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Amberlite XAD-4 Functionalized with 1-amino-2-naphthole for Determination and Preconcentration of Copper (II) in Aqueous Solution by Flame Atomic Absorption Spectrometry

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Abstract**—**A new chelating resin is prepared by coupling Amberlite XAD-4 with 1-amino-2-naphthole through an azo spacer. The resulting sorbent has been characterized by FT-IR, elemental analysis and thermogravimetric analysis (TGA) and studied for preconcentrating of Cu (II) using flame atomic absorption spectrometry (FAAS) for metal monitoring. The optimum pH value for sorption of the copper ions was 6.5. The resin was subjected to evaluation through batch binding of mentioned metal ion. Quantitative desorption occurs instantaneously with 0.5 M HNO_3. The sorption capacity was found 4.8 mmol.g^{-1} of resin for Cu (II) in the aqueous solution. The chelating resin can be reused for 10 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 99% was obtained the metal ions with 0.5 M HNO_3 as eluting agent. The method was applied for metal ions determination from industrial waste water sample.

Keywords**—**Amberlite XAD-4; Copper (II); Flame atomic absorption; Chelator; 1-amino-2- naphthole

I. Introduction

THE direct determination of trace elements in real samples is a difficult task. The main restrictions come from the complexity of the matrix and the extremely low concentrations of analytes in those samples, which are often below the detection limits of available techniques [1, 2]. Thus, highly sensitive and selective techniques are required. Although the sensitive and accurate determination of trace elements by some instrumental techniques including inductively coupled plasma mass spectrometry, graphite furnace atomic absorption spectrometry is possible, Flame atomic absorption spectrometry [3, 4] is preferred for trace element determination due to its cheap coast and simplicity.

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However, the determinations of elements at μgL^{-1} concentration level by flame atomic absorption spectrometry are not possible. To solve this problem, preconcentration–separation procedures have been proposed. Preconcentration is a very important issue for achievement of low detection limits [5-7]. There are many methods of preconcentration and separation such as liquid–liquid extraction [8] ion exchange techniques [9], coprecipitation [10, 11], membrane filter techniques [12], cloud point extraction [13, 14].

In this work, Amberlite XAD-4 (1-amino-2-naphthole) was prepared by chemically bonding to be used as an adsorbent. 1-amino-2-naphthole could form chelates with metallic ions on the surface of the resin. Absorption of metal ions from aqueous solution using modified Amberlit XAD-4 was studied under different experimental conditions to assess its affinity towards the chelator.

II. Experimental

Reagents

Amberlite XAD-4 resin (surface area 745 m^2/g, pore diameter 5 nm and bead size 20-60 mesh) was obtained form serva. 1-amino-2-naphtole was synthesized in Ethanol [51]. The metal ion solution was prepared by dissolving following metal salts: Cu $(NO_3)_2.4H_2O$. The following buffers were used to control the pH of the solutions: Hydrogen disodium phosphate (pH=7-9), Sodium Hydroxide-Acetic acid (pH=5), Acetic acid (pH=3-4). CH_3COOH, NaH_2PO_4, Na_2HPO_4 , $CoCl_2.6H_2O$, $SnCl_2$, HCl , H_2SO_4 , HNO_3 , $NaNO_2$, NaOH , β-Naphthole , Aniline, Iodide-Starch Paper were products of Merck (Darmstadt, Germany).

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 a FT-IR spectrometer Jasco / FT-IR-410 by KBr pellet method. Elemental analysis was carried out on an elemental analyzer

from Thermo-Finnigan (Milan, Italy) model Flash EA. TGA analysis was carried out by using TGA-50H (Shimadzu, Japan).

Synthesis of XAD-4- (1-amino-2-naphthole)

Amberlite XAD-4 bead (5g) were treated with 10 cm³ of concentrated HNO_3 and 25 cm³ of concentrated H_2SO_4 and the mixture stirred at 60ºC for 1h on an oil bath. There after, the reaction mixture was poured into an ice water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid and there after treated with a reducing mixture of 40g of $SnCl_2$, 45 cm³ of concentrated HCl and 50 cm³of Ethanol. The mixture was refluxed for 12h at 90ºC. The solid precipitate was filtered and washed with water and 2mol/dm³ 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/dm³ HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice-water mixture (350 cm³) and treated with 1mol/dm³ HCl and 1mol/dm³ $NaNO_2$ (added in small aliquits of 1cm³) 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 react with 1-amino-2-naphthole 0.03 mol in 200 cm³of 10% NaOH solution. The reaction mixture stirred at 0-3ºC for 24h. The resulting colored beads were filtered, washed with water and dried in air. The methodology used to synthesize modified XAD-4 resins is summarized in Fig.1.

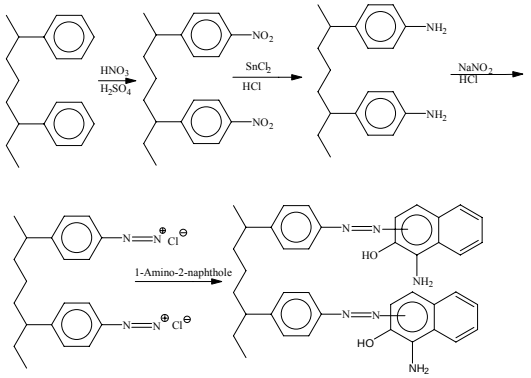


Fig. 1. The methodology of synthesize of 1-amino-2-naphthole – Amberlite XAD-4.

Batch method

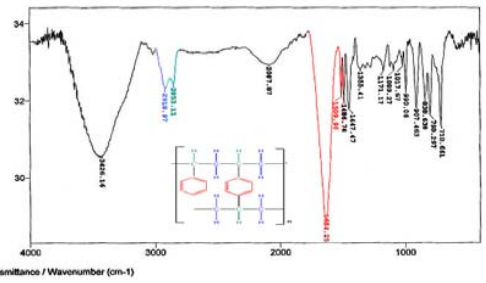
A sample solution (100ml) containing 0.1-30 µg.mL of Cu (II) was placed in glass stopper bottle after adjusting its pH to the optimum value. The modified Amberlite XAD-4 (0.1g) was added. The bottle was shaken for 5h. The resin was filtered and the metal ions were desorbed by shaking the resin beads with 10ml HNO_3 1M. The resin was filtered off and the filtrate was aspirated in to FAAS.

III. Results and Discussion

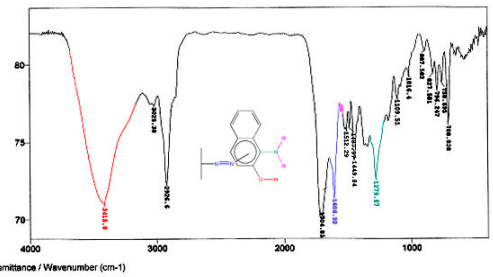
Characterization of modified Amberlite

IR Spectrum

The IR spectrum of 1-amino-2-naphthole loaded Amberlite XAD-4 (Fig. 2) is compared with that of free Amberlite XAD-4 (Fig. 2). There are 4 additional bands at 1557,1606,1279 and 3415 cm^{-1} which appear to originate due to modification of N-H (bending), N=N, C-N (bending) and O-H, NH_2 vibrations, respectively.



a)



b)

Fig. 2 IR spectrum of a) Amberlite XAD-4 b) 1-amino-2-naphthole – Amberlite XAD-4.

Elemental Analysis

The instruction used in this study is reported in ThermoFinnigan elemental analyzer manual. Elements of C, H and N in the sample and standards in a column containing oxidant at 900 ºC were converted to CO_2, H_2O and N_2, respectively. They 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 (1-Amino-2-Naphtole) (found: C,75.85; H,9.02; N:4.11%,calculated for $(C_8H_7)_6$ $C_{10}N_3H_8O(H_2O)_6$: C,77.67; H,6.91; N,4.68%) show that on an average one (1-amino-2-Naphtol) molecule is present in each 6 repeat unit of the polymer.

Thermal Analysis

TGA of the resins shows two-step weight loss up to 510 °C. The weight loss up to 130°C was due to the water molecules in the polymer. The major weight loss after 290°C is due to the dissociation of chemically immobilized moiety and the polymeric matrix.

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 µg.mL^{-1} Cu (II) was taken. Their pH values were adjusted in range 3-9 with 0.01 M acetate and/or phosphate buffer solutions. The 0.1 g of 1-amino-2-naphthole loaded Amberlite XAD-4 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 Cu (II) is shown in figure 3. The maximum recovery was 99% at pH 6.

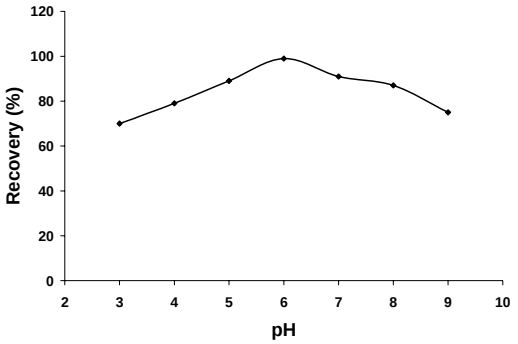


Fig. 3 Effect of pH sorption of Cu (II) onto1-amino-2-naphthole – Amberlite XAD-4.

Stability and reusability of the resin

The mentioned metal ions were sorbed and desorbed on 1g of the resin several times. It was found that sorption capacity of resin after 10 cycles of its equilibration with the 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 month under ambient conditions has been found to be practically unchanged.

Total sorption capacity

The 0.01g of resin beads were stirred for 5 h with 100 mL solution containing 30 $\mu g.mL^{-1}$ of Cu (II), at optimum pH. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the resin for each 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 for Cu (II) is 4.8 $mmol.g^{-1}$ of resin.

Application of method

Solid phase extraction with1-amino-2-naphthole loaded Amberlite XAD-4 coupled with FAAS determination was supplied to determine the Ni (II), Zn (II) and Cu (II) in plating waste water sample. The sample solution (100 mL) was taken in a glass stoppered bottle (250 mL), after adjusting its pH to the optimum value. The 0.5g of 1-amino-2-naphthole – Amberlite XAD-4 was added to the bottle and the mixture was shaken for 30 min. 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 a pre-standardized FAAS. The results are shown in Table 1.These results demonstrate the applicability of the procedure for Ni, Cu and Co determination in samples.

TABLE I RESULTS OBTAINED FOR METAL DETERMINATION IN PLATING WASTE WATER SAMPLE

Analyte	Ni (II)	Zn (II)	Cu (II)
Before preconcentration	**779**	**0.5**	**0.7**
After preconcentration	**6986**	**4.8**	**6.8**
Preconcentration factor	**10**	**10**	**10**
Recovery %	**94**	**96**	**97**
Standard deviation[a]	**1.12**	**0.84**	**0.99**
Relative standard deviation (%)[a]	**1.5**	**1.95**	**3.26**

a: For three determinations

IV. CONCLUSION

A new resin was synthesized by coupling of Amberlite XAD-4 with 1-amino-2-naphthol. Amberlite XAD-4-1-amino-2-naphthole has a good potential for enrichment of trace amounts of Cu from large sample volumes. The synthesis of the resin is simple and economical. The resins can be applied over a wide pH range (3-9) for collection of trace metals. All the resins also present the advantage of high adsorption capacity, good reusability and high chemical stability. Preconcentration by this resin combine with FAAS can be applied to the determination of trace Cu (II), Zn (II) and Ni (II) ions in water and mineral reference sample with satisfactory results.

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