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Modification and characterization of amberlite XAD-2 with calcein blue for preconcentration and determination of copper(II) from environmental samples by atomic absorption spectroscopy

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Abstract−A chelating resin is produced by coupling a dye calcein blue to Amberlite XAD-2 through an azo spacer. The resulting resin has been characterized by FT-IR, elemental analysis, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) studied for the preconcentration and determination of trace Cu(II) from solution samples. The optimum pH for adsorption of copper ions was 6. The sorption capacity of functionalized resin is 27 mg·g^{-1}. The chelating resin can be reused for 10 cycles without any significant changes in sorption capacity. A recovery of 100% was obtained for Cu(II) when eluted with 0.5 M nitric acid. Scatchard analysis revealed that homogeneous binding sites were formed in the resin. The equilibrium adsorption data of Cu(II) on modified resin were analyzed by Langmuir, Freundlich and Temkin models. Based on equilibrium adsorption data the Langmuir, Freundlich and Temkin constants were determined 0.036, 2.196 and 0.348 at pH 6 and 20 °C, respectively. The method was applied for Cu(II) assay in environmental samples.

Key words: Copper, Preconcentration, Solid Phase Extraction, Determination, Amberlite XAD-2, Isotherm Study

INTRODUCTION

Heavy metal pollution has become a serious environmental problem as a result of its toxicity and insusceptibility to the environment, and therefore rapid and sensitive methods must be accessible for determination of toxic metals in actual samples [1]. Copper is an important bioelement that is present in animals, plants and microorganisms. It is both vital and toxic to many biological systems, depending on the level of concentration. In biosystems copper exists in two characteristic forms, with oxidation numbers of I and II, and takes part in oxidation–reduction processes. One notable function of copper is its influence on the metabolism of iron; another is its direct influence on the activity of some enzymes [2]. The determination of trace metals by FAAS among the determination techniques has a number of advantages including high selectivity, speed and fairly low operational cost. However, preconcentration is usually required for the determination of trace metals in various samples by FAAS because of complex matrices of samples and low concentrations of some metals, which are near or below the limit of detection of the instrument [4]. For this purpose, numerous separation and preconcentration procedures have been developed for trace metal ion determination in various matrices. These methods include ion exchange [5], solvent extraction [6], cloud-point extraction [7], co precipitation [8] and solid phase extractions [9-12]. Solid phase extraction based on a solid support impregnated with a chelating agent, has gained special attention due to the advantages in the use of these substances in metal ion enrichment for the determination of their trace levels in various matrices. There is a continued interest in the development of modified solid supports that can provide good stability and high sorption capacity for metal ions [13-17].

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

EXPERIMENTAL

1. Instruments

A 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 was measured 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 done by using a TGA-50H (Shimadzu Corporation).

2. Reagents and Solutions

$SnCl_2$, HCl, H_2SO_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, CH_3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4, Pb $(NO_3)_2$, $FeSO_4·7H_2O$, $CuSO_4·5H_2O$, $Co(NO_3)_2·6H_2O$, Ni $SO_4·6H_2O$, Zn $SO_4·7H_2O$, calcein blue, ethanol, ethylenediaminetetraacetic acid

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(EDTA), CH_3COCH_3, C_2H_5OH and Sn powder were products of Merck (Darmstadt, Germany). Amberlite XAD-2 resin (surface area 745 m^2/g, pore diameter 5 nm, and bead size 20 to 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 $mg \cdot L^{-1}$) of Cu(II) was prepared by dissolving appropriate amounts of $Cu(NO_3)_2$, in deionized water. To adjust the pH of the solution, 10 mL of 0.1 M acetic acid - acetate buffer (pH 3-6.5) or 0.01 M phosphate buffer (pH 6.5-9) was used wherever suitable.

3. Synthesis of Amberlite XAD-2-Calcein Blue (Amberlite XAD-2-CAL)

Amberlite XAD-2 beads (5 g) were treated with 10 mL of con-

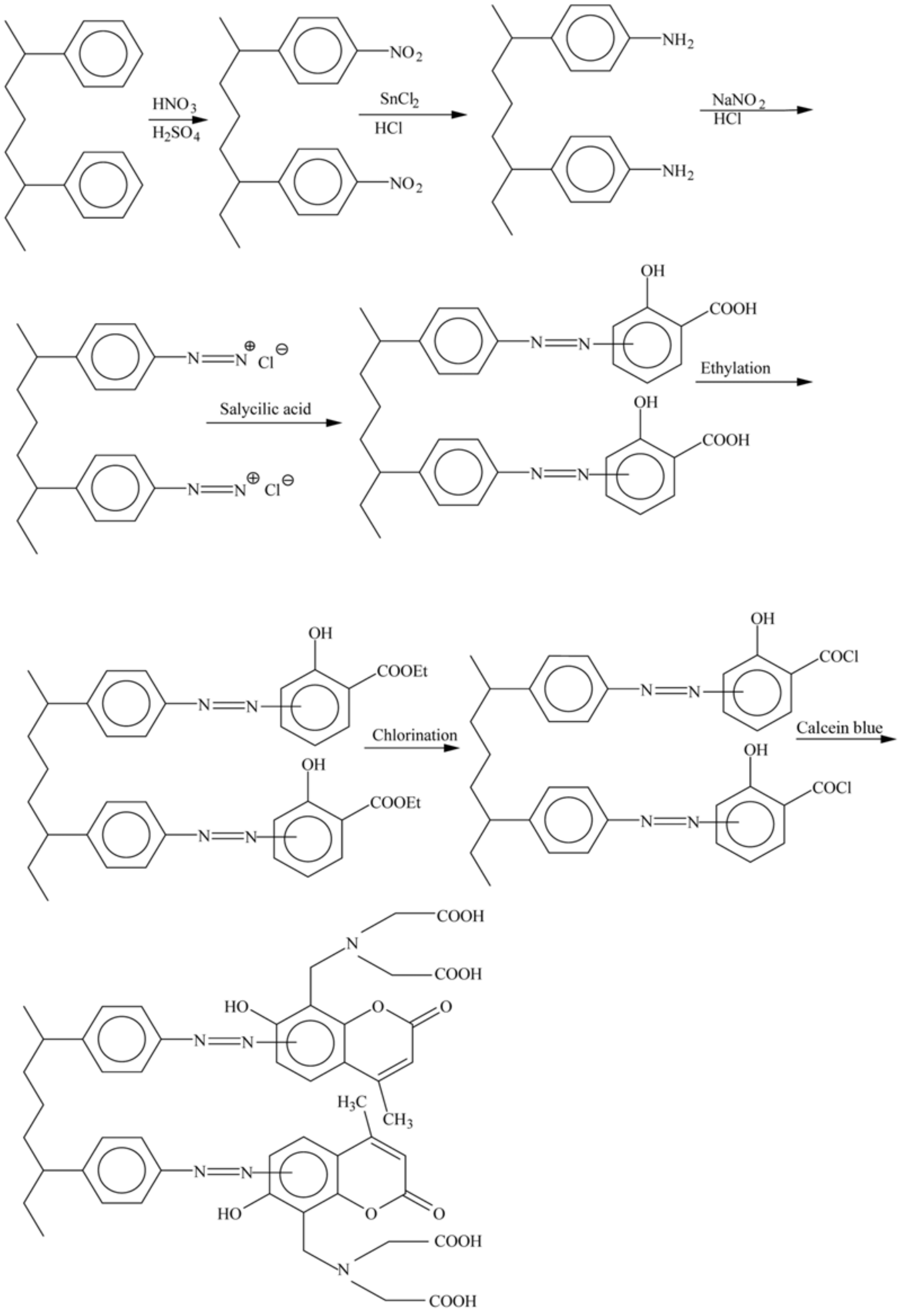


Fig. 1. The methodology of synthesis of Amberlite XAD-2-CAL.

centrated HNO_3 and 25 mL of concentrated H_2SO_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 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 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 calcein blue (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 beads were filtered and washed with water. The methodology used to synthesize modified XAD-2 resin is summarized in Fig. 1.

4. Batch Method

A sample solution (100 mL) containing (0.5 μg·mL^{-1}) of Cu(II) was taken in a glass stoppered bottle, and the pH was adjusted to optimum value. Then 0.05 g of Amberlite XAD-2-CAL 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 eluent was determined by FAAS.

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 Cu(II) (10-100 μg·mL^{-1}). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with the required adsorbent time (4 h) at 20, 30 and 40 °C and optimum pH (6). pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Cu(II) in the solution was measured by FAAS. The amount of Cu(II) at equilibrium q_e (mg·g^{-1}) on Amberlite XAD-2-CAL 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 Cu(II) at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

RESULT AND DISCUSSION

Characterization of the Resin

1. IR Spectrum

The IR spectrum of calcein blue loaded Amberlite XAD-2 is compared with that of free Amberlite XAD-2. There are some additional bands at 1,619 and 3,445 cm^{-1} which appear to originate due to modification of N=N and (O-H, NH_2) vibration, respectively.

2. Elemental Analysis

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

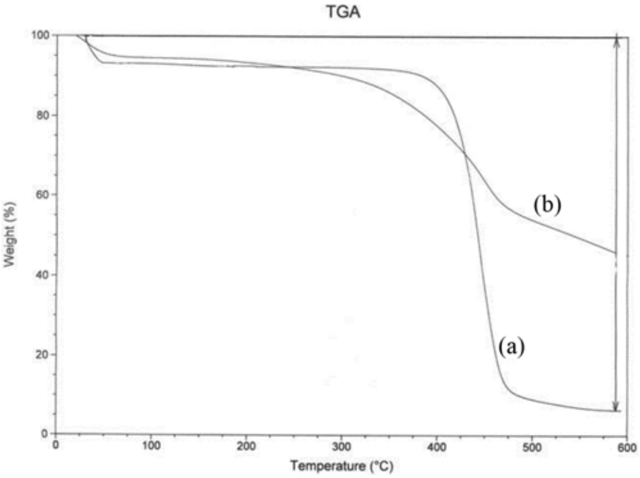


Fig. 2. Thermogravimetric analysis of Amberlite XAD-2 (a) and Amberlite XAD-2-CAL (b).

The elemental analysis for Amberlite XAD-2-SAL (found: C, 66.14; H, 6.78; N: 7.71%, calculated for $(C_8H_8.C_8H_7)$ $C_{15}H1_5N_3O_7$: C, 67.02; H, 5.20; N, 7.56%) show that on an average one calcein blue molecule is present in each two repeated units of the polymer.

3. Thermal Analysis

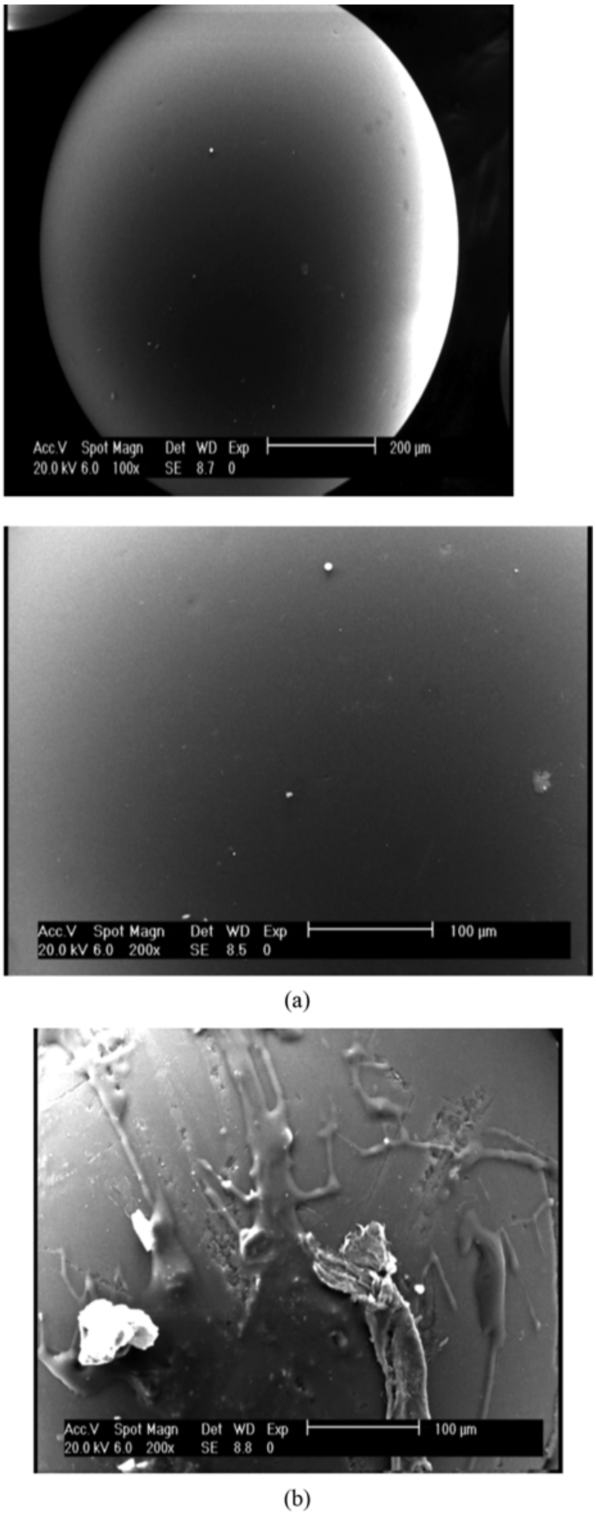
TGA of the Amberlite XAD-2 shows two-step weight loss up to 600 °C (Fig. 2). The weight loss up to 100 °C was due to the water molecules in the polymer. The major weight loss after 400 °C is due to decomposition of the polymer. Amberlite XAD-2-CAL shows completely different thermal behavior. The weight 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.

4. Scanning Electron Microscopy

In this investigation Amberlite XAD-2 resin with surface area 745 m^2/g, pore diameter 5 nm, and bead size 20 to 60 meshes was used. The surface morphology and internal structure of polymer beads were investigated by scanning electron microscopy (Fig. 3). As clearly seen here, Amberlite XAD-2 is comprised of heterogeneous and smooth small particles. In comparison with the unmodified Amberlite, the surface of Amberlite XAD-2-CAL was more coarse and groovy, most probably due to partial matrix degradation during the harsh chemical treatment used for calcein blue immobilization.

5. Metal Sorption as a Function of pH

The degree of 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 Cu(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-2-CAL 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 Cu(II) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the



(a)

(b)

Fig. 3. SEM photograph of Amberlite XAD-2 (a) and Amberlite XAD-2-CAL (b).

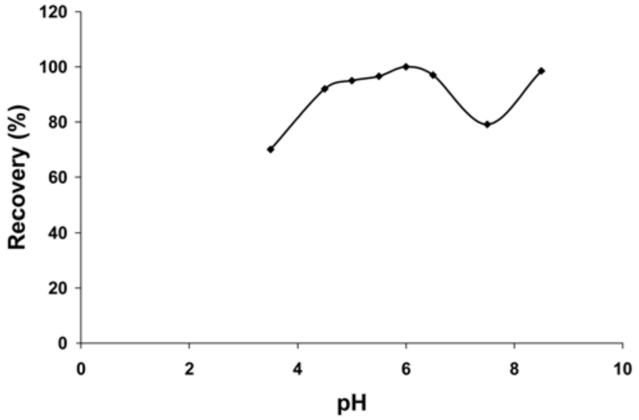


Fig. 4. Effect of pH sorption of Cu(II) onto Amberlite XAD-2-CAL.

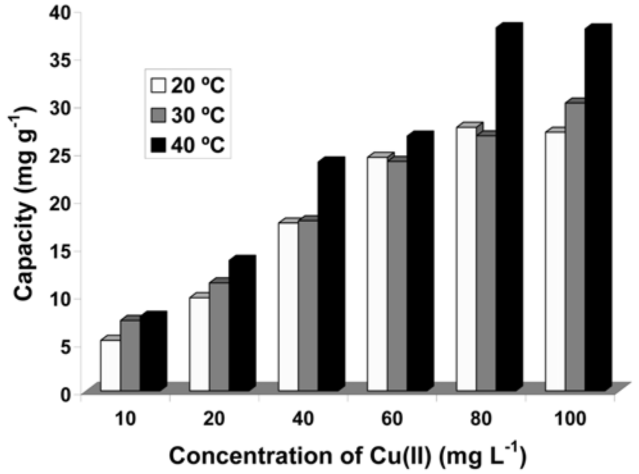


Fig. 5. Effect of initial concentration of the Cu in the solution and temperature on capacity sorption of Cu(II) onto Amberlite XAD-2-CAL.

metal ion from Amberlite XAD-2-CAL 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 6.

6. Total Sorption Capacity

At this point, 0.05 g of Amberlite XAD-2-CAL was stirred for 4 h with 50 mL solution containing 10-100 $\mu g \cdot mL^{-1}$ of Cu(II) at optimum pH and 20, 30 and 40 ºC. 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 Cu(II) in the solution and temperature on sorption capacity of Cu(II) by Amberlite XAD-2-CAL. The adsorption capacity in initial concentration of 100 $\mu g \cdot mL^{-1}$ of Cu(II) at optimum pH and 20 ºC was obtained at 27 $mg \cdot g^{-1}$.

7. Stability and Reusability of the Sorbent

The Cu(II) was sorbed and desorbed on 1 g of the Amberlite XAD-2-CAL several times. It was found that sorption capacity of resin after 10 cycles of its equilibration with Cu(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 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.

8. Sorption Kinetic Studies

Amberlite XAD-2-CAL (0.05 g) was shaken with 50 mL of solu-

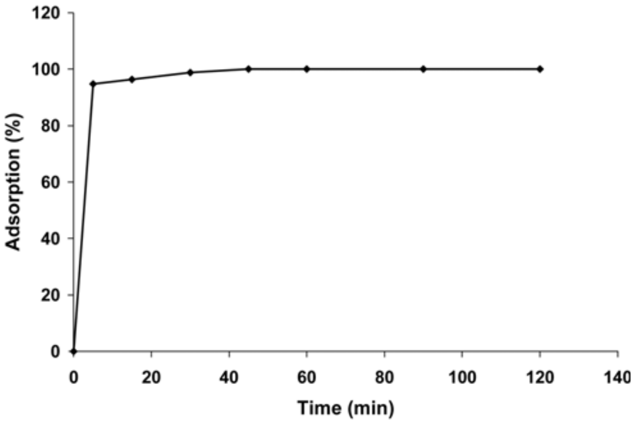


Fig. 6. Kinetics of copper sorption on Amberlite XAD-2-CAL.

tion containing 80 µg·mL^{-1} of Cu(II) for different length of time (5, 15, 30, 45, 60, 90 and 120 min) under optimum pH. After filtration of the sorbent, the concentration of copper 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 5 min shaking was required for 95% sorption. The profile of copper uptake on this sorbent reflects good accessibility of the chelating sites in the Amberlite XAD-2-CAL.

9. Adsorption Isotherms

In chromatographic operation, both the rate of adsorption and the dynamic approach to the equilibrium state will influence the quality of separation; this is usually described in terms of an adsorption isotherm. Adsorption isotherm has been widely used as a diagnostic for the characterization of ion exchangers and affinity adsorbents proposed for bioproduct adsorption. The adsorption isotherms are usually generated by contacting adsorbent with the solute in solution characteristically in batch process conditions which permit equilibrium to occur. Subsequent to such adsorption/desorption batch binding experiments, the maximum binding capacity of an adsorbent solid phase can be estimated by other methods. Several isotherm models have been proposed for determining both the dissociation constant (K_d) and the maximum binding capacity (q_{max}) including linear, Freundlich and Langmuir isotherm models.

The Langmuir equation was given in the following form [18]:

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

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

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

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 into the Langmuir isotherm model indicates the homogeneous nature of Amberlite XAD-2-CAL 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 [19]:

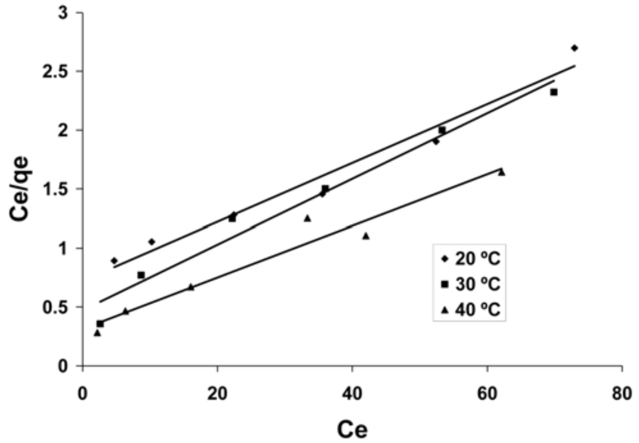


Fig. 7. Langmuir isotherm for Cu(II) adsorption onto Amberlite XAD-2-CAL at different temperatures.

Table 1. Isotherm parameters obtained by using linear method

Langmuir isotherm model

Temperature	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
20	40.00	0.035	0.224	0.9671
30	35.84	0.059	0.145	0.9724
40	45.66	0.070	0.125	0.9500

Frendlich isotherm model

Temperature	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2
20	2.196	1.58	0.9609
30	4.632	2.26	0.9934
40	5.565	2.07	0.9735

Temkin isotherm model

Temperature	A (L/g)	B (J/mol)	b (J/mol)	R^2
20	0.348	8.941	272.59	0.9686
30	0.792	7.049	357.56	0.9515
40	0.847	9.366	277.98	0.9329

Redlich-Peterson isotherm model

g	B (dm^3/mg)^g	A (dm^3/g)	R^2
1.03	0.025	1.25	0.9929

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

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

Table 1 shows the values of RL (0.125-0.224) were in the range of 0-1 at optimum pH, which confirms the favorable uptake of the Cu(II) (Table 2).

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

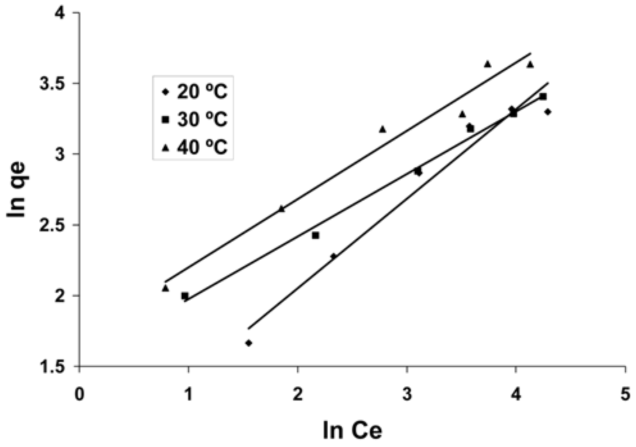


Fig. 8. Freundlich isotherm for Cu(II) adsorption onto Amberlite XAD-2-CAL at different temperatures.

by the heterogeneity factor 1/n. Hence, the empirical equation can be written as [20]:

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

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 the Eq. (5):

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

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 Cu(II) concentration on the adsorbent will increase as long as there is an increase in the Cu(II) concentration in the liquid.

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

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

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

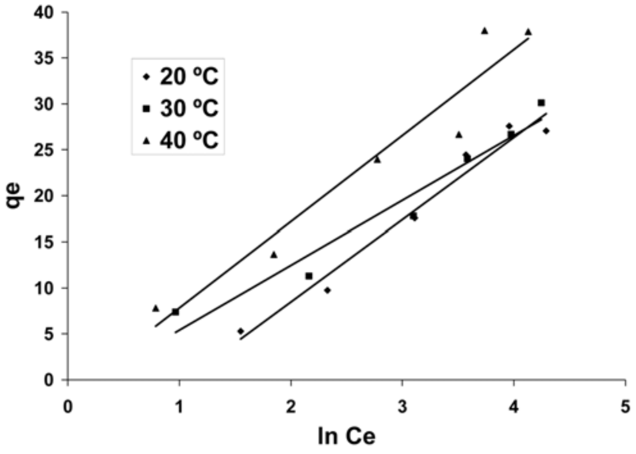


Fig. 9. Temkin isotherm for Cu(II) adsorption onto Amberlite XAD-2-CAL at different temperatures.

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 Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol. K) 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 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:

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

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

Where g=1

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

i.e., the Langmuir form results.

Where constants A and B are much greater than unity [21]

$$q_e=\frac{AC_e}{1+BC_e} \tag{11}$$

i.e., the Freundlich form results.

Where g=0

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

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 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 Cu(II) on to Amberlite XAD-2-CAL 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 equilib-

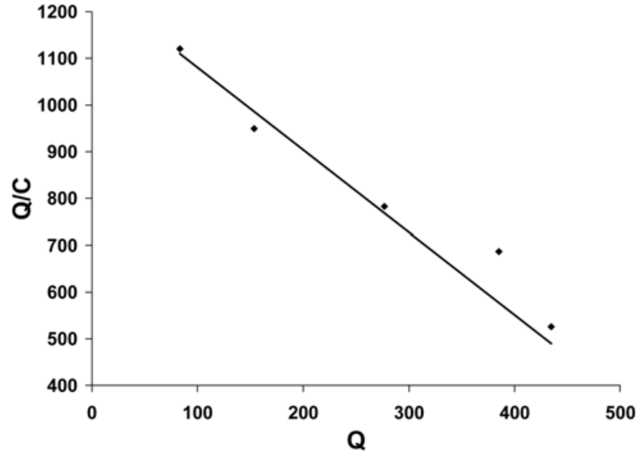


Fig. 10. Scatchard plots of Cu(II) adsorption onto Amberlite XAD-2-CAL at 20 °C.

rium data for adsorption of Cu(II) on Amberlite XAD-2-CAL.

10. 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 copper; 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. 10 shows the Scatchard plots of the binding of copper to the resin. It is clear that the Scatchard plot for resin is a single straight line. The linear regression equation was $Q/C=-1.7649\ Q+1256.8$ ($R^2=0.9127$), suggesting that homogeneous recognition sites for copper were formed in the SPE resin. From the slope (–1.7649 ($1/K_d$)) and intercept (1,256.8 (Q_{max}/K_d)), K_d and Q_{max} for the affinity binding sites were calculated to be 0.567 μmol·mL^{-1} and 712.1 μmol·g^{-1}, respectively.

Table 3. Effect of other ions on sorption

Interfering	A	L (%)	E (%)	D
___	6.81	0.00	65.93	1.935
Hg(II)	7.59	5.92	37.97	1.633
Ni(II)	8.01	9.05	40.04	1.498
Ba(II)	7.10	2.19	35.51	1.816
Zn(II)	7.76	7.19	38.82	1.576
Ag(I)	7.64	6.28	38.21	1.617
Co(II)	7.51	5.28	37.55	1.663
K(I)	7.03	1.64	35.16	1.844
Mn(II)	7.43	4.66	37.14	1.692
Al(III)	7.92	5.38	39.62	1.524
Pb(II)	8.13	10.00	40.66	1.459
Mixed above ions	7.52	5.38	37.61	1.658

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

11. 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 Cu(II) ion (concentration 20 mg·L^{-1}) was investigated. The result is shown in Table 3. This Table indicates that the most effective ions on adsorption of Cu(II) on Amberlite XAD-2-CAL are Pb(II), Ni(II). The adsorption of Cu(II) on the Amberlite XAD-2-CAL in presence of all mentioned ions (with each ion having the concentration of 20 mg·L^{-1}) shows that the Cu(II) can be determined quantitatively in the environmental samples.

12. Comparison with Other Methods

Comparative information from a number of studies on preconcentration of Cu(II) by various methods for the figure of merits is given in Table 4. The sorption capacity and recovery of the present sorbent is superior in comparison to all the matrices shown in Table 4. This new developed method has been successfully applied to the

Table 4. Comparison of recovery, preconcentration and capacities with some literatures

Resin used	R	P	C	D	T	Ref.
2,2_-Bipyridyl and erythrosine	94-98	50	-	10.3	FAAS	[23]
Manganese dioxide	96-105	80	-	5	FAAS	[24]
Cerium(IV) hydroxide	95	-	-	1.8	FAAS	[25]
Erbium hydroxide	95	25	-	0.11	FAAS	[26]
Indium hydroxide	94-103	-	-	0.6	FAAS	[27]
Modified silica gel with aminothioamidoanthraquinone	105	-	-	1	FAAS	[28]
Gallic acid-modified silica gel	98.6	200	15.38	0.65	FAAS	[29]
Benzothiazole-based chelating	74	20	-	18	FAAS	[30]
Chromosorb-102	95	-	-	0.44	FAAS	[31]
Metal alkoxide glass immobilized 8-quinolinol	99	-	-	0.05	ICP/MS	[32]
Activated carbon	101	-	-	0.02	CPI-MIP-AES	[33]
Diaion SP-850 resin	95	-	-	0.47	FAAS	[34]
5-Formyl-3-(1V-carboxyphenylazo) salicylic acid-bonded silica gel	98	-	-	0.07-14	FAAS	[35]
Amberlite XAD-2-CAL (Our resin)	100	10	27.01	3.9	FAAS	-

R: Recovery (%), P: Preconcentration factor, C: Capacity (mg·g^{-1}), D: Detection limit (μg·L^{-1}), T: Technique

ICP/MS: inductively coupled plasma mass spectrometry

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

Table 5. Results obtained for Cu(II) determination in river water sample (I) and (II) and well water sample (III)

Analyte	(I)	(II)	(III)	(IV)
Sample (without spiking of Cu(II)) ($\mu g \cdot mL^{-1}$)	N.D.	N.D.	0.11	0.11
Added Cu(II) ($\mu g \cdot mL^{-1}$)	0.20	0.60	-	0.20
Found Cu(II), after preconcentration ($\mu g \cdot mL^{-1}$)	2.02	5.98	1.06	3.04
Preconcentration factor	10	10	10	10
Recovery %	100	100	96	98
Standard deviation	0.056	0.080	0.047	0.088
Relative standard deviation (%)[a]	2.8	1.3	4.4	2.9

[a]For three determinations

analysis of trace copper ions in natural water sample.

13. Application of Method

Amberlite XAD-2-CAL was used to preconcentrate and determine Cu(II) ions in the Jajrod River (Teran state, Iran) and well water (Pishva, Varamin, Iran). The collected samples were filtered on site, acidified to pH 2 with HNO2 and kept in a plastic container. In this condition the holding time for copper ions is about 6 months [22]. The pH of water sample was adjusted to the optimum pH. Solid phase extraction with Amberlite XAD-2-CAL coupled with FAAS was applied to determination of Cu(II) in water sample. After no detection of Cu(II) in the water, a 100 mL water sample was spiked with 0.02 and 0.06 mg of Cu(II) before subjecting it to the recommended procedure. The results are shown in Table 5. These results demonstrate the applicability of the procedure for Cu determination in samples with high recovery (100%).

14. Characteristics Performance of Method

Seven replicate determinations of 0.5 mg L^{-1} Cu(II) solutions gave a relative standard deviation of 4.3. The limit of detection corresponding to three times the blank standard deviation was found to be 2.9 $\mu g\ L^{-1}$. The limit of quantification corresponding to ten times the blank standard deviation was found to be 9.7 $\mu g\ L^{-1}$. The regression equation (after preconcentration) was $A=2985C_{Cu}+35.47$ ($R^2=0.9585$), and the conventional regression equation was $A=1214\ C_{Cu}+19.72$ ($R^2=0.9566$). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 2.46. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10.

CONCLUSION

A new chelating resin is prepared by coupling Amberlite XAD-2 with calcein blue. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Cu(II) from large sample volumes. The resins also have 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 40.00, 35.84, 45.66 ($mg \cdot g^{-1}$) at 20, 30, and 40 °C, respectively. The R_L values showed that the Amberlite XAD-2-CAL was favorable for the adsorption of Cu(II). Preconcentration by this resin combined with FAAS and ICP-AES can be applied to the determination of trace copper(II) ions in water and the mineral reference sample with satisfactory results.

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