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A Simple Procedure for Preconcentration of Trace Amounts of Co (II), Cu (II) and Ni (II) Using A New Chelating Resin

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Original Research Article

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Abstract: A new method for preconcentration of ultratrace amounts of Co (II), Ni(II) and Cu(II) ions in various matrices has been proposed. The method is based on the adsorption and chelation of the metal ions on Amberlite XAD-4 resin modified with Quinol via azotisation prior to their determination by standard spectrophotometric method. The effect of pH, type, concentration and volume of eluent, sample volume,flow rates of sample and elution solutions, and interfering ions have been investigated. The optimum pH for retention of the metal ion were10.0, 7.0 and 7.0 respectively. Eluent for quantitative elution was 5 ml of 2 mol l−1 HCl. The optimum sample and eluent flow rates were found to be 2.5 ml min−1. The sorption capacity of the resin was found to be 0.60, 0.45 and 0.52mmolg^{-1} for Co (II), Ni (II) and Cu (II) respectively. The preconcentration factor of the method was 250 for all the metals. The detection limit values were in the range of 3.0- 5.0 μgl^{-1}. The accuracy of the method was confirmed by analyzing standard synthetic mixtures and standard addition methods. This procedure was applied to the determination of Cobalt, Nickel and Copper from various water samples and SRM's.

Keywords: Amberlite XAD-4, Functionalization, Quinol, Preconcentration, Trace metal.

INTRODUCTION

Accumulation of metal ions in the environment is posing a serious threat to living system as their intake beyond a certain limit is toxic [1-3].

A serious problem in the removal of the toxic metal ions is that they are in low concentration and exist in association with complex matrices. In rapidly expanding analytical fields such as environmental, biological and material monitoring of trace metals, there is an increasing need to develop simple, sensitive and selective analytical techniques that do not use expensive or complicated test equipment. A wide variety of procedures have been proposed for diverse matrices depending on the nature of the sample, the type and concentration of the analyte, and the methods used for determination [4, 5].Considering all separation techniques for preconcentration and separation of analytes from different matrices, chelating resins promises better results by virtue of their large domain of sites with chelating functionality [4, 6]. The design of chelating devices anchoring the active site to a solid support in a polymer matrix, provides an immobilized active surface capable of selective and quantitative separation of cations from aqueous solution and this solid-phase extraction systems can be operated indefinitely for the purification of water and industrial effluents, etc., without loss of the expensive ligating groups [6-8]

Copper is introduced into the environment from natural sources and as a result of human activities. It is accumulated in the soil (especially in its surface layers) with all its negative consequences [9]. Copper is indispensable for normal development of living organisms, but its excess may lead to biochemical changes in the liver and also has the potential to damage kidneys, brain tissue, coronary vessels and myocardium. Nickel(II) is an important metal in the environmental, marine and aquatic chemistry, in food and in biological samples, because of its possible interaction with the environmental compartments [10]. Nickel occurs in aquatic systems as soluble salts adsorbed, or associated with organic particles. Moreover, changes in physical and chemical parameters or due to the microbial activity, nickel may be released from the sediments', deposited through precipitation, adsorption or complexation on clay particles, by virtue of the reversibility of the sorption processes. Cobalt is an important element, not only for industry but also for biological systems [11]. The preconcentration and separation methods based on the solid phase extraction of trace heavy metal ions in aqueous solutions are considered to be superior to liquid-liquid extraction [12, 13]. Solid phase extraction is a multi-element separation/preconcentration method because of its simplicity, rapidity and ability to attain a high preconcentration factor. In solid phase extraction, various sorbents including activated carbon, C-18,C-60, C-70, Diaion HP-20, Ambersorb 563, chelating resins, silica gel and others[14, 15] have been used for the preconcentration/separation of trace heavy metal ions from various media such as seawater and mineral waters, urine and geological samples. Amberlite XAD adsorption resins have good physical properties such as porosity, uniform pore size distribution, and high surface area as chemically homogeneous non-ionic structures for large amounts of uncharged compounds, and they have been used as solid sorbents for the enrichment/separation of metal complexes [6]. Amberlite XAD-4 is a polystyrene-divinyl benzene copolymer. It has been used for the separation and preconcentration of traces of metal ions in various media including natural waters [16, 17].

The aim of the present work is to investigate the optimal analytical conditions, including pH and sample volume, for the preconcentration/separation of Cu, Co, and Ni on Amberlite XAD-4 funtionalized with a chelating agent.

EXPERIMENTAL

Instrumentation

A Shimadzu UV 160A spectrophotometer was employed for measuring absorbance; an ELICO (Hyderabad, India) digital pH meter (LI-120) was used for pH measurements. A thermostat shaker (Scientific, New Delhi, India), 200 strokes min. $^{-1}$ was used for carrying out equilibrium studies. Infrared (IR) spectra were recorded on a Nicolet- 5DX Fourier transform IR spectrophotometer (Madison, USA), in potassium bromide pellets.

Reagents and Solutions

In this study, all chemicals and solutions were of analytical reagent grade and were prepared in triple distilled/triply de-ionised water. Stock solutions of nitrate salts of the studied metals at the concentration of 1000 mg l^{-1} in1% HNO_3 were used. The model and standard solutions of the metals were prepared by appropriately diluting the stock solutions. Buffer solutions were used for pH adjustment. For this, solutions containing appropriate amounts of Na2SO4-NaHSO4 for pH 2, HAc-NH4Ac for pH 4-6, NH3-NH4Cl for pH 8-10, and NaOH-Na2HPO4 for pH 12 were prepared in water [18]. Amberlite XAD-4 resin (Sigma Chemical Co.) was purchased as 20-60 mesh particle size with $725m^2$ g^{-1} of surface area.

Procedure for functionalization of Amberlite XAD-4 resin with Quinol

Air dried AmberliteXAD-4 resin pretreated for removal of any impurities was used as the starting material. The resin beads were initially nitrated followed by reduction to the amino compound. The amino compound was washed thoroughly with 2M NaOH and then with 4M HCl in order to remove the excess $SnCl_2$. The product was diazotized according to the procedure that has already been described in the reference [19]. The diazotized product was rapidly filtered off, washed with cold distilled water until free from acid and then subjected to coupling reaction by treating it with a solution of Quinol (2.5 g) in 10% NaOH at a temperature as low as 0-5 ◦C over a period of 24 hrs.

Procedure for adsorption

Static method

A weighed amount of Quinol-modified resin was equilibrated at shaking speed of 80 rpm with 50 ml of metal solution (50 - 150 µg) maintained at constant pH at 25 ± 1 ◦C for 2 hrs. The resin was filtered and the sorbed metal ions were desorbed by shaking with 2 M HCl and analyzed by spectrophotometry [20].

Dynamic method

A sample of modified resin was slurried in water and then poured into a glass column (1 × 25 cm). A small amount of glass wool was used to plug the column to prevent any loss of resin beads during the sample loading. A solution of metal ions containing100 µg was passed through the column at the optimum flow rate after adjusting to appropriate pH with suitable buffers. After the sorption operation, recovery experiments were performed; for this purpose the column was washed with water and then 3 ml of 2 M HCl was made to percolate through the bed of loaded resin whereby the sorbed metal ions get eluted. The eluents were collected in 10mL volumetric flasks for the subsequent determination spectrophotometrically.

RESULTS AND DISCUSSIONS

Table-1: Optimum parameters for sorption characteristics of XAD-4-HQ

Experimental conditions	Metals		
	Ni(II)	Cu(II)	Co(II)
Optimum pH	7.0	7.0	10
Optimum flow rate(mL min^{-1})	2.5	2.5	2.5
Overall adsorption capacity(mmolg^{-1})	0.45	0.52	0.60
Loading time, $t_{1/2}$ (min)	≤2.5	≤2.5	≤2.5
Average recovery (%)	98($n^{\#}$=3)	97(n=3)	98(n=3)

n= number of readings.

Table-2: Recovery of metal ions from natural water samples (mean ±S.D, n=3)

Samples	Ni(II)			Cu(II)			Co(II)		
	Added, µgL^{-1}	Found, µg L^{-1}	Recovered %	Added, µg L^{-1}	Found, µg L^{-1}	Recovered %	Added, µg L^{-1}	Found, µ L^{-1}g	Recovered %
Waste water	0	n.d^{+}	-	0	n.d	-	0	n.d	-
	10	9.8 ±1.1	98	10	10.5±1.6	105	10	10.4±0.6	104
	20	19.2±0.6	96	20	19.1±1.5	96	20	19.1±1.5	96
Tap water	0	n.d	-	0	n.d	-	0	n.d	-
	10	9.3±1.3	93	10	10.5±1.6	105	10	10.5±1.6	105
	20	20.9±0.5	98	20	20.9±0.5	98	20	19.1±1.5	96
Mineral water	0	n.d	-	0	n.d	-	0	n.d	-
	10	9.5±0.5	86	10	9.8 ±1.1	98	10	9.5±0.5	86
	20	20.9±0.5	98	20	19.2±0.6	96	20	20.9±0.5	98
Spring water	0	n.d	-	0	n.d	-	0	n.d	-
	10	10.5±1.6	105	10	10.4±0.6	104	10	9.8 ±1.1	98
	20	19.1±1.5	96	20	19.1±1.5	96	20	19.2±0.6	96

+ n.d = not detected

Table-3: Tolerance limits of common matrix ions on adsorption of the metal ions

Foreign species	Co(II)	Cu(II)	Ni(II)
Na^{+} (mg)	1000	1000	1000
NO$_3^{-}$(mg)	500	500	500
SO$_4^{2-}$(mg)	500	500	500
K^{+}(mg)	1000	1000	1000
NH$_4^{+}$(mg)	1500	1400	1500
Cl^{-}(mg)	1500	1500	1500
CO$_3^{2-}$(mg)	2000	2000	2000

Table-4: Comparison of the sorption capacities and preconcentration factors

Type of chelating resin	Metal	Sorption capacity mmolg^{-1}	Enrichment factor(s)	*Ref.
Support:Amberlite XAD-2				
o-aminophenol	Co/Cu/Ni	0.056/0.053/ 0.055	100/50/65	19
Tiron	Co/Cu/Ni	0.11/0.22/ 0.21	55/200/150	22
Pyrocatechol	Co/Cu/Ni	0.023/0.092/ 0.053	200/100/200	23
Chromotropic acid	Co/Cu/Ni	0.065/0.133/ 0.103	150/100/200	24
Support:Amberlite XAD-7				
Xylenol Orange	Co/Cu/Ni	0.044/0.025/ 0.044	100/50/100	25
Salicyldoxime	Co/Cu/Ni	0.04/ 0.060/0.0800	40/40/40	26
Support: Amberlite XAD-4				
2-Acetylmercaptophenyl-diazoaminoazo -benzene	Co/Cu/Ni	0.10/.095/ 0.17	80/80/80	27
2,6- dihydrophenyl-diazoaminoazobenzene	Co/Cu	0.160/0.195	33/28	28

*References

Fig.1: Variation of adsorption of Cu(II),Ni(II)and Co(II)with pH on Amberlite XAD-4-HQ.

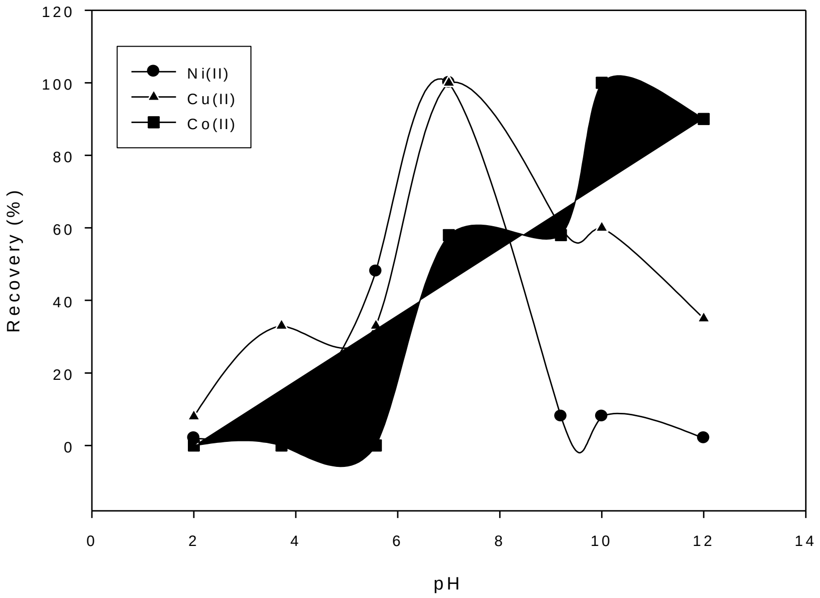


Fig.2: Variation of adsorption capacity with the variation of the initial concentration of Ni(II), Cu(II) and Co(II).

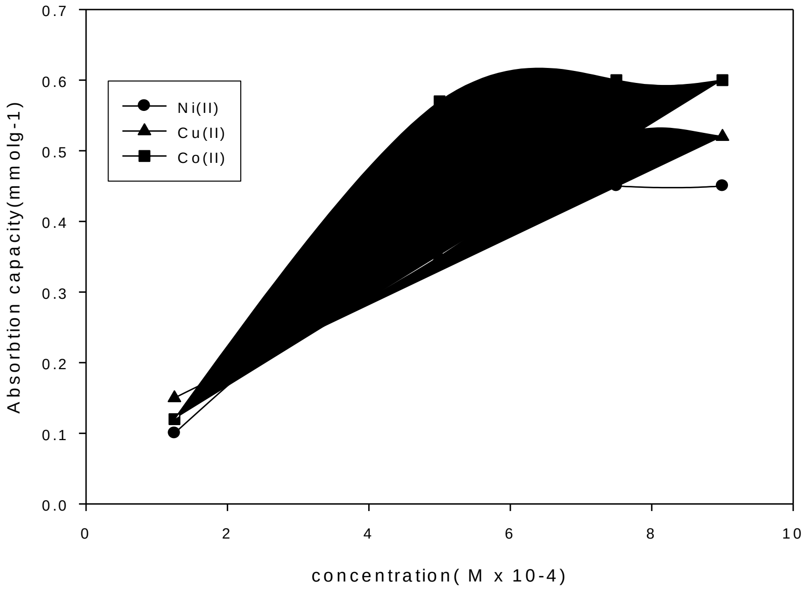
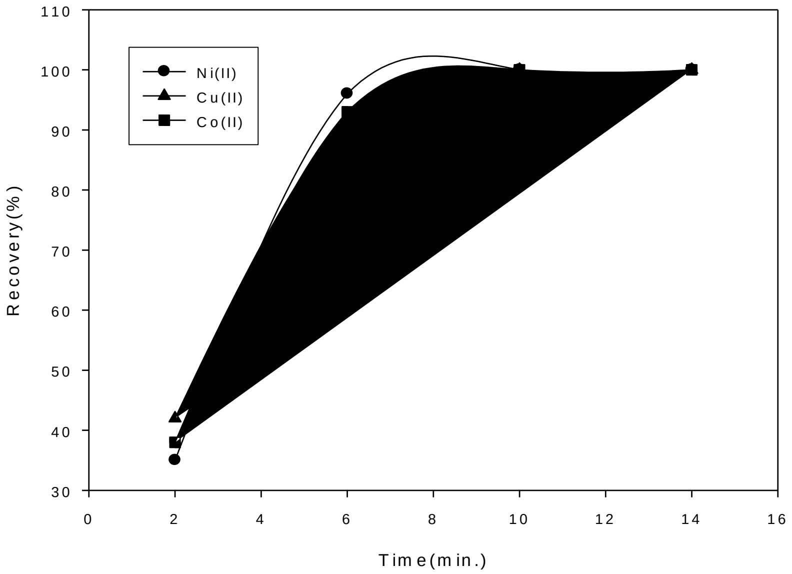


Fig.3: Effect of time on the adsorption of the metal ions onto the resin.



Characterization of the synthesized resin with FT-IR

The appearance of additional peaks at 3437.23 cm^{-1} and 1631.12 cm^{-1}, as compared to that of XAD-4, implies the proper incorporation of Quinol [21]. The red shifts of the two peaks for metal loaded resin suggest the involvement of both the groups in retaining the metal through chelation.

Optimum pH of metal ion uptake

Optimum pH of metal ion uptake was determined by static method. Excess of metal ion (50, 100µg) was shaken with 50 mg of resin for 120 minutes. The pH of metal ion solution was adjusted prior to equilibration over a range pH 2 – 10 with the corresponding buffer system.

Total sorption capacity

Total sorption capacity (Table 1) of the resin was determined by shaking an excess of metal ion solution (50 mL, 150 μgmL^{-1}) with 50 mg resin for 6 hrs. at the optimum pH at room temperature to ensure complete equilibrium. A breakthrough curve was obtained by plotting the concentration (mg/L) vs. the µmol of metal adsorbed per gram. The results are shown in Figure 2.

Sorption kinetics

The rate of loading of metal ions on the resin was determined by static method. 50 mL of each metal ion solution, contained in a 100 mL conical flask, was shaked with 50mg of the resin at room temperature in a thermostat shaker for preselected intervals of time. The loading halftime, $t_{1/2}$, that is, the time required to reach 50 % of the resins total loading capacity was evaluated from the resulting isotherm (Fig. 3).

Effect of matrix

The effect of cations and anions namely NO_3^{2-} , CO_3^{2-} , NH_4^+ , SO_4^{2-}, PO_4^{2-},Cl^- , K^+ and Na^+ on the quantitative absorption of Co(II), Ni(II), and Cu(II) ions on AmberliteXAD-4-Quinol resin was studied. For every combination of one of these electrolytes with any of the above ions, a set of solutions containing 100 µg each of the three metals in 50 mL and the matrix ions at different concentration levels was taken. The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5 % related to the preconcentration and determination of the analytes. Table 3 illustrates the interference effect.

Lower limit of metal ion detection

Sensitivity of the developed method was studied using analyte solutions in the concentration range (50 ml, 0.01- .0001 $\mu g\ ml^{-1}$) equilibrated with 100 mg of resin. The lower limit of detection for the three metals were found to be 3.0, 3.5 and 5.0 $\mu g\ ml^{-1}$ for Co (II), Cu(II) and Ni(II) respectively.

Resin durability test

The resin was subjected to several loading and elution cycles by the dynamic method. The resin beads (300 mg) were packed into the column and 50 mL(100µg)of each metal solutions were allowed to percolate through the bed of resin locked between two glass wool at a flowrate of 2.5 $mLmin^{-1}$.

Analytical performance of the method

The analytical performance of the method can be shown with standard addition method. The developed method has been applied for the determination of trace Co(II),Cu(II), and Ni(II) in tap water, mineral water, waste water and synthetic samples. For analysis, 50mL of sample water studied by the developed method. The results are given in Table 2.The correctness of the procedure was confirmed by the recoveries of spiked analytes from the 50 mL of water sample. The results indicated a recovery value, for each metal, of higher than 95% which implies the accuracy of the procedure.

CONCLUDING REMARKS

The AXAD-4-Quinol resin synthesized was successfully tested for performance. The results reflect its promising nature for trace metal ion analysis. Its credibility can also be assessed by comparison with many of the previously reported chelating resins (Table 4).

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