SORPTION PROFILE AND THERMODYNAMIC CHARACTERISTICS OF NITROSONAPHTHOL FUNCTIONALIZED SORBENT FOR METAL ION ENRICHMENT

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Received January 5, 2005
Accepted May 16, 2005

A simple and reliable method has been developed using styrene–divinylbenzene-based polymeric material containing 1-nitroso-2-naphthol as chelating agent, to concentrate ultratrace amounts of Ni(II) and Cu(II) ions in aqueous samples. Sorption of both the ions on the new synthetic resin under static and dynamic conditions has been investigated. The sorption has been optimized with respect to pH, shaking and contact time of two phases. Maximum sorption has been achieved from solution of pH 5–8 after 8 min of agitation. Total saturation capacities were 516 ± 2 and 316 ± 2.5 μmol g^{-1} for Ni(II) and Cu(II) ions, respectively. The lowest concentration for quantitative recovery (98 ± 1%) is 1.33 and 5 ppb with the preconcentration factor of 750 and 200 for Ni(II) and Cu(II), respectively. Monitoring of the influence of diverse ions on the sorption of metal ions has revealed that phosphate, hydrogencarbonate and citrate reduce the sorption to some extent. Under optimum conditions the sorption data followed Langmuir, Freundlich, and Dubinin–Radushkevich isotherms. The kinetics and thermodynamics of sorption are studied in detail. The sorption procedure is utilized to preconcentrate these ions prior to their determination in tea, human hair, and tap water samples by atomic absorption spectrometry using direct and standard addition methods.

Keywords: Sorption; Thermodynamics; Functionalized sorbent; Preconcentration; Nickel; Copper; Azo compounds; Ion exchangers; Atomic absorption spectroscopy; Functionalized resins; Metal ions; Nitroso compounds.

Analytical determination of metal ions at trace or subtrace levels requires versatility, specificity, sensitivity and accuracy. In certain cases direct determination of metal ions using various instrumental methods is not possible due to matrix interference and their low concentrations in analyte samples. These difficulties can be overcome by employing effective separation and preconstruction techniques to improve the detection limits and selectivity of their determination. Several methods have been proposed and employed

doi:10.1135/cccc20051341

for the preconcentration/separation of elements at trace or subtrace levels depending upon the nature of the samples, analyte concentration and analytical procedures of measurement. Solvent extraction, precipitation, adsorption, distillation, evaporation, electrophoresis, ion-exchange[1–3] and chelating resins have been utilized to achieve these objectives. Solid phase extraction has become popular because of numerous advantages over other methods such as its simplicity, rapidity and ability to attain a high concentration factor. Chelating solid phases may be tailored by immobilizing appropriate ligands on insoluble functionalized polymers having good stability and high capacity for metal ions.

Recently, several chelating matrices have been developed using resins of Amberlite XAD series a support with very high capacity increasing the number of chelating sites and making them accessible. This can be achieved by selecting a ligand of small size and a polymeric support of moderate crosslinking. A number of ligands such as pyrocatechol[4], thiosalicylic acid[5], poly (dithiocarbamate)[6], tiron[7], 2-aminophenol[8], pyridylazonaphthol (PAN)[9], dithizone[10], *o*-vanillinethiosemicarbazone[11] and *N*-(2-hydroxyethyl)ethylenediamine[12] have been used to develop resins of XAD series as a support. 1-Nitroso-2-naphthol forms strong complexes with divalent nickel and copper ions[13]. Therefore, macroporous Amberlite XAD-2 resin has been functionalized using 1-nitroso-2-naphthol ligand through an azo spacer. It is a multidentate ligand containing binding sites for metal ions. The resulting resin has been characterized and its sorption potential for Ni(II) and Cu(II) ions has been investigated in detail and used in a preconcentration procedure before their estimation in tea, human hair and tap water using atomic absorption spectrometry. The present communication reports the results of this study in detail.

EXPERIMENTAL

Apparatus and Reagents

A Varian AA-10 atomic absorption spectrophotometer (AAS) is used for the determination of metal ions in solution. The pH measurements are made on digital (inoLab pH level I) pH meter. A Gallenkamp automatic shaker model BKS 305-010, U.K. is used the batch experiments. The liquid flow through the column was controlled by a peristaltic pump. Nicolet Avatar FT-IR spectrometer was employed to record IR spectra.

All chemicals used were of analytical or equivalent grade. Stock standard solutions of Ni(II) and Cu(II) have been prepared by dissolving appropriate amounts of their nitrates in deionized water (conductivity 0.5 μS cm^{-1} and pH 6) and acidified with small amounts of nitric acid.

Buffer solutions of pH 1–3, 4–6, and 7–9 were prepared by mixing in appropriate ratios 0.1 M HCl and KCl, 0.5 M acetic acid and sodium acetate and 0.5 M ammonia and NH_4Cl solutions, respectively.

Amberlite XAD-2 (surface area 300–750 m^2/g, pore diameter 90–50 Å and bead size 200–400 mesh) was procured from Fluka, Germany.

Synthesis of the Sorbent

A 5-g sample of Amberlite XAD-2 was mixed with 10 ml of concentrated HNO_3 and 25 ml of concentrated H_2SO_4 and stirred at 60 °C for 30 min. Thereafter, the reaction mixture was poured into an ice–water mixture. The nitrated resin was filtered, washed with water until free from acid and mixed with 40 g of $SnCl_2$, 45 ml of concentrated HNO_3 and 50 ml of ethanol. The mixture was refluxed for 10 h. The solid precipitate was filtered and washed with water and 2 M NaOH. The amino resin was first washed with 2 M HCl and finally with an excess of water. The resin was than slurried in an ice–water mixture (350 ml) and treated with 1 M HCl and 1 M $NaNO_2$ (added in small aliquots of 1 ml) until the reaction mixture began to give a dark blue color with starch iodide paper. The diazotized resin was filtered, washed with cold water and reacted with 1-nitroso-2-naphthol (2.5 g in 350 ml of glacial acetic acid and 150 ml of acetone) at 4 °C for 24 h. The resulting brown color beads were filtered and washed with water. For $C_{18}H_{15}N_3O_2 \cdot H_2O$ (323.4) calculated: 66.87% C, 5.26 % H, 13.00% N; found: 66.90% C, 5.25% H, 12.91% N.

Sorption Procedure

Static sorption of metal ions. A weighed amount of nitrosonaphthol modified resin was equilibrated with 10 ml of a metal ion solution (1.57×10^{-4} mol l^{-1}) maintained at constant pH and ionic strength at 25 °C. The resin was filtered off. The sorbed metal ions were desorbed by shaking with 2 M HNO_3/HCl and analyzed with flame atomic absorption spectrophotometer at 232 and 324.8 nm, respectively for Ni(II) and Cu(II) using air-acetylene flame.

Dynamic Sorption of Metal Ions

Synthesized resin (500 mg) was slurried in water, and then poured into a glass column (5 × 50 mm). A small amount of glass wool was placed on the top to prevent any loss of resin beads during the sample loading. A solution of metal ion (3.14×10^{-4} mol l^{-1}) was passed through the column at flow rates between 1–10 cm^3 min^{-1} after adjusting its pH with a suitable buffer. After the sorption the column was washed with water and then 1–2 M HCl/HNO_3 was passed to elute the sorbed metal ion. The concentration of metal ion was determined by AAS.

The sorption of metal ions onto the functionalized XAD-2 resin was computed using the following equation

$$\% \text{ sorption} = \frac{A_\mathrm{i} - A_\mathrm{f}}{A_\mathrm{i}} \times 100 \qquad (1)$$

where A_i is absorbance of solution before sorption and A_f is absorbance of solution after sorption.

The results are the average of at least triplicate measurements. The precision is in most cases close to ±2%.

RESULTS AND DISCUSSION

Characterization of Modified Resin

The chemically modified resin (Fig. 1) was characterized by thermal, IR and elemental analyses before sorption studies. The TGA plot of functionalized resin (Fig. 2) shows a two-step weight loss up to 500 °C. The 5.43% weight loss up to 115.7 °C in the first step is due to sorbed water and suggests that approximately one water molecule per repeat unit of polymer is present. The second step mass loss starts above 200 °C, which indicates a high thermal stability of modified resin

The results of elemental analysis (66.9% C, 5.25% H, 12.91% N) also suggest that one water molecule is present per repeat unit of polymer.

The functionalized XAD-2 resin was also characterized by FT-IR spectroscopy. The important IR bands of the modified resin (Fig. 3) at 1244 and 1180 cm^{-1} are due to the aromatic nitroso group and C–N stretching vibrations, respectively. A characteristic band at 1410 cm^{-1} can be assigned to the azo group indicating the conversion of amino resin to the diazotized resin[14].

Optimization of Sorption onto Functionalized Resin

Initially, the experiments were carried out to select the most appropriate medium to give maximum sorption. Buffers of pH 1–10 were investigated to observe the effect of pH on the sorption of divalent Ni and Cu ions. The results are shown in Fig. 4. The sorption increases with increasing pH of metal solution and attains a maximum value at pH 8 for Ni(II) and pH 9 for Cu(II) ions. Maximum (>90%) sorption of Ni(II) and Cu(II) ions has been reported for dithizone-loaded resin[10] at pH 8 and 9, respectively. Quantita-

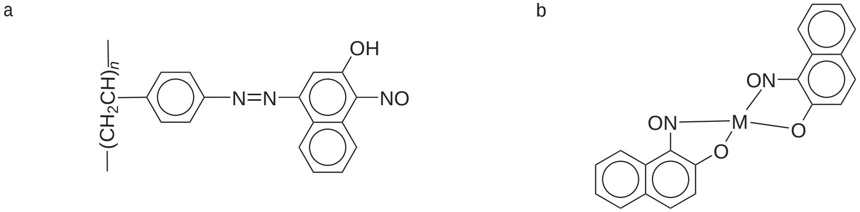

FIG. 1
Single unit of 1-nitroso-2-naphthol functionalized XAD-2 resin (a); metal-1-nitroso-2-naphthol complex (b)

tive sorption of (>95%) of Ni(II) is shown between pH 6.5–11.5 for PAN immobilized on XAD resin[9]. Similarly quantitative sorption (96–98%) for Ni(II) and Cu(II) ions has been reported on XAD resin functionalized with 2-aminophenol[8]. This indicates that the sorption process involved the release of H^+ ions allowing firm complexation of metal ions to XAD-2/1-nitroso-2-naphthol. The reaction scheme can be represented as follows:

$$M^{2+} + 2\text{-nitrosonaphthol} \rightarrow M(\text{nitrosonaphthol})_2 .$$

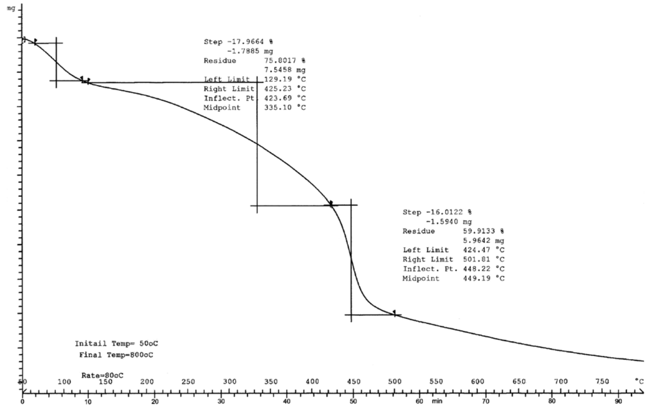

FIG. 2
Thermogram of 1-nitroso-2-naphthol modified XAD-2

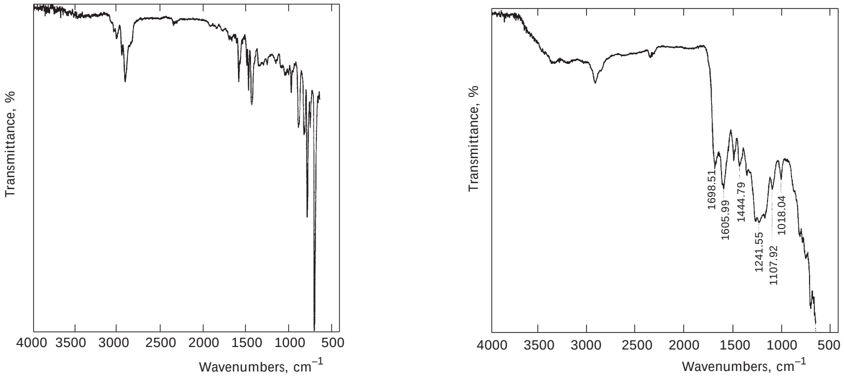

FIG. 3
IR spectra of unmodified XAD-2 (a) and XAD-2 modified with 1-nitroso-2-naphthol (b)

The structure of possible complex is shown in Fig. 1b. However, the amount of metal ions sorbed decreased when pH was greater than 8 for Ni(II) and 9 for Cu(II) ions this may be due to the hydrolysis of the metal ions in strong basic solution. Up to pH 8 the main species of Ni(II) is Ni^{2+} and Cu(II) is Cu^{2+}.

Sorption of metal ions as a function of the shaking was studied in the range 30–120 rpm (Fig. 5). It was found that the sorption increases with increasing shaking speed and attains a maximum at 90 rpm; it decreased above 90 rpm. For further studies the shaking speed of 90 rpm was employed for both metal ions.

The sorption of both the metal ions on the synthesized resin has also been studied as a function of shaking time. The results are depicted in Fig. 6. Sorption in both the cases is very rapid (≥92% within 10 min), which indicates diffusion of solute through a hypothetical film or hydrodynamic boundary[15]. Similarly, 10 and 5 min were found to be sufficient to attain maximum sorption of Ni(II) and Cu(II) ions on tiron[7] and thiosalicylic acid[5]-loaded XAD resin, respectively. The fast resin–metal interaction at an optimum pH may be attributed to better accessibility of the chelating sites of the modified resin to metal ions. Beyond 10 min no further increase in sorption was observed; therefore, for further investigations 10-min agitation time was applied.

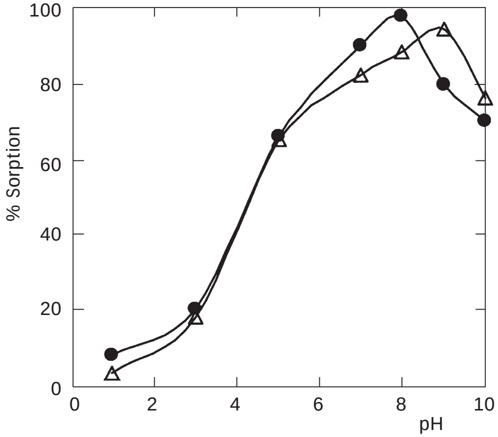

FIG. 4
Sorption of Ni(II) (●) and Cu(II) (△) ions as a function of pH

Kinetics of Sorption

The change of sorption with time was subjected to the Morris–Weber and Lagergren kinetic equations. The sorbed concentration at time t, q_t (μmol g^{-1}) is plotted against '$\sqrt{t}$' to test the Morris–Weber equation[16] in the following form:

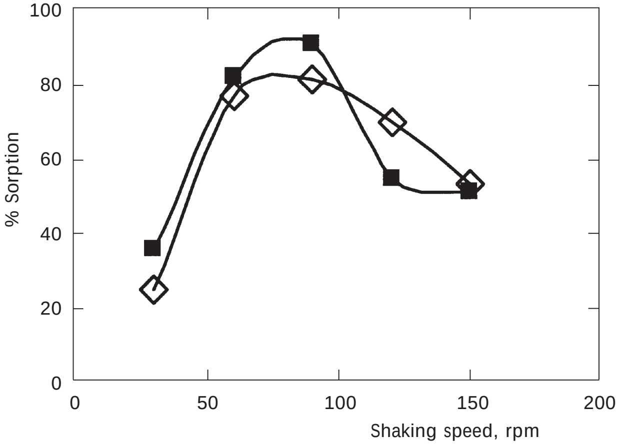

FIG. 5
Effect of equilibration speed on the sorption of Ni(II) (■) and Cu(II) (◇) ions on modified XAD-2

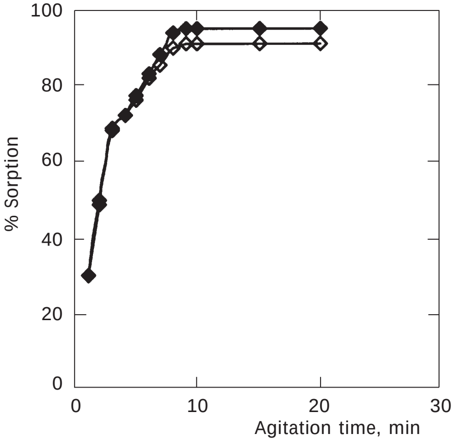

FIG. 6
Effect of agitation time on the sorption of Ni(II) (◆) and Cu(II) (◇) ions

$$q_t = R_d\ (t)^{1/2}. \qquad (2)$$

Up to 8 min, Eq. (*2*) holds good with correlation coefficient 0.98 both for Ni(II) and Cu(II) ions, but deviates as the agitation time is increased. From the slope of the plot in the initial stage, the value of R_d, the rate constant of intraparticle transport, is estimated to be 3.96 ± 0.32 μmol g^{-1} $min^{-1/2}$ for both the metal ions. The Lagergren equation[17]

$$\log (q_e - q_t) = \log q_e - kt/2.303 \qquad (3)$$

was tested by plotting log ($q_e - q_t$) versus time, t, where q_e is the sorbed concentration of metal ions onto modified resin (mol g^{-1}) at equilibrium. In the early stages (up to 7 min), the plot appears to be linear with correlation coefficient 0.988 for both the metal ions. The slope gives the value for the overall rate constant k = 0.356 ± 023 and 0.345 ± .023 min^{-1} for both Ni(II) and Cu(II) ions. Beyond 7 min, the slope becomes very steep.

Sorption Isotherms

The sorption of both the metal ions was also investigated as a function of their concentration in the range 1.7×10^{-4}–8.6×10^{-6} mol l^{-1} using 100 mg sorbent and 10 min shaking time at a shaking speed of 90 rpm. The sorption data were tested with different sorption isotherms such as Langmuir, Freundlich, and Dubinin–Radushkevich (D-R). The data followed all three isotherms over the entire concentration of Ni(II) and Cu(II) ions investigated.

The Freundlich isotherm, the most widely used mathematical model, gives an empirical expression encompassing the surface heterogeneity and exponential distribution of active sites and their energies[18a]. The Freundlich sorption isotherm was tested in the following form:

$$\log C_{ads} = \log A + 1/n \log C_e \qquad (4)$$

where C_{ads} is the amount of sorbate (mol g^{-1}) and C_e is the concentration of sorbate in liquid phase at equilibrium (mol l^{-1}), A is a constant related to the sorption capacity and $1/n$ is a constant associated with the strength of sorption which should be always <1. The log C_{ads} was plotted against log C_e which is linear for both metal ions. Another sorption model that of Langmuir[18b] represents chemisorption on a set of well-defined localized sorption sites having same energy, independent of surface coverage and with no interactions between sorbed species. The Langmuir model was tested in the following form:

$$\frac{C_\mathrm{e}}{C_\mathrm{ads}} = \frac{1}{Qb} + \frac{C_\mathrm{e}}{Q} \tag{5}$$

where C_e and C_ads are same as that for Freundlich, Q is the maximum amount of metal ions sorbed corresponding to a monolayer coverage of sorbent surface and b is a constant related to the binding energy of sorbate, independent of temperature. The plot of $C_\mathrm{e}/C_\mathrm{ads}$ versus C_e gives a straight line for both Ni(II) and Cu(II) ions indicating that Langmuir sorption is followed by the sorption data very well. A characteristic of Langmuir isotherm can be expressed in terms of dimensionless constant, R_L [19], using the relationship

$$R_\mathrm{L} = 1/(1 + bC_\mathrm{i}) \tag{6}$$

where b is Langmuir constant and C_i is the initial concentration of metal ions. The values of R_L falls in the range 0.3–0.9 for Ni(II) and 0.2–0.9 for Cu(II) ions indicating highly favorable sorption.

The Dubinin–Radushkevich isotherm is postulated within a sorption ‘space’ close to sorbent surface[18c]. The model features the heterogeneity of energies over the surface. The linearity of D-R isotherm is tested in the following form:

$$\ln C_\mathrm{ads} = \ln X_\mathrm{m} - \beta\varepsilon^2 \tag{7}$$

where X_m is the total sorption capacity, β is the coefficient having dimensions of energy and ε is Polanyi potential which is equal to

$$\varepsilon = RT \ln (1 + C_\mathrm{e}) \tag{8}$$

where R is gas constant in kJ mol^{-1} and T is temperature (in K). β is related to the mean sorption energy (E) as envisaged[20]

$$E = \frac{1}{\sqrt{-2\beta}}\ . \tag{9}$$

This is the Gibbs energy of the transfer of one mol of solute to the surface of the sorbent.

Freundlich, Langmuir and D-R constants were evaluated using slope and intercept of linear plots of both the metal ions studied. The results are listed in Table I. The numerical value of Freundlich constant $1/n < 1$ shows that sorption capacity is only slightly suppressed at lower equilibrium concentrations.

The value of sorption capacity is different for all three sorption isotherms. This difference can be interpreted in terms of the assumptions taken into consideration while deriving these sorption models.

The numerical values of sorption energy were calculated from D-R isotherm (13.13 ± 0.3–9.3 ± 0.19 kJ mol^{-1}), ranging from 9 to 16 kJ mol^{-1}. They are expected for chemisorption or ion exchange[21]. Hence, it is very likely that the trace metal ions are sorbed on nitrosonaphthol modified XAD-2, predominantly by chemisorption.

Thermodynamics of Sorption

The effect of temperature on the sorption of Ni(II) and Cu(II) ions on nitrosonaphthol-loaded XAD-2 was studied in the range of 15–40 °C under optimum conditions. Log $K_C = F_e/1 - F_e$, where F_e is the fraction sorbed at

TABLE I
Sorption parameters of Ni (II) and Cu (II) ions on modified XAD-2 resin

Isotherm	Parameter	Cu(II)	Ni(II)
Freundlich	$1/n$	0.45 ± 0.01	0.44 ± 0.03
	K, mmol g^{-1}	3.5 ± 0.5	4.46 ± 0.5
	Correlation factor, γ	0.9967	0.992
Langmuir	Q, mmol g^{-1}	0.06 ± 0.03	0.104 ± 0.03
	b, l mol^{-1}	$(7.1 \pm 0.8) \times 10^4$	$(9.7 \pm 0.01) \times 10^3$
	Correlation factor, γ	0.9797	0.989
	R_L, dimensionless factor	0.2–0.9	0.3–0.9
D-R	X_m, mmol g^{-1}	0.24 ± 0.04	1.18 ± 0.1
	E, kJ mol^{-1}	13.13 ± 0.3	9.3 ± 0.19
	Correlation factor, γ	0.993	0.997
	ΔH, kJ mol^{-1}	–50.8 ± 3.2	–47.82 ± 3.1
	ΔS, J mol^{-1} K^{-1}	–159 ± 25	–148 ± 20
	ΔG, kJ mol^{-1}	–3.27 ± 1.2	–3.43 ± 1.3
	Correlation factor, γ	0.996	0.999

equilibrium, was plotted against $1/T$ (in K). The values of ΔH, ΔS and ΔG were estimated using the relationships

$$\log K_c = -\Delta H/2.303RT + \Delta S/2.303R \tag{10}$$

$$\Delta G = -RT \ln K_c \,. \tag{11}$$

From the slope and intercept of the plots the values of $\Delta H = -47.82 \pm 3.1$ and -50.8 ± 3.2 kJ mol^{-1}, $\Delta S = -148 \pm 20$ and -159 ± 25 J mol^{-1} K^{-1}, $\Delta G_{298K} = -3.43 \pm 1.3$ and -3.27 ± 1.2 kJ mol^{-1} have been estimated both for Ni(II) and Cu(II) ions with the correlation factor 0.999 for Ni and 0.996 for Cu. The negative values of ΔH and ΔG indicate the exothermic and spontaneous nature of the sorption.

Dynamic Sorption

Effect of flow rate. The effect of flow rate on the sorption was studied at flow rates 1–8 cm^3 min^{-1} (Fig. 7) at the pH chosen for maximum sorption. It was observed that at flow rates higher than three there was decrease in % sorption.

Recovery studies. Different mineral acids were used to desorb the metal ions from the resin. The efficiency of stripping mineral acids was studied by using different volumes (1–10 cm^3) and concentrations of mineral acids. It

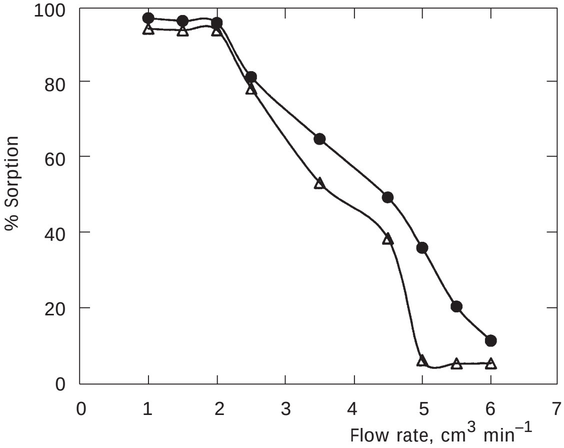

FIG. 7
Effect of flow rate on the sorption of Ni(II) (●) and Cu(II) (△) ions on modified resin

was found that 3 cm^3 of 2 M HCl or HNO_3 was sufficient for more than 98% recovery of Ni(II) and Cu(II) ions. Therefore for complete recovery 3 cm^3 of 2 M HCl was used.

Limit of preconcentration and preconcentration factor. The limit of preconcentration was determined by increasing the volume of metal ion solution and keeping the total amount of loaded metal ion constant at 10 μg. Quantitative collection of Ni(II) and Cu(II) ions was possible from solutions of concentration in the order 1–5 ppb with recovery up to 98%. Preconcentration factor for Ni(II) and Cu(II) ions was found to be 750 and 200, respectively.

Break through studies. In sorption studies the breakthrough is depicted when the effluent concentration of any chemical species from the column is ca. 3–5% of the influent concentration. The breakthrough volume of both the metal ions was observed and noted on *x*-axis of the plot (Fig. 8) at the initial rise of the curves. Similarly the total saturation volume (where $C_e \approx C_i$) was observed and noted on *x*-axis (top) of the plot at the final shape of the curves. The breakthrough occurs at 975 ml for Ni(II) and at 750 ml for Cu(II). The total sorption capacities in mmol g^{-1} were calculated on the basis of total saturation volumes and were found 0.516 ± 0.001 and 0.316 ± 0.005 mmol g^{-1} for Ni(II) and Cu(II) ions, respectively. The sharp profile of the curve shows the favorable equilibrium[22].

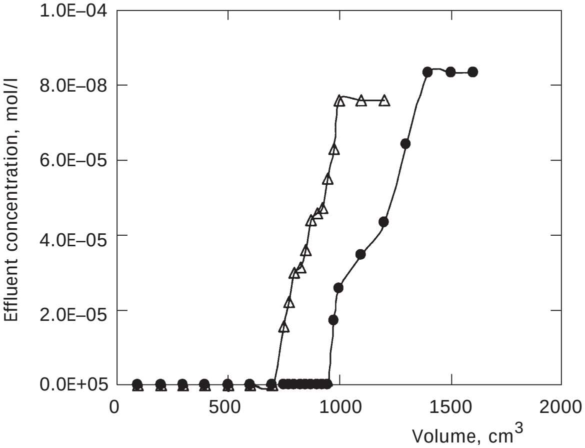

FIG. 8
Break through curve for the sorption of Ni(II) (●) and Cu(II) (△) on modified resin

Resin stability. The resin stability was checked by subjecting the resin to several loading-and-elution experiments. The capacity of the resin was found to be practically constant (variation 1–2%) after its repeated use for more than ten times, thus the multiple use of resin column is feasible.

Influence of Common Ions

Because common ions influence the sorption of metal ions in aqueous solutions their effect (in the ratios 1:100 and 1:10 for anions and cations, respectively) was examined on the sorption for the synthesized resin. The results are given in a histogram shown in Fig. 9. It is evident from Fig. 9 that phosphate; hydrogencarbonate and citrate reduce the sorption by 3–17%. This decrease in the presence of anions may be due to the replacement of metal ions by these anions themselves or lower sorption affinity for anionic complexes of Ni(II) and Cu(II) ions with these anions. The strong complexes of Ni(II) and Cu(II) ions with phosphate, nitrate, hydrogencarbonate and citrate have been reported in the literature[23,24].

Applications of the Method

Human hair and tea samples. The proposed method was used for the determination of nickel and copper in tea leaves and human hair. 0.1 g sample dissolved in concentrated nitric acid (5 cm^3) with heating. The solution was

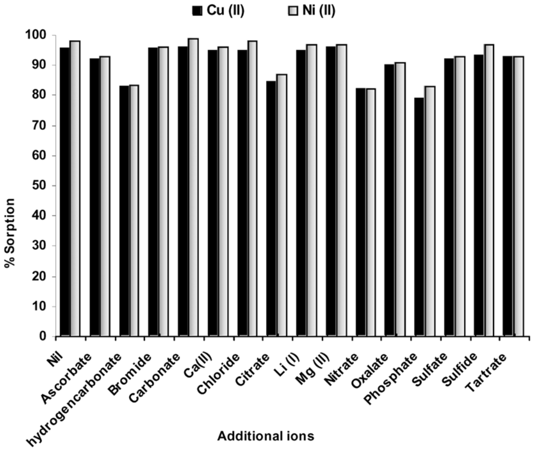

FIG. 9
Effect of common anions and cations on the sorption of Ni(II) and Cu(II) ions on functionalized XAD-2

cooled, diluted and filtered. The filtrate was made to 100 cm^3 with deionized water after adjusting its pH to the optimum value. The estimation of both the metal ions were made with and without standard addition by passing 100 ml of a sample through a column packed with 0.5 g of resin and determining the metal by FAAS after elution as described in the procedure.

Water samples. Water samples were filtered and estimation of both the metal ions was made with and without standard addition by following the described procedure.

The concentration reported in Table II as evaluated by standard addition (SA) method are the values obtained by subtracting the amount of the metal added for spiking from the total metal recovered. The results are given in Table II and reflect the suitability of the present modified resin for preconcentration before actual measurement of both the metal ions using atomic absorption spectrometry.

TABLE II
Analysis of Ni(II) and Cu(II) ions in real samples using atomic absorption spectrometry

Sample	Method	Metal ions, μg g^{-1}			
		Cu(II)[a]	%RSD	Ni(II)[a]	%RSD
Tea 1	Direct	20.5	2.5	9.7	2.0
	SA	20.3	3.0	9.0	2.5
Tea 2	Direct	18.85	1.5	2.57	1.1
	SA	18.2	1.2	2.50	2.0
Human hair 1	Direct	15.34	2.4	5.54	2.5
	SA	14.98	2.5	5.50	2.3
Human hair 2	Direct	16.89	1.5	3.32	1.0
	SA	16.0	1.0	3.1	1.6
S.U.C, Pakistan tap water		15.2	0.2	2.8	2.0
	SA	15.5	1.8	2.8	0.5
Hyderabad, Pakistan		22	1.0	3.5	0.8
	SA	22.1	1.9	3.7	0.5

SA, Standard addition = 5 mg; S.U.C, Sindh University Colony; [a] Average of three determinations.

CONCLUSIONS

XAD-2-nitrosonaphthol resin has been found useful for preconcentration of trace amounts of Ni(II) and Cu(II) ions and their separation from aqueous solutions. Fast equilibration of metals on the resin makes it also applicable for the conventional column method. The low affinity of resin towards alkali metals, alkaline earth metals and common anions indicates its use for environmental application. The sorption data are followed quantitatively by three isotherms namely Langmuir, Freundlich and Dubinin–Radushkevich. The negative values of ΔH and ΔG indicate the exothermic and spontaneous nature of the sorption for both the metal ions.

Comparison of preconcentration factor of both the metal ions on nitrosonaphthol functionalized resin with different ligands showed that nitrosonaphthol has 3.5–11 times greater value for Ni(II) and 0–4 times greater for Cu(II) ions (Table III).

TABLE III
Comparison of sorption capacities for Ni(II) and Cu(II) ions using XAD resins with different ligands

Ligand	Cu(II)		Ni(II)		Reference
	Capacity mmol g^{-1}	Preconcentration factor	Capacity mmol g^{-1}	Preconcentration factor	
Pyrocatechol	0.0925	100	0.053	200	4
Thiosalicylic acid	0.214	–	0.309	–	5
Tiron	0.22	200	0.20	150	7
2-Aminophenol	0.053	50	0.055	65	8
1-(2-Pyridylazo)-2-naphtol (PAN)	–	–	0.0018	_	9
Dithizone					
o-Vanillinthiosemicarbazone	0.08	–	0.04	_	10
N-(2-hydroxyethyl)-ethylenediamine	0.013	90	–	–	11
1-Nitroso-2-naphtol	0.48	–	0.42	–	12
	0.316	**200**	0.516	**750**	This work

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