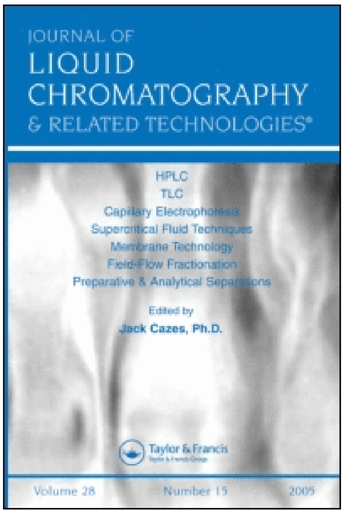

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Synthesis, Characterization, and Analytical Applications of a New Chelating Resin Containing p-Bromophenylhydroxamic Acid

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Abstract: A new chelating resin based on salicylic acid formaldehyde copolymer, containing hydroxamic acid as a functional group, has been synthesized and characterized on the basis of FTIR analysis, elemental analysis, and sorption capacity. The resin is highly stable in acidic and alkaline solutions and has been studied as a chelating sorbent for heavy metals. The sorption capacity order is: Cu(II) > Zn(II) > Pb(II) > Co(II) > Ni(II). The sorption for copper (II) was 1.80 mmol/g of dry resin. The distribution coefficients (K_d) for eight metal ions were determined in acetate buffers at pH = 2, 4, and 6. The effect of nature and concentration of different electrolytes on K_d values for Zn(II), Cd(II), Cu(II), and Pb(II) has been investigated. The quantitative separations achieved on the column of the chelating resin include Co(II)-Cu(II), Ni(II)-Cu(II), Cd(II)-Zn(II), and Pb(II)-Cu(II). The resin columns were studied for the removal of iron (III) up to 0.0005% level in cobalt acetate and analysis of bauxite. The developed procedure was also tested for the removal and recovery of copper (II) and iron (III) from synthetic seawater.

Keywords: Synthesis, Characterization, Chelating resin, p-Bromophenylhydroxamic acid

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INTRODUCTION

Removal, separation, and enrichment of trace metals in aqueous solutions play an important role for the analysis of wastewaters, industrial and geological samples, as well as for environmental remediation. In addition, there is also a growing interest to recover the precious metals due to both environmental and economic reasons.[1,2] Many separation techniques using solvent extraction and ion exchange chromatography have been applied for this purpose. Ion exchange is a popular method owing to its applicability to both preconcentration and separation. But, the use of chelating resins for separation and removal of metal ions is the method of choice due to its high separation efficiency, good reproducibility of retention parameters, and simplicity.[3–6] The strong chelating power of hydroxamic acid ligands has been utilized in the manufacture of chelating resins. Poly(hydroxamic acid) resins have been synthesized from polymetharylate,[7] Amberlite IRC 50,[8] Amberlite XAD-4,[9] and styrene-divinyl benzene copolymer.[10] Introduction of the bromo group at the para-position increases the basicity of the ligand and, hence, its chelating power for various metal ions. Shah and Devi have studied a chelating resin based on acrylonitrile-divinylbenzene copolymer containing p-bromophenylhydroxamic acid.[11] So far poly-(hydroxamic acid) chelating resin based upon salicylic acid–formaldehyde copolymer has not been reported.

The present paper describes the synthesis and characterization of a new chelating resin, salicylic acid-formaldehyde, containing p-bromophenylhydroxamic acid as functional groups. The resin has been studied for complexation of Cu(II), Zn(II), Cd(II), Ni(II), Pb(II), Co(II), and Fe(III) from aqueous solutions. The quantitative separations of Co(II)-Cu(II), Ni(II)-Cu(II), Cd(II)-Zn(II), and Pb(II)-Cu(II) were achieved on the columns of the chelating resin. The chelating resin has also been studied for the analysis of bauxite, removal of iron (III) from cobalt acetate, and recovery of Cu(II) or Fe(III) from synthetic seawater.

EXPERIMENTAL

Reagents

Salicylic acid (AR) and formaldehyde solution (37–41% W/V, AR) were obtained from CDH, India. All other reagents used were of analytical reagent grade.

Metal Ion Solutions

Metal ion solutions were prepared by dissolving their acetate salts in demineralized water and standardized by EDTA titration[12] or a spectrophotometeric method.[13]

Synthesis of the Chelating Resin

A mixture of salicylic acid (0.1 mol) and formaldehyde (0.8 mol) was refluxed for 10 h in the presence of 20 mL of 2 M HCl. Thus, obtained salicylic acid-formaldehyde copolymer was filtered and washed thoroughly with demineralized water until the filtrate was free from acid, dried in a vacuum oven at 50°C, ground, and sieved to (60–100 mesh). p-Bromophenylhydroxyl amine was synthesized by partial reduction of p-bromonitrobenzene with zinc powder at 60°C in the presence of ammonium chloride. The product was recrystallized using a mixture of petroleum ether and benzene. Then, chelating resin samples were prepared by treating salicylic acid-formaldehyde copolymer (2.5 g) with the varying amounts of p-bromophenylhydroxylamine (0.2–0.6 g) at 70–80°C for 8 h using a magnetic stirrer. The schematic diagram for synthesis of chelating resin is shown in Figure 1. The resulting chelating resins were washed thoroughly with methanol, then with 2 M hydrochloric acid, and finally with demineralized water until free from chloride. The resin samples were converted into H^+ form by treatment with 2 M HCl, for 24 h with occasional shaking and removal of the acid.

FTIR Studies

FTIR spectrum of the chelating resin was obtained by the KBr disc method using a FTIR spectrophotometer (Shimadzu 8201 PC).

Elemental Analysis

Elemental analysis of resin was carried out using Heraeus-carlo-Erba 1108 analyzer.

Sorption Capacity

The chelating resin was equilibrated with acetate buffers (pH 1–6) for 12 h. The buffer solutions were decanted and the resin samples (0.10 g) were equilibrated by shaking for 6 h with 20 mL of 0.1 M metal acetate solutions at appropriate pH. The metal ion concentration in the supernatant liquid was estimated. The results were also crosschecked by eluting the sorbed metal ions from the resin using appropriate eluents (Table 4).

Breakthrough Studies

For the column experiments, metal ion solution (1 mg/mL) buffered to pH 5 was passed through a Pyrex glass column (i.d. 0.5 cm), packed with 1 g of resin

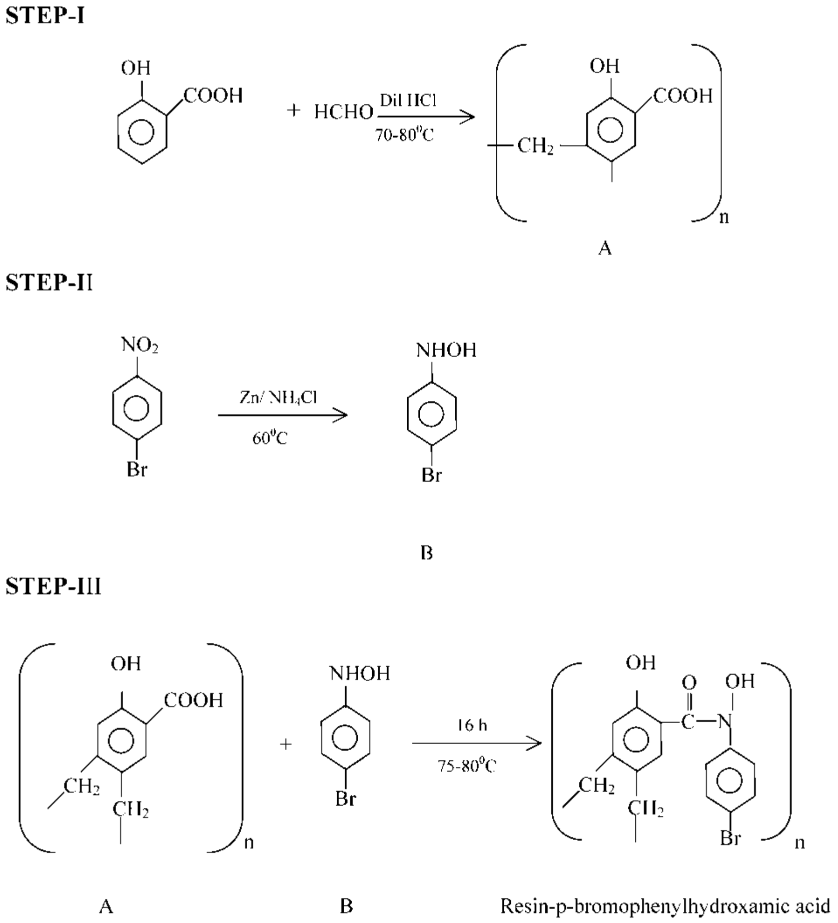

Figure 1. Schematic diagram for synthesis of chelating resin.

suspended in demineralized water. The flow rate was maintained at 0.4 mL/min. The effluent fractions were collected in 10 mL portions and analyzed for metal ions.

Distribution Coefficients (K_d) of Metal Ions

The K_d values of Cu(II), Zn(II), Cd(II), Co(II), Ni(II), Pb(II), Fe(III), and Al(III) were determined at pH 2, 4, and 6 by the batch method.[15] A metal ion solution (0.005 M, 20 mL) was shaken with 0.10 g of chelating resin at 25 ± 1°C for 6 h, which was found to be sufficient for attaining maximum sorption. The distribution coefficients, K_d (mL/g) are defined as:

$$K_d = [(C_i - C_f)/C_f] \times V/m\,(\mathrm{mL/g}),$$

Where C_i and C_f are the concentrations of metal ions at initial and at equilibrium stages, respectively; m (g) is the weight of chelating resin, and V (mL) is the volume of metal ion solution.

Effect of Different Electrolytes on K_d Values of Metal Ions

A 0.10 g portion of resin in H^+ form was suspended in 19 mL of electrolyte solution (0.05-1.0 M), adjusted to the pH value at which the resin shows the maximum sorption capacity for the metal ions. The mixture was shaken for 6 h. Then, 1 mL of 0.1 M solution of the metal ion under investigation was added. The solution was further shaken for 6 h and filtered. The filtrate was analyzed for the metal ion and K_d values were determined.

Analytical Separations

The chelating resin in H^+ form was packed into a chromatographic column to form a bed ~15 cm height and 0.4 cm diameter. Mixtures of metal ions (10 mg of each per 20 mL) at appropriate pH were passed through the column at a flow rate of 0.4 mL/min. The chelated metal ions were eluted using appropriate eluents. During elution, a flow rate of 0.4 mL/min was maintained.

Analysis of Bauxite

A 1 g sample of bauxite was heated with the mixture of concentrated nitric acid and hydrochloric acid (1:9). After dissolution, the mixture was evaporated to dryness and residue was dissolved in 5 mL of 0.1 M hydrochloric acid. Silica was filtered off and the filtrate and washings were diluted to volume in a 100 mL standard flask with demineralized water. A 10 mL aliquot of 100 mL of sample solution containing iron and aluminum was adjusted to pH 2 and passed through the chelating resin column at a flow rate of 0.4 mL/min.

Recovery for Spiked Synthetic Seawater Sample

Synthetic seawater was prepared as described by Riley and Skirrows,[16] A 1000 mL portion of the synthetic sea water was spiked with 50–100 μg of

Cu(II) or Fe(III), and filtered through Whatman No. 4 filter paper. The spiked synthetic seawater was passed through chelating resin column (i.d. 0.4 cm, height of resin bed ~15 cm), at a flow rate of 5 mL/min. The preconcentrated Cu(II) and Fe(III) were recovered by successive elution with 20 mL of 2 M and 4 M HCl solutions, respectively, at a flow rate of 0.4 mL/min. The effluents were analyzed for Cu(II) and Fe(III).

RESULTS AND DISCUSSION

Characteristics of Chelating Resin

The increased amount of p-bromohydroxyl amine (0.20–0.60 g) in the preparation of chelating resin results in increased sorption capacity for Cu(II) from 1.16 to 1.80 mmol/g. However, further addition to p-bromohydroxyl amine had no change in sorption capacity. The increase in capacity seems due to an increased amount of hydroxamic acid (a chelating group) in the resin. On the basis of maximum sorption capacity, the chelating resin prepared by adding 0.6 g of p-bromohydroxyl amine was taken for detailed studies. The chelating resin possesses 3.2% moisture content, 0.50 g/mL apparent density, and 0.38 void volume fraction. The infrared spectra of the chelating resin (Figure 2) showed bands at 1660 cm^{-1} (C=O), 3550–3300 cm^{-1} (intramolecular hydrogen bonded O-H), 513 cm^{-1} (C-Br), 3050 cm^{-1} (benzene aromatic C-H stretching), 1593–1456 cm^{-1} (ring

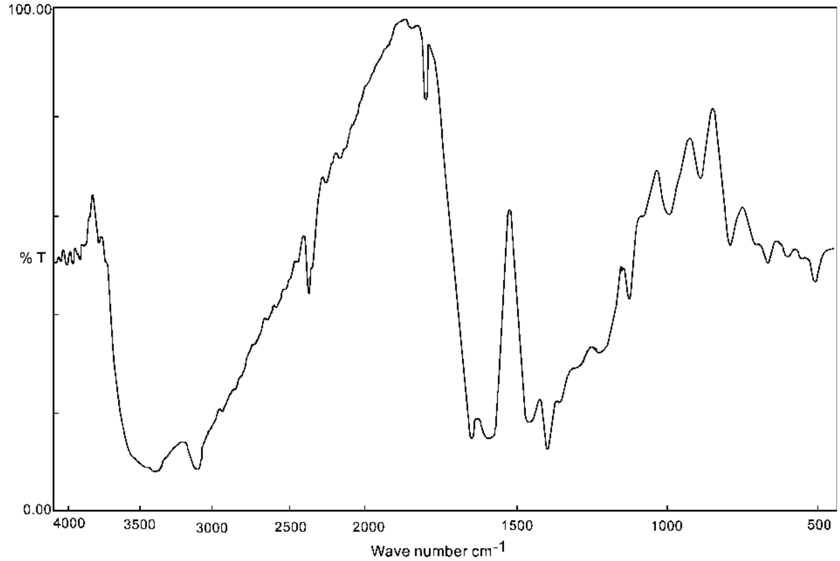

Figure 2. FTIR spectrum of chelating resin.

skeleton vibrations of -C═C-), and 1396 cm^{-1} (C-N). From the elemental analysis it was found that the conversion of carboxylic acid into hydroxamic acid was ~80% complete. The concentration of chelating groups (hydroxamic groups) found was 1.02 mmol/g from nitrogen stoichiometry.

The chemical stability was evaluated by measuring the change in sorption capacity for Cu(II) after successive contact of resin with acidic and alkaline solutions in the various concentration ranges. As a result, the chelating resin was stable in acidic solutions up to 5 M and alkaline solutions up to 1 M.

Sorption of Metal Ions on Chelating Resin

The sorption capacity of the chelating resin as a function of pH, for the metal ions under investigation, is shown in Figure 3. The sorption of metal ions on the resin is dependent on the pH of the sample solution, probably due to varying stability of metal ions—hydroxamic acid group complexes formed at different pH. The sorption capacities of Cu(II), Zn(II), and Ni(II) were found to be maximum at pH 5, while the optimum pH was 4 for Cd(II), Pb(II), and Co(II). The selectivity order of metal ions was evaluated as follows: Cu(II) > Zn(II) > Cd(II) > Pb(II) > Co(II) > Ni(II). The same

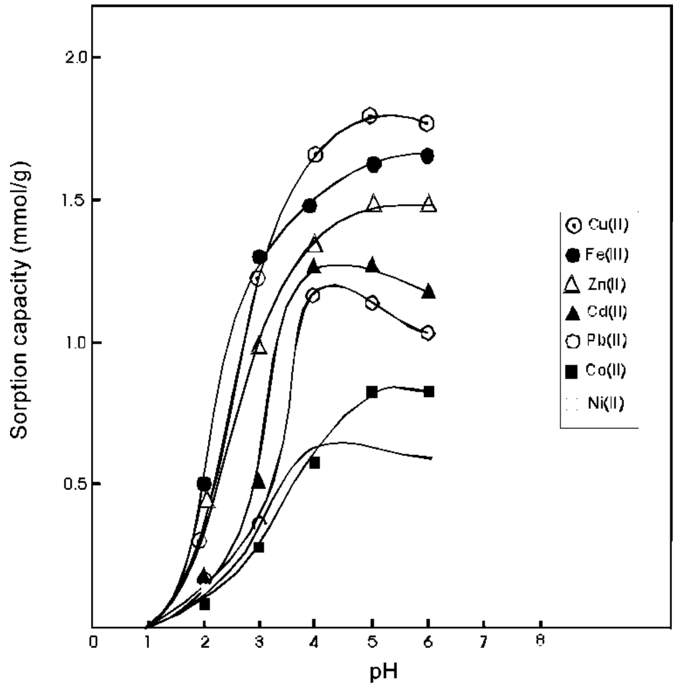

Figure 3. Effect of pH on sorption capacity of metal ions.

order is reported for macroreticular iminodiacetate resin[17] and acronitrile-divinylbenzene copolymer containing p-bromophenylhydroxamic acid.[11] It seems that the metal capacities of the resin increase with increasing stability of the metal complexes formed with the chelating resin. The ratio of metal ions uptake to the amount of hydroxamic groups were found as 1.8:1.0, 1.5:1.0, 0.82:1.0 for Cu(II), Zn(II) and Ni(II), respectively, at pH 5. The adsorption isotherm for Cu(II) plotted against the equilibrium concentration (Figure 5) shows that sorption capacity increases with equilibrium concentration of Cu(II). The maximum sorption capacity was found to be 2.5 mmol/g.

The capacities for the transition metal ions follow the Irving William order, except for Co(II). The capacity of the resin for Co(II) is higher than that for Ni(II). This may be due to aerial oxidation of Co(II) to Co(III), resulting in higher crystalfield stabilization energy for the cobalt complex than for the nickel complex. However, in the case of Cd(II) and Pb(II) purely electrostatic factors are responsible. The lower capacity of Cd(II) than Zn(II) may be explained due to greater hydrated—ion radius of Cd(II) than that of Zn(II). This will result in lower electrostatic interaction between Cd(II) and the coordinating groups and, hence, lower complex stability.

Column Breakthrough Studies

In the present work, the metal sorption capacity of resin was measured to estimate how large a quantity of the chelating resin would be needed for quantitative recovery of a metal ion from its aqueous solution. The breakthrough curves for Cu(II), Zn(II), Co(II), and Ni(II) are shown in Figure 4. This study revealed that as many as 11 bed volumes of Cu(II) corresponding to (110 mg retention), 9 bed volumes of Zn(II) corresponding to (90 mg retention), 4 bed volumes of Co(II) corresponding to (40 mg retention), and 2 bed volumes of Ni(II) corresponding to (20 mg retention), can be passed through the column of the chelating resin without any trace being detected in the effluent. The order of breakthrough capacity for the studied metal ion is: Cu(II) $>$ Zn(II) $>$ Co(II) $>$ Ni(II). The observed order of selectivity is further confirmed by sorption studies (Figure 3).

Distribution Coefficients (K_d) of Metal Ions

The distribution coefficients of metal ions under investigation determined in acetate buffers (pH 2, 4, and 6) are summarized in Table 1. The K_d values decreased with the decrease in pH of metal ions due to competitive reaction between chelating groups and hydrogen ions at lower pH; probably desorption increases at lower pH due to greater solubility of metals in acidic solutions.

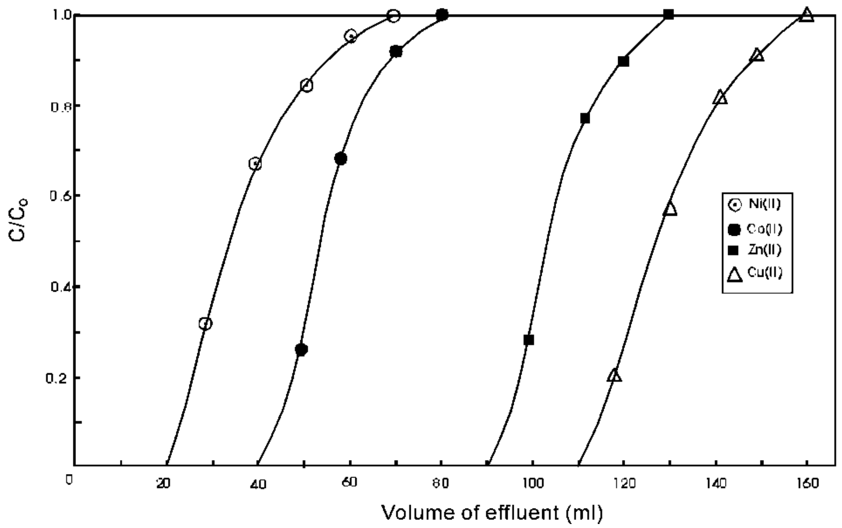

Figure 4. Breakthrough curves of metal ions with chelating resin.

Effect of Different Electrolytes on K_d Values of Metal Ions

The distribution coefficients (Table 2) for Cu(II), Cd(II), Pb(II), and Zn(II) increase with the decreasing concentration of sodium chloride, nitrate, and sulphate. This is because the heavy metal ions chelate with the hydroxamic

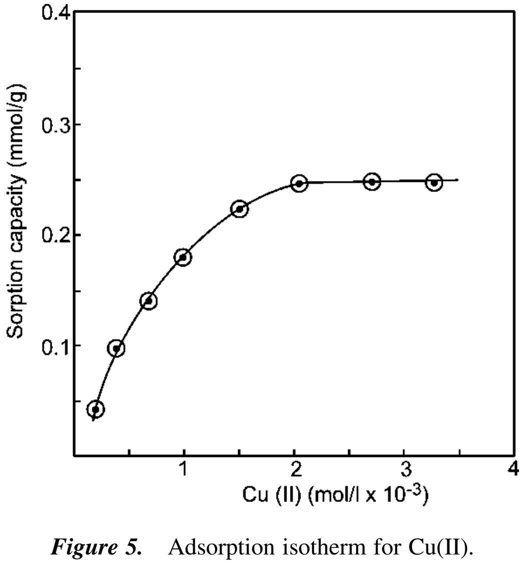

Figure 5. Adsorption isotherm for Cu(II).

Table 1. K_d values (mL/g) of metal ions in different pH systems

Metal ions	pH 2	pH 4	pH 6
Fe(III)	205	312	825
Zn(II)	165	210	46
Cd(II)	52	64	103
Co(II)	24	45	82
Ni(II)	20	32	45
Pb(II)	42	50	112
Cu(II)	825	904	1458
Al(III)	5	16	36

acid groups in the resin, whereas the background electrolyte is simply sorbed in the resin. The efficiency of exclusion of electrolyte (Donnan potential effect) increases with decreasing electrolyte concentration and, thus, favours an increase in K_d of metal ions. The electrolyte exclusion is found to be more efficient for counterions of low charge and co-ions of high charge. However, the decrease in K_d at 0.05 M background electrolyte concentration is regarded as a deviation from ideal behaviour, similar to that reported for metal ions by Kraus et al.[18] and Shah et al.[11]

Table 2. Effect of different electrolytes on K_d values of metal ions

		K_d		
Metal ion	Concentration of electrolyte, (M)	Sodium chloride	Sodium nitrate	Sodium sulphate
Cu(II)	1.0	101	121	225
	0.5	175	190	324
	0.1	300	512	1074
	0.05	202	260	398
Cd(II)	1.0	50	24	72
	0.5	80	58	122
	0.1	108	154	191
	0.05	64	25	45
Pb(II)	1.0	18	32	62
	0.5	40	64	80
	0.1	45	80	155
	0.05	18	19	32
Zn(II)	1.0	20	67	28
	0.5	26	102	58
	0.1	28	187	201
	0.05	15	38	22

Removal of Iron (III) from Cobalt Acetate

Iron (III), present in cobalt acetate can be removed by passing a solution of the salt at pH 2 through a column of the resin; Co(II) does not form the complex with hydroxamic acid at pH 2, and passes through the column. Iron (III), preconcentrated on the resin can be eluted from column using 4 M hydrochloric acid. A cobalt acetate sample containing 0.025% of iron was purified by the proposed method, iron content being reduced to 0.0005%.

Analytical Separations

Separations of Cu(II) from Pb(II) and Zn(II) from Cd(II) (10 mL of 1 mg/mL) solution of each metal ion) were performed at pH 5 by selective elution of Pb(II) with 4 M sodium chloride solution and of Cu(II) with 2 M hydrochloric acid solution and by gradient elution of Cd(II) and Zn(II) with 0.1 M and 0.5 M hydrochloric acid solutions, respectively.

Separation of Cu(II) from Co(II) and Ni(II) (10 mL of 1 mg/mL solution of each metal ion) was achieved by selective sorption of Cu(II) at pH 2 and gradient elution of Co(II) and Ni(II) with 0.1 M nitric acid and Cu(II) with 2 M hydrochloric acid. The results of these separations are summarized in Table 3. The % error observed was −0.40 to 0.50.

Analysis of Bauxite

Bauxite solution was passed through the resin column at pH 2. Aluminium (III) does not form the complex with hydroxamic acid at pH 2, and is thus separated from iron (III), the adsorbed iron (III) was eluted with 4 M

Table 3. Separations achieved on the columns of chelating resin

Mixture No.	Metal ion	Eluent	Eluate (mL)	Amount found (mg)	Error (%)
1	Co(II)	0.01 M HNO_3	25	10.01	0.10
	Cu(II)	2 M HCl	20	9.96	− 0.40
2	Ni(II)	0.01 M HNO_3	25	10.00	0.00
	Cu(II)	2 M HCl	20	9.97	−0.30
3	Cd(II)	0.1 M HCl	20	10.02	0.20
	Zn(II)	0.5 M HCl	25	9.97	−0.30
4	Pb(II)	4 M NaCl	30	10.05	0.50
	Cu(II)	2 M HCl	20	9.96	−0.40

Amount of each metal ion loaded = 10 mg.

Table 4. Recovery of Cu(II) and Fe(III) from synthetic seawater sample[a] (n = 5)

Metal ions	Added (μg/L)	Found (μg/L)	Total recovery (%)	RSD (%)
Cu(II)	50	50.0	100.0	—
	100	99.9	99.9	1.0
Fe(III)	50	49.8	99.6	—
	100	99.5	99.5	1.2

[a] Volume of sample 1000 mL (pH 2); total volume of eluent 20 mL.

hydrochloric acid. The bauxite sample contained 1.8% iron, which was determined with 1.3% relative error.

Recovery for Spiked Synthetic Seawater Samples

To verify the applicability of the present chelating resin to the preconcentration of trace Cu(II) or Fe(III) from seawater, the extraction and elution of 100 μg of Cu(II) or Fe(III) from 1000 mL of synthetic seawater was studied. In this study, the preconcentrated Cu(II) and Fe(III) were recovered with 20 mL of 2 M and 4 M hydrochloric acid, respectively. Table 4 shows the results of five independent determinations of 100 μg of Cu(II) or Fe(III) in synthetic seawaters. Quantitative recoveries were obtained from the highly saline sample with good reproducibility, even though 1000-fold enrichment was applied. The results indicate that the extraction and elution of Cu(II) or Fe(III) is little affected by the coexistence of salt matrices, and suggests that the present chelating resin is applicable to real natural water samples, such as seawater.

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