



METAL ION UPTAKE PROPERTIES OF 1-NITROSO-2-NAPHTHOL LOADED XAD-16 RESIN

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A stable resin matrix has been functionalized by coupling through an –N=N– group with 1-nitroso-2-naphthol. The resin has been used for preconcentrating Ni (II) and Cu (II) ions prior to their determination by flame atomic absorption spectrophotometry. The optimum pH values for quantitative sorption of Cu (II) and Ni (II) are 9 and 8, respectively. The metal ions can be desorbed (recovery 97-99 %) with 2M HNO₃ solution. The sorption capacity of the resin calculated from breakthrough curve is 0.35 and 0.68 mmol g⁻¹ of resin, for Cu (II) and Ni (II), respectively. The limits of tolerance of some electrolytes like NaCl, NaF, NaNO₃, Na₂SO₄ and Na₃PO₄ have been reported. The preconcentration factor for Cu (II) and Ni (II) is 833 and 1250 respectively.

Keywords: Sorption, Preconcentration, Chelating resins, Amberlite XAD-16, Metal ions, Nitrosonephthol.

1. Introduction

The selective and quantitative separation and preconcentration of metal ions related to water pollution problems has received increasing importance in recent years. Methods widely used for preconcentration are based on liquid-liquid extraction [1-3], ion exchange and chelating resin.

The ion exchange resins have shown better metal ion separation but with conventional resins the selectivity factor and preconcentration factor is relatively low. This problem can be overcome by chemical bonding of a suitable moiety to the solid substrate. So chemically bonded chelating agents on suitable chromatographic supports would be appropriate medium for ion separation and preconcentration. Chelating sorbents obtained by immobilization of organic reagents on solid support (adsorbed or chemically bonded) have found wide spread application in preconcentration of trace metals from a variety of matrices [4-14].

In the present paper we describe the synthesis and characterization of a 1-nitroso-2-naphthol grafted XAD-16 resin which is highly effective towards the removal of trace metal ions. This matrix has been studied for its use in the

preconcentration of Cu (II) and Ni (II).

2. Experimental

2.1. Apparatus and reagents

A Varian AA-10 atomic absorption spectrophotometer was used for the determination of metal ions in solution. The pH measurements were made on digital (inoLab pH level I) pH meter. The flow of liquid through the column was controlled using a peristaltic pump.

All chemicals used were of analytical grade. Stock standard solutions of Cu (II) and Ni (II) were prepared by dissolving the appropriate amount of Cu (II) and Ni (II) nitrates in deionized water, acidified with small amount of corresponding acid.

Amberlite XAD-16, surface area 825 m²/g., pore diameter 144 Å and bead size 300-600 µm mesh was procured from Fluka (Germany).

2.2. Synthesis of the sorbent

The styrene-divinylbenzene copolymer was modified according to the procedure reported in the literature [10]. The synthesis involves nitration of XAD-16, followed by the reduction to form an aromatic amine. This amine facilitates the

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formation of a stable diazonium salt. The diazotized resin was treated with nitrosonaphthol at 0-3 °C.

2.3. Experimental technique

Amberlite XAD-16 (0.5g), loaded with nitrosonaphthol, was packed in a glass column of 100 mm length and 10 mm internal diameter. Resin was treated with 3M HCl and washed with water until free from the acid. A solution containing known concentration of metal ion was passed through the column, after adjusting pH to its optimum level (Table 1) at a flow rate (Table 1) controlled by the peristaltic pump. The column was washed with HNO₃ (optimum value is given in Table 1). The volume of eluate was made upto 10 cm³ and its Cu (II) and Ni (II) contents were determined directly at 324.8 nm and 232 nm, respectively, by aspirating it into the air- acetylene flame.

Table 1. Optimum conditions for sorption and desorption of metal ions on Amberlite XAD-16 loaded with nitrosonaphthol.

Experimental Parameter	Cu (II)	Ni (II)
pH	9	8
Flow rate (ml/min)	2	2
HNO ₃ /HCl concentration for desorption	2M (3ml)	2M (3ml)
Average recovery (%)	97	99
Preconcentration factor	833	1250
Adsorption Capacity (mmol/g)	0.35	0.68

3. Results and Discussion

3.1 Characterization

The functionalized XAD-16 resin (Fig. 1) was characterized by FT-IR spectroscopy. The IR spectrum of nitrosonaphthol loaded Amberlite XAD-16 in comparison of pure XAD-16 depicted

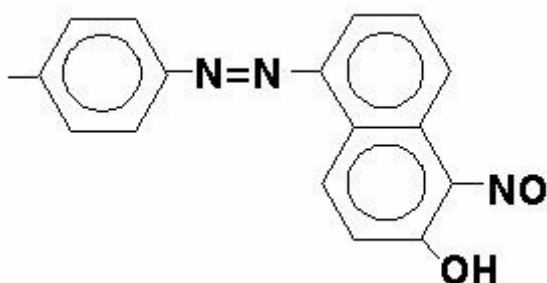


Figure 1. Repeat unit of nitrosonaphthol modified XAD-16.

Additional bands at 3240-3100, 1580, 1345, 1280, 1240 and 1180 cm⁻¹. These appear to originate from -OH stretching, -N=N- (1575~1650 cm⁻¹), C_{arom}-N stretching (1360~1250 cm⁻¹ higher position due to increase in bond is also possible), -NO stretching (1300-1200 cm⁻¹), - and phenolic -OH (~ 1200 cm⁻¹ shift upto 30 cm⁻¹ is possible) [15].

3.2. Optimum conditions for sorption

The column packed with 0.5 g of XAD-16 loaded with nitrosonaphthol, treated with 20 cm³ of 3M HCl and washed several times with deionized water to remove the acid. The sorption and desorption (under optimum conditions) of Cu (II) and Ni (II) on this column were quantitative. The optimum conditions for their sorption (pH and flow rate) and desorption (acid concentration) were established by varying one of them and following the recommended procedure. The results are summarized in Table 1. The variation of sorption with pH was investigated in the range of 1-10 at fixed concentration of metal ions (Fig. 2). As can be seen from the figure, increasing pH led to an increase in the amount of metal ion adsorbed. This indicates that the adsorption process involved the release of H⁺ ions to allow the firm complexation of metal ions to XAD-16/nitrosonaphthol. Reaction scheme is as follows :

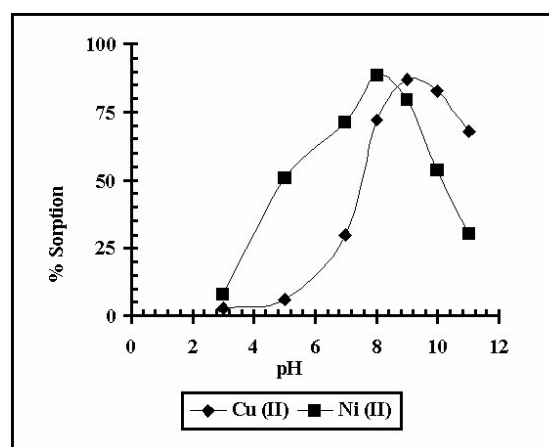
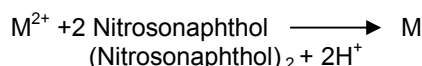


Figure 2. Metal ion sorption as a function of pH

However, the amount of metal ions adsorbed decreased when pH was greater than 8 for Ni (II) and pH 9 for Cu (II) this may be attributed to the hydrolysis of the metal ions in strong basic solution [16]. The obvious precipitation of Cu (II) at pH

values greater than 9 provides support for this suggestion.

The degree of metal ion sorption was studied by varying the flow rate of feed solution. It was found that the optimum flow rate for both metal ions was $\sim 2.0 \text{ ml min}^{-1}$. However at flow rate greater than 3 ml min^{-1} , there was a decrease in percentage sorption (Fig. 3). Desorption conditions were optimized by eluting the metal ions with the mineral acids of different volume of different concentrations. The percentage recovery was found to be $>97\%$ with 3 ml of 2 M HNO_3 for both metal ion. 2M HCl is equally good ($\% \text{ recovery } 95\%$) for quantitative desorption of Ni (II) (Fig 4). To test the resin stability metal ions were sorbed and desorbed many times on the same resin beads and the amount of metal eluted was estimated. The variation in the results obtained for both metal ions was within 2-3% (Fig. 5). Thus the multiple use of resin column is feasible.

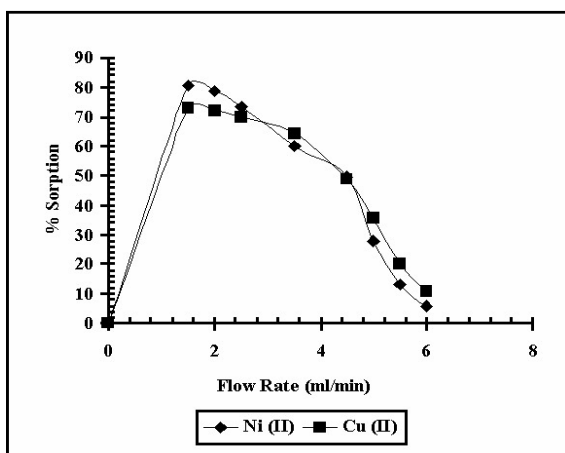


Figure 3. Effect of flow rate on metal ion sorption.

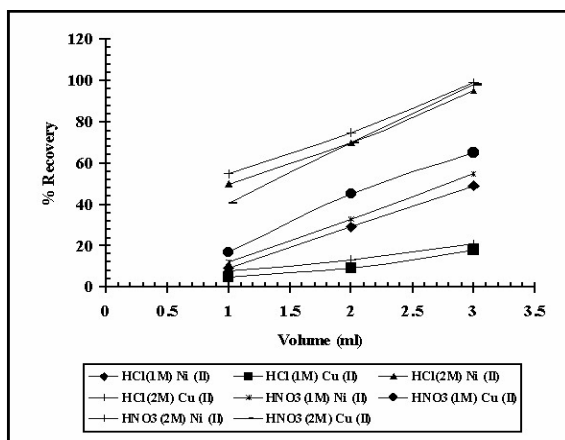


Figure 4. % Recovery of metal ions with mineral acids.

3.3. Total sorption capacity (Breakthrough curve)

The breakthrough volumes in ml g^{-1} for metal ions were observed and noted on x-axis of the plot at the initial rise of the curves. Similarly the total saturation volumes (where $C_e = C_i$) in ml g^{-1} were observed and noted on x-axis of the plot at the final shape of the curves. The total sorption capacities in mmol g^{-1} were calculated on the basis of total saturation volumes and were found 0.346 and 0.68 mmol g^{-1} for Cu (II) and Ni (II) respectively. The sharp profile of the curve shows the favorable equilibrium (Fig. 6).

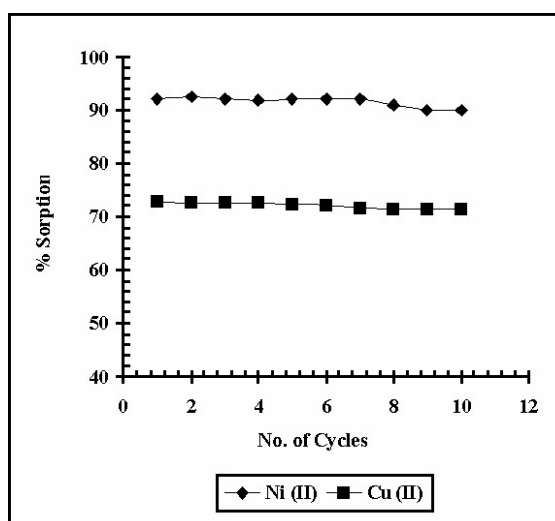


Figure 5. Effect of reuse of nitrosophthal loaded XAD-16 resin on % sorption

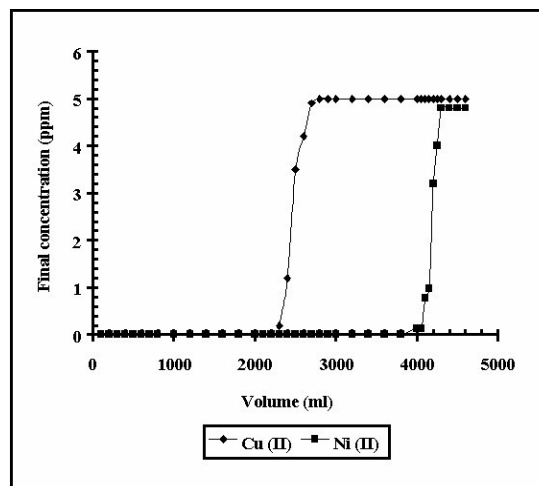


Figure 6. Break through curve for Cu (II) and Ni (II) .

3.4. Effect of electrolytes

The effect of various electrolytes likes NaCl, NaF, NaNO₃, Na₂SO₄ and Na₃PO₄ on the sorption of both metal ions with nitrosonaphthol loaded Amberlite XAD-16 was studied. It was observed that all the electrolytes were tolerated in the concentration range of 0.1-1.0 M.

3.5. Limit of preconcentration and preconcentration factor

The limit of preconcentration was determined by increasing the dilution of the metal ion solution and keeping the total amount of loaded metal at 10 µg. Both metal ions can be collected quantitatively from solutions of concentration of 4 µg l⁻¹ (recovery 98%), resulting in the preconcentration factors, 833 and 1250 respectively, for Cu (II) and Ni (II).

3.6. Applications of the method

Amberlite XAD-16 modified was used to preconcentrate and determine Cu (II) and Ni (II) in tap water sample from city water supply. The tap water sample was filtered to remove the suspended particles. The estimation of both the metal ions were made by passing 500 ml of water sample through the column packed with 1g of resin and determining the metal ions by FAAS after elution as described in the procedure. The amount of metal ions found was 6.6 mg/L ± 2.5% and 1.1 mg/L ± 2. % for Cu²⁺ and Ni²⁺ ions respectively.

4. Conclusions

The Amberlite XAD-16-nitrosonaphthol resin has high sorption capacities and large preconcentration factors for Cu (II) and Ni (II) compared with many other analogous resins reported in the literature [4-8]. The sorbed ions can readily be desorbed with common mineral acids with the percentage recovery of ~98. The resin could be recycled many times without affecting its sorption capacity. The synthesized resin has minimum matrix interference with common anions.

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