

Synthesis, characterization and application of allyl phenol modified amberlite XAD-4 resin for preconcentration and determination of copper in water samples

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Abstract—A new chelating resin was prepared by coupling Amberlite XAD-4 with phenol through an azo spacer, then modified by allyl bromide and characterized (by elemental analysis and IR) and studied for preconcentration of Cu(II) using flame atomic absorption spectrometry (FAAS) for metal monitoring. The optimum pH value for sorption of the above mentioned metal ion was 4.5. The resin was subjected to chemical evaluation through batch binding and column chromatography of Cu(II). The chelating resin can be reused for 15 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 98% was obtained for the metal ion with 0.5 M HNO₃ as eluting agent. 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 to be 0.061, 0.193 and 0.045 at pH 4.5 and 25 °C. The method was applied for the copper determination from industrial waste water sample.

Key words: Solid Phase Extraction, Amberlite XAD-4, Immobilization, Trace Element, Water Samples

INTRODUCTION

There is a continued interest in the synthesis of insoluble functionalized polymers that can provide good stability, high sorption capacity for metal ions and good flexibility under working conditions. In the recent two decades, the design of good chelating resins and use of them [1-13] for metal enrichment has increased very significantly because of their good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics. They also have many applications in solid phase extraction [5].

Amberlite XAD is a sort of resin widely used to develop several chelating materials due to its good physical and chemical properties such as porosity, high surface area, durability and purity. Advantage factors in the chelating resin are high capacity and weak metal binding [2,14]. Small amounts of high capacity resin could concentrate metal ion from a large sample volume; on the other hand, weak metal binding can be an advantage in the elution step. Selectivity is often related to the functional group of the chelating resin.

Two methods are frequently adopted for designing of good chelating resins. The first is the sorption of chelating ligands onto a matrix. The other is based on covalent coupling of a ligand with a polymer backbone through a spacer arm, generally -N-N- or -CH₂- group. Many ligands, such as salicylic acid [15], chromotropic acid [16], pyrocatechol [17], o-amino benzoic acid [3], 2-(methylthio) aniline [18], succinic acid [19], 2-aminothiophenol [8], and derivative of benzoic acid [6] were covalently coupled with a polymer backbone

through an Azo (-N=N-) [13,20] methylene (-CH₂-) [21] or other groups [11,22].

In the present work, Amberlite XAD-4-[2-(allyl-phenol)], was prepared via covalent bonding on the surface of Amberlite XAD-4 resin to be used as an adsorbent. The procedures of adsorbing/stripping elements on new polymers, measurement of concentration by atomic absorption spectroscopy (AAS), and optimization of pH conditions are described in this paper. Trace element was pre-concentrated on the synthesized modified Amberlite XAD-4 by column method for atomic absorption spectrometric determination.

MATERIALS AND METHODS

1. Instruments

A flame atomic absorption spectrometer of the Shimadzu, model AA-680, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L·min⁻¹, respectively) was used for measuring the concentration of metal ions. The pH measurements were made with Metrohm model 744 (Switzerland). IR spectra were recorded on an FT-IR spectrometer Jasco/FT-IR-410 by KBr pellet method. Elemental analysis was performed on an elemental analyzer from Thermo-Finnigan (Milan, Italy) model Flash EA. TGA analysis was carried out by using TGA-50H (Shimadzu, Japan). A pump (DV-42 N-250) was used control the flow of liquid through column. The sorption and desorption studies of metal on the chelating matrix were generally done on columns of 7 mm diameter and 7 cm in length.

2. Reagents and Solutions

CH₃COOH, NaH₂PO₄, Na₂HPO₄, Cu (NO₃)₂·3H₂O, SnCl₂, HCl, H₂SO₄, HNO₃, NaNO₂, NaOH, allyl bromide, phenol and iodide-starch paper were products of Merck (Darmstadt, Germany). Amberlite XAD-4 resin (surface area 745 m²/g, pore diameter 5 nm and

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bead size 20-60 mesh) was obtained from Serva.

Standard solutions were prepared in deionized water using analytical grade reagents. The stock solution ($1,000 \text{ mg} \cdot \text{L}^{-1}$) of Cu(II) was prepared by dissolving appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in deionized water. 10 mL, 0.01 M acetic acid - acetate buffer (pH 3-5), 0.01 M phosphate buffer (pH 6-9) were used to adjust the pH of the solutions, wherever suitable.

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 cm^3 of concentrated H_2SO_4 and the mixture stirred at 60°C for 1 h in an oil bath. Then the reaction mixture was put 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 NaOH which released amino resin (R-NH_2) from $(\text{RNH}_3)_2 \text{SnCl}_6$ (R =resin matrix). The amino was first washed with 2 mol/L HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice-water mixture (350 L) and treated with 1 mol/L HCl and 1 mol/L 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 phenol (0.03 mol) in sufficient amount of 10% NaOH solution. The reaction mixture was stirred at $0-5^\circ\text{C}$ 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 a previous step, the resulting new resin Amberlite XAD-4-[2-(allyl-phenol)] was filtered, washed with water and dried in air. The procedure used to synthesize modified XAD-4 resin is summarized in Fig. 1.

4. Batch Method

A sample solution (100 mL) containing ($0.3 \text{ } \mu\text{g} \cdot \text{mL}^{-1}$) of one of Cu(II) was taken in a glass stoppered bottle, after adjusting its pH

to the optimum value. 0.1 g of Amberlite XAD-4-[2-(allyl-phenol)] 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 HNO_3 (10 mL). The concentration of metal ion in the eluate was determined by flame atomic absorption spectrometry.

5. Column Method

Amberlite XAD-4-[2-(allyl-phenol)] (0.1 g) was packed in the polypropylene column ($0.7 \times 7 \text{ cm}^2$) and treated with 20 mL of 1 M HNO_3 and washed with double-distilled water until the resin was free from acid. 50 mL aliquot of the solution containing of Cu(II) in the concentration $0.3 \text{ } \mu\text{g} \cdot \text{mL}^{-1}$ was passed through this column after adjusting its pH to an optimum value at flow rate of $0.08-0.56 \text{ mL} \cdot \text{min}^{-1}$. The stripping of the metal ions from the resin column was carried out by 0.5 M HNO_3 (10 mL). The eluate was collected in 10 mL capacity volumetric flask. The collected solution was aspirated into the flame for atomic absorption spectrometer standardized prior to determination.

6. Adsorption Isotherm Studies

Adsorption experiments were carried out at 25°C by adding a fixed amount of adsorbent (0.05 g) to a series of beakers filled with 25 mL diluted solutions of Cu(II) ($50-750 \text{ } \mu\text{g}/\text{mL}$) at optimum pH (5.5). pH adjustments were done using 0.01M acetate buffer. The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (5 h). The beakers were then removed from the shaker, and the final concentration of Cu(II) in the solution was measured by flame atomic absorption spectrometer. The amount of Cu(II) at equilibrium q_e (mg/g) on modified Amberlite XAD-4 was calculated from the following equation:

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

Where C_0 and C_e (mg/L) 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.

RESULTS AND DISCUSSIONS

1. Characterization of Resin

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, 1,721, 3,433 cm^{-1} which appear to originate due to the contribution of vinyl OOP, C-N, CH_2 (bending), $\text{N}=\text{N}$, C=O and OH vibrations, respectively.

1-2. Elemental Analysis

The instruction used in this study is reported in the 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. 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.

The elemental analysis for Amberlite XAD-4-[2-(allyl-phenol)] (found: C, 73.38; H, 7.04; N, 4.97%; calculated for $(\text{C}_8\text{H}_8)_2\text{C}_9\text{N}_2\text{H}_8\text{O}(\text{H}_2\text{O})_1$: C, 77.31; H, 6.73; N, 7.25%) show that on an average one 2-(allyl-phenol) molecule is present in each 2 repeat units of the polymer.

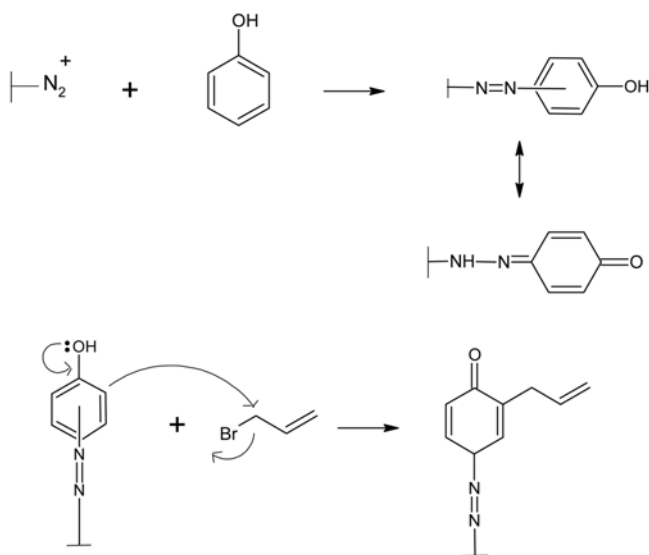


Fig. 1. The methodology of the synthesis of Amberlite XAD-4-[2-(allyl-phenol)].

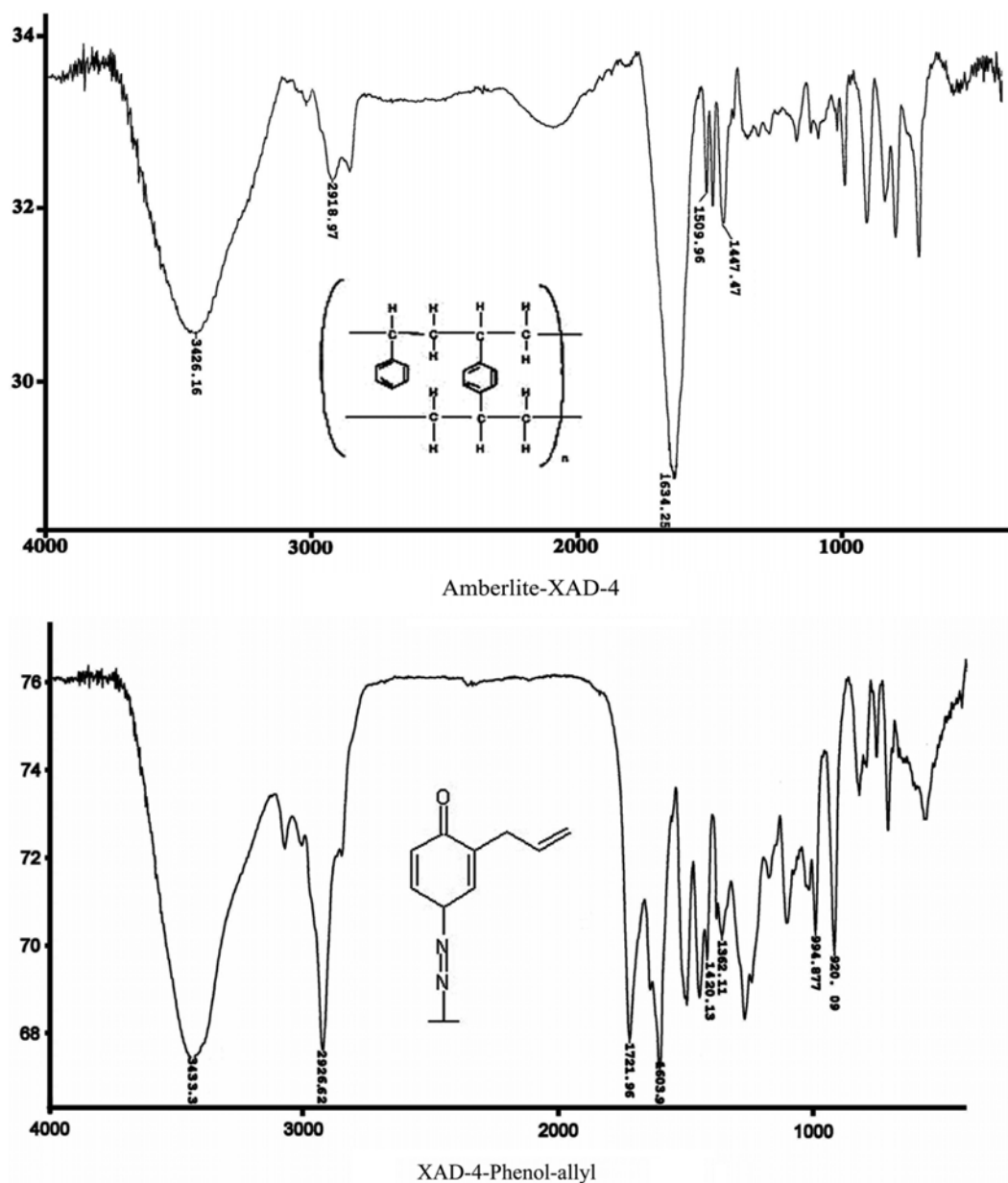


Fig. 2. The IR spectrum of Amberlite XAD-4 and Amberlite XAD-4-[2-(allyl-phenol)].

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 (volume of each 50 mL) containing $0.3 \mu\text{g}\cdot\text{mL}^{-1}$ of Cu(II) was taken. Their pH values were adjusted in the range 3-9 with 0.01 M acetate and/or phosphate buffer solutions. Then 0.1 g of Amberlite XAD-4-[2-(allyl-phenol)] was added to each solution and the mixture was shaken for 5 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the metal ions content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from resin with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of each metal ion is shown in Fig. 3. The maximum recovery was 98% for Cu(II).

3. Stability and Reusability of the Resin

The metal ions were sorbed and desorbed on 1 g of the resin sev-

eral times. It was found that sorption capacity of resin after 15 cycles of its equilibration with each of metal ions changes less than 5%. Therefore, repeated use of the resin is feasible. The resin cartridge after loading it 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 was found to be practically unchanged.

4. Effect of Flow Rate

The metal ion sorption on an Amberlite XAD-4-[2-(allyl-phenol)] (0.1 g) packed column was studied at various flow rates of the Cu(II) solutions (Fig. 3). All flow rates for loading Cu(II) on to resin were excellent. A flow rate less than $0.08 \text{ mL}\cdot\text{min}^{-1}$ was not employed to avoid the longer time of analysis. It was observed that more than 99% sorption of Cu(II) on the resin occurred at these flow rates. For stripping off the bounded Cu(II) on the modified Amber-

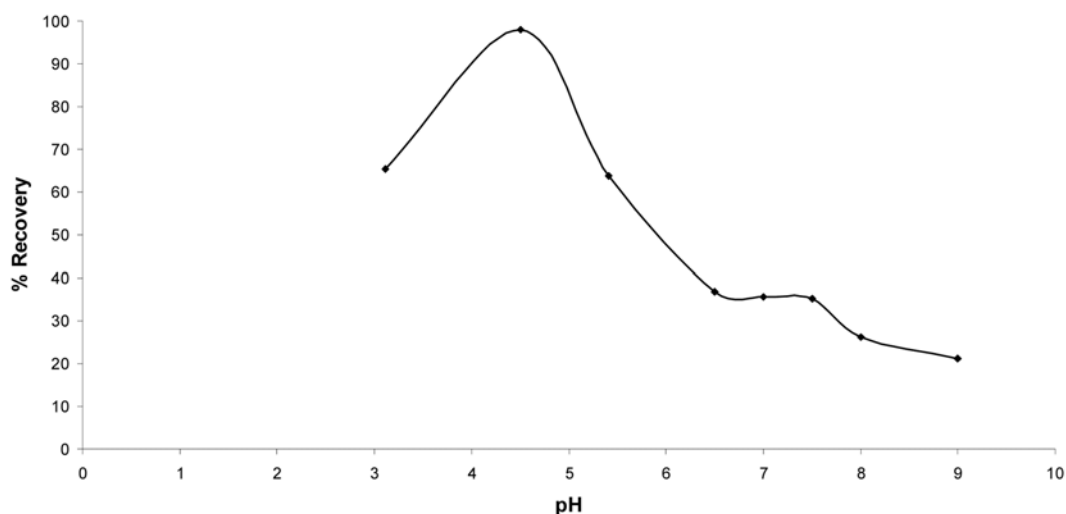


Fig. 3. Effect of pH sorption of Cu(II), onto Amberlite XAD-4-[2-(allyl-phenol)].

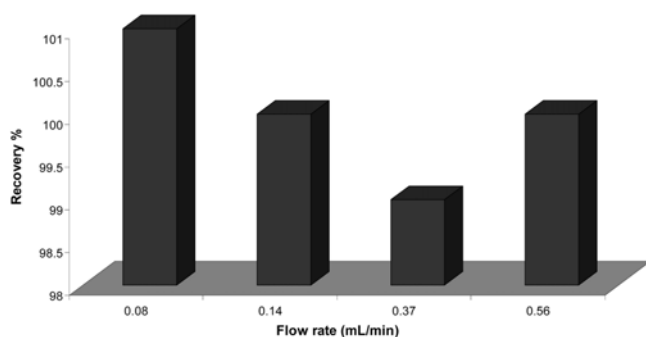


Fig. 4. Effect of flow rate on sorption of metal ions on modified Amberlite XAD-4.

lite XAD-4, the optimum flow rate of 0.5 M nitric acid was found to be $<1 \text{ mL} \cdot \text{min}^{-1}$. In this flow rate maximum recovery was obtained.

5. Adsorption Isotherms

The Langmuir equation is given in the following Eq. (23).

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

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). 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. 5).

Conformation of the experimental data to the Langmuir isotherm model indicates the homogeneous nature of the 5-amino-2-benzot-

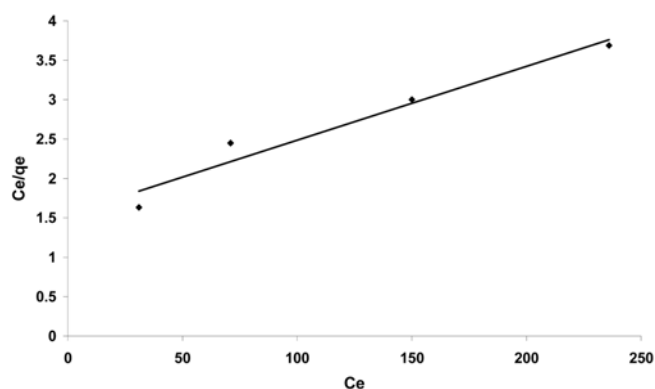


Fig. 5. Langmuir isotherm isotherm for Cu(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at optimum pH.

riazol-2-yl-phenol 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 (24):

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

Table 1 shows the value of R_L (0.35) was in the range of 0-1 at pH studied, which confirms the favorable uptake of the Cd(II) (Table 2).

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 (25):

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

Table 1. Langmuir, Freundlich and Temkin isotherm and separation factors (R_L) for adsorption of Cd(II)

T (°C)	Langmuir isotherm model				Freundlich isotherm model			Temkin isotherm model			
	q_{\max}	K_L	R^2	R_L	K_F	n	R^2	A	B	b	R^2
25	106.38	0.061	0.9536	0.35	0.193	0.791	0.9148	0.045	46.85	52.91	0.9948

q_{\max} (mg/g), K_L (L/mg), K_F (mg/g) (L/mg) $^{1/n}$, A (L/g), b (J/mol)

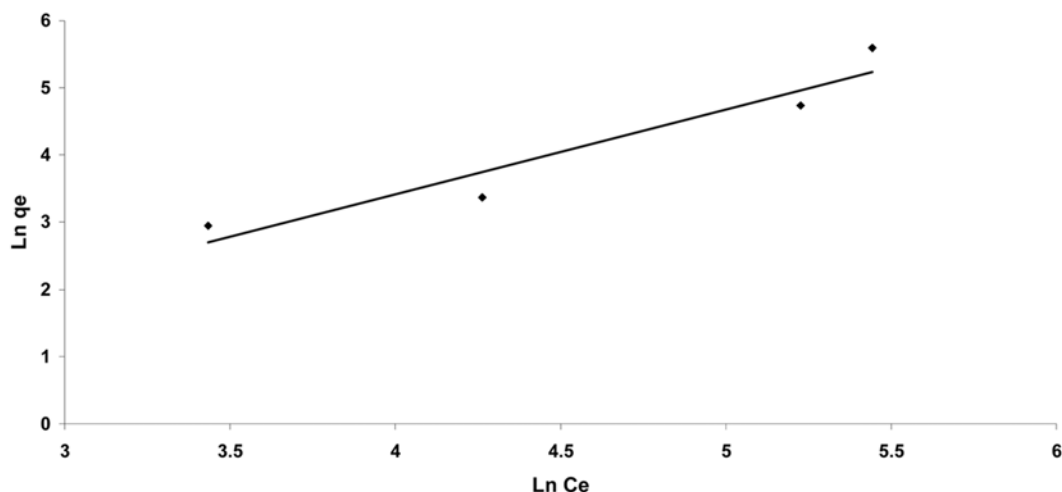


Fig. 6. Freundlich isotherm for Cu(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at optimum pH.

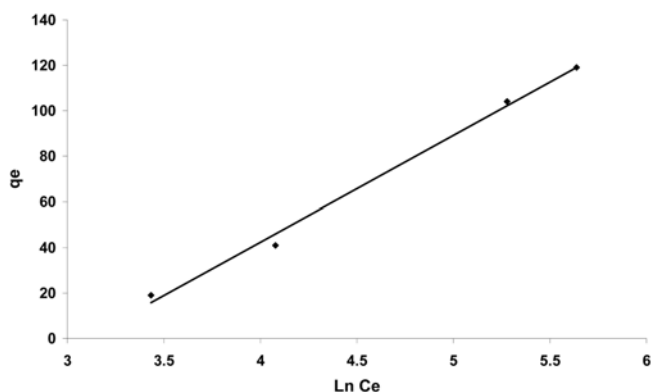


Fig. 7. Temkin isotherm for Cu(II) adsorption onto Amberlite XAD-4-[2-(allyl-phenol)] at optimum pH.

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):

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

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ (Fig. 6) enables the constant K_F and exponent 1/n to be determined. The Freundlich equation predicts that the Cd(II) concentration on the adsorbent will increase so long as there is an increase in the Cd(II) concentration in the liquid.

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

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

and can be linearized:

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

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. 7) enables one to determine the constants A and B . Temkin parameters calculated from Eq. (7) and

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

Table 3. Results obtained for metal determination in plating waste water sample

Analyte	Cu(II) ppm	Cr(III) ppm	Ni(II) ppm	Co(II) ppm
Sample before contacting with resin	170	3120	63	0.32
Sample after contacting with resin	50	2006	26	0.16
Standard deviation ^a	0.039	0.082	0.064	0.071
Percentage of sorption	70.6	35.7	58.7	50

^aFor three determinations

(8) are listed in Table 1.

6. Application of Method

Solid phase extraction with Amberlite XAD-4-[2-(allyl-phenol)] coupled with FAAS determination was supplied to determine the Cu(II), Ni(II), Cr(III) and Co(II) in plating waste water sample. The batch method was applied for preconcentration of metal ions. The results are shown in Table 3. These results demonstrate the applicability of the procedure for Cu, Ni, Cr and Co determination in samples.

CONCLUSIONS

A new chelating resin shows higher adsorption selectivity for Cu(II) ions, and adsorbed ions can be readily desorbed from the resin column by 10 mL of 0.5 M nitric acid solution. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 106.38 (mg/g) at 25 °C. The R_L values showed that the Amberlite XAD-4-[2-(allyl-phenol)] was favorable for the adsorption of Cu(II). The Freundlich isotherm best-fit the equilibrium

data for adsorption of Cu(II). The resin also presents the advantage of good reusability and high chemical stability. The synthesis of the resin is simple and economical. This resin combined with FAAS can be applied to the adsorption of trace Cu(II), Cr(III), Ni(II) and Co(II) ions in water and mineral reference sample with satisfactory results.

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