	11.46	226.99	0.9930

Redlich–Peterson isotherm model

	g	B (dm^3 mg^{-1})^g	A (dm^3 g^{-1})	R^2
	1.03	1.163	110	0.9998

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

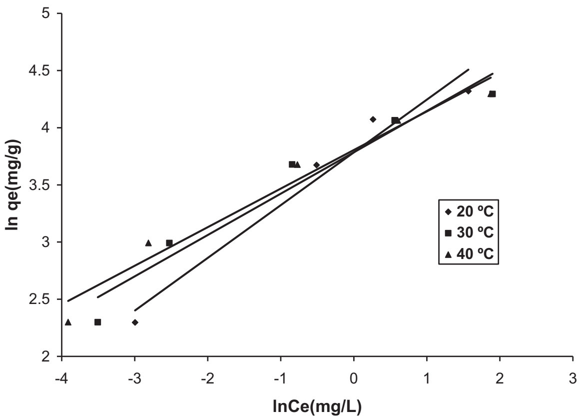


Fig. 7. Freundlich isotherm for Pb(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at optimum pH.

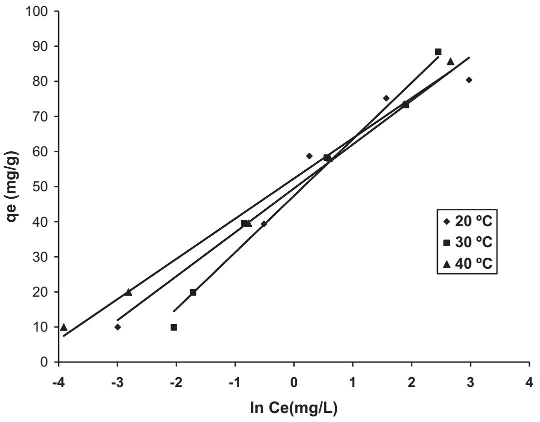


Fig. 8. Temkin isotherm for Pb(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at optimum pH.

i.e. the Langmuir form results.
where constants A and B are much greater than unity [20]:

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

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

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

i.e. the 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 optimization to maximize the coefficient of determination, R^2, for a series of values of A for 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-4-[2-(allyl-phenol)] 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 Pb(II) on Amberlite XAD-4-[2-(allyl-phenol)].

3.7. 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 [21–22]:

Table 3
Thermodynamic parameters of Pb(II) adsorption on Amberlite XAD-4-[2-(allyl-phenol)]

Temperature (˚C)	Thermodynamic parameters		
	ΔG°_a (kJ mol^{-1})	ΔH°_a (kJ mol^{-1})	ΔS°_a (J mol^{-1} K^{-1})
20	−2.485	48.960	170.09
30	−3.494		
40	−3.828		

$$\Delta G^\circ_a = -RT \ln K_L \tag{14}$$

$$\ln K_L = \frac{\Delta S^\circ_a}{R} - \frac{\Delta H^\circ_a}{RT} \tag{15}$$

where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature, and K_L (L/mg) is the Langmuir thermodynamic constant. By plotting a graph of ln K_L vs. $1/T$ (figure not shown) the values δH°_a and ΔS°_a can be estimated from the slopes and intercepts. Table 3 shows the negative values of ΔG°_a and positive ΔH°_a obtained indicated that the Pb(II) adsorption process is spontaneous and endothermic. The positive value of ΔS° suggests that increased randomness at the solid/solution interface occur in the internal structure of the adsorption of Pb(II) onto Amberlite XAD-4-[2-(allyl-phenol)].

3.8. Scatchard analysis

Scatchard analysis was employed to further analyze the binding isotherms, which is an approximate model commonly used in solid phase extraction (SPE) characterization. The Scatchard equation can be expressed as, $Q/C = (Q_{max} - Q)/K_d$, where C (μmol mmL^{-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. Fig. 9 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 $Q/C = -273.83Q + 115{,}728$ ($R^2 = 0.9872$), suggesting that the homogeneous recognition sites for lead were formed in the SPE resin. From the slope (−273.83 ($1/K_d$)) and intercept (115,728 (Q_{max}/K_d)), K_d and Q_{max}

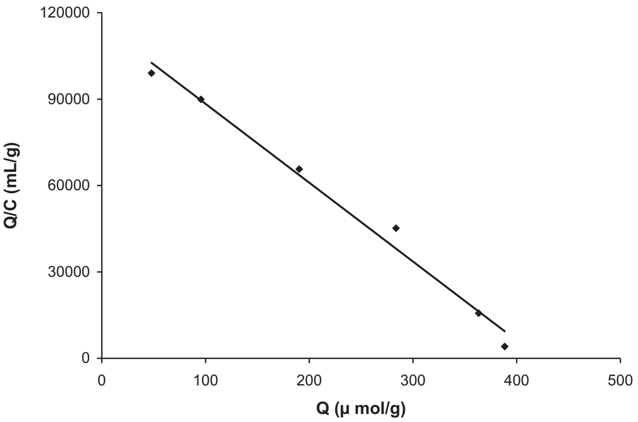


Fig. 9. Scatchard plots of Pb(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at 20˚C.

Table 4
Effect of other ions on sorption

Interfering ions	Amount of adsorbed Pb(II) (mg L^{-1})	Loss adsorption%
—	19.90	0
Ni(II)	18.80	5.5
Co(II)	19.70	1.0
Fe(II)	19.64	1.31
Hg(II)	19.40	2.51
Zn(II)	19.26	3.22
Ba(II)	19.60	1.51
Ag(I)	19.64	1.31
Cu(II)	19.45	2.26
K(I)	19.40	2.51
Al(III)	18.28	8.14
Na(I)	19.90	0
Ca(II)	19.11	3.97
Mg(II)	19.48	2.11
Mixed above ions	18.00	9.55

for the affinity binding sites were calculated to be 0.0037 µmol mL^{-1} and 422.6 µmol g^{-1}, respectively.

3.9. Effect of foreign ions

In order to evaluate the selectivity of the preconcentration system, the effect of some metal ions at the concentration 20 mg L^{-1} on the sorption behavior of Pb(II) (20 mg.L^{-1}) was investigated. Table 4 indicates the Pb(II) adsorption by Amberlite XAD-4-[2-(allyl-phenol)]is mostly affected by Al (III), Ni (II), and Zn (II) whereas the effects of other foreign ions at given concentrations are is negligible allowing for quantitative Pb(II) determination in environmental samples.

3.10. Comparison with other methods

The data available in the literature on preconcentration of Pb(II) by various methods are compiled in Table 5. The sorption capacity of the Amberlite XAD-4-[2-(allyl-phenol)] and recovery of the present sorbent are superior in comparison to all the matrices shown in Table 5. This new developed method has been successfully applied to the analysis of trace lead ions in natural water sample.

3.11. Application of method

Amberlite XAD-4-[2-(allyl-phenol)] preconcentration followed by ICP-AES was used for the determination of Pb(II) in the water samples from The Persian Gulf (Boshehr, Nuclear Power Plant, Iran) and well water (Pishva, Varamin, Iran). The results are shown in Table 6 and based on the average of three replicates. These results demonstrate the applicability of the procedure for lead determination in samples with high recovery.

Adsorption of Pb(II) by Amberlite XAD-4-[2-(allyl-phenol)]from human plasma was also studied batch

Table 5
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	[23]
Microcrystalline triphenylmethane loaded with quinolin-8-olate	98	100	—	[24]
Gallic acid-modified silica gel	96	25	12.63	[25]
Cellulose modified with triethylenetetramine	—	—	192.3	[26]
Sugarcane bagasse chemically modified with succinic anhydride	—	—	416.7	[27]
Chitosan modified ordered mesoporous silica	95	—	22.9	[1]
Macroporous epoxy resin-based polymer monolithic matrix	97	10	106.8	[28]
Thioureasulfonamide resin	97	20	0.5	[29]
Dibenzyldithiocarbamate chelates on Dowex Optipore V-493	96	4–8	8.6	[30]
Amberlite XAD-2 with chromotropic acid	97	4–10	186.3	[31]
Amberlite XAD-2 with pyrocatechol	94	4–10	104.7	[31]
Amberlite XAD-2 with thiosalicylic acid	93	4–10	89.3	[31]
Amberlite XAD-7 with xylenol orange	91	4–10	16.9	[31]
Amberlite XAD-4-[2-(allyl-phenol) (Our resin)	100	10	80.4	—

Table 6
Results obtained for Pb(II) determination in plasma and water sample of The Persian Gulf (I), (II), and (III), and well water (IV) and (V)

Analyte	Plasma	(I)	(II)	(III)	(IV)	(V)
Sample (without spiking of Pb(II))	N.D.	N.D.	N.D.	N.D.	0.06	0.06
Added Pb(II) (μg mL^{-1})	0.4	0.20	0.40	0.60	—	0.20
Found Pb(II), after preconcentration (μg mL^{-1})	1.78	1.85	3.70	5.6	0.57	2.42
Preconcentration factor	5	10	10	10	10	10
Recovery (%)	89	92.5	92.5	93.3	95.0	93.1
Standard deviation[a]	0.017	0.068	0.14	0.10	0.014	0.056
Relative standard deviation (%)[a]	1.9	3.7	3.7	1.8	2.5	2.3

[a] For three determinations.

wise. Human blood was collected from thoroughly controlled voluntary blood donors. Each unit 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 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 Pb(II) in the plasma, 25 mL plasma was spiked with 0.005 mg of Pb(II) before subjecting it to the preconcentration procedure. Then 25 mL sample of human serum containing 0.4 μg mL^{-1} of Pb(II) was treated with 0.1 g of Amberlite XAD-4-[2-(allyl-phenol)] resin at room temperature and stirred magnetically at a speed of 600 rpm. After the defined treatment periods, the sorbent was taken out and adsorbed Pb(II) was eluted with 0.5 mol L^{-1} nitric acid (5 mL). The results are shown in Table 6 and indicate the suitability of the present sorbent for the preconcentration of lead from plasma samples.

3.12. Analytical performance of the proposed system

Seven replicate determinations of 0.6 mg L^{-1} lead solutions gave a relative standard deviation of 2.6%. The limit of detection corresponding to three times the standard deviation blank was found to be 14.9 μg L^{-1}. The limit of quantification corresponding to 10 times the standard deviation blank was found to be 49.7 μg L^{-1}.The regression equation (after preconcentration) was $A = 0.014C_{Pb}—0.002$ ($R^2 = 0.99970$), and the conventional regression equation was $A = 0.005C_{Pb} + 0.005$ ($R^2 = 0.9975$).The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 2.9. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10.

4. Conclusion

New polymeric sorbent shows higher adsorption selectivity for Pb(II) ions and adsorbed ions can be readily desorbed from the resin by 10 mL of 0.5 mol/L nitric acid solution. 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 83.33, 84.49, and 86.95 (mg g^{-1}) at 20, 30, and 40˚C, respectively. The R_L values showed that the Amberlite XAD-4-[2-(allyl-phenol)] was favorable for the adsorption of Pb(II). The sorbent was successful for Pb(II) capture from biological and environmental samples (recovery > 90% with preconcentration of 10 and capacity of 80 mg/g). It seems the combination of OH groups beside π electrons on the polymeric sorbent for capturing the heavy metal ions was too successful to surprise the authors.

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