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Characterization and Application of 1-(2-Pyridylazo)-2-naphthol Functionalized Amberlite XAD-4 for Preconcentration of Trace Metal Ions in Real Matrices

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Amberlite XAD-4 resin (AXAD-4) has been functionalized by coupling it through an $-N{=}N-$ group with 1-(2-pyridylazo)-2-naphthol (PAN). The resulting chelating resin, PAN-AXAD-4, has been characterized by using elemental and thermogravimetric analysis, infrared spectra, water regain value, and hydrogen ion capacity. The sorption capacity was found to be (285, 145, 135, 85, and 76) μmol·g^{-1} for Zn(II), Co(II), Ni(II), Cu(II), and Pb(II), respectively. The kinetics was studied at different temperatures, and the corresponding rate constants were also determined. All the metals could be eluted with 5 mL of HNO_3 resulting in a high preconcentration factor of 300 to 500. The detection limits were found to be (0.65, 0.80, 0.85, 0.95, and 1.40) μg·L^{-1} for Zn(II), Co(II), Ni(II), Cu(II), and Pb(II), respectively. The validity of the method was checked by analyzing standard reference materials and performing recovery studies. The analytical utility of the PAN-AXAD-4 for preconcentration and determination of metal ions was explored by analyzing river, canal, sewage, tap water, multivitamin formulation, and infant milk substitute by direct as well as the standard addition method.

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1. Introduction

With growing industrialization and urbanization, diversified uses of metals in varied forms have become a significant source of pollution resulting in environmental deterioration. Metals constitute a major category of persistent, bioaccumulative, and toxic (PBT) chemicals and pose a significant threat to public health through occupational as well as environmental exposures. Quantification of toxic metal ions in industrial effluents, various water resources, and environmental and biological samples is important, especially in environment monitoring and assessment of environmental exposure to toxic metals. However, the direct determination of trace metals in real matrices is difficult even with frequently used sophisticated instrumental techniques[1,2] such as inductively coupled plasma atomic emission spectrometry, electrothermal atomic absorption spectrometry, etc. because of the low concentrations of the metals and strong interference from the sample matrix. Solid-phase extraction (SPE) addresses these two problems by virtue of its ability to concentrate the desired trace elements and remove interfering constituents whereby the detection limits, precision, and accuracy of the analytical methods get improved. It has been demonstrated in various procedures[3,4] to be a very effective preconcentration technique in combination with atomic absorption spectrometry. The main advantage of this technique is the possibility of using a relatively simple detection system with flame atomization instead of a flameless technique, which requires more expensive equipment and is usually much more sensitive to interference from macro components of various natural matrices.[5] The use of a chelating resin in SPE as metal ion extractants has turned out to be an active area of research in the field of separation science in recent years.[6−8] The possibility to extract selectively a number of analytes over a wide pH range, quantitative sorption and elution, kinetically faster sorption and desorption mechanisms, good retention capacity, high preconcentration factor, and regenerability are frequently quoted as an advantage.[8] The Amberlite XAD series resins with a polystyrene-divinyl benzene copolymer matrix have proved themselves as efficient support for anchoring chelating ligands due to their good porosity, uniform pore size distribution, high surface area, and excellent chemical and physical stability. High surface area and porosity of the resin increases the sorption capacity and chelating site accessibility of the metal ions. Selective chelating resins with high metal ion uptake capacity may be designed by immobilizing a small polydentate ligand moiety onto Amberlite XAD resins either through surface sorption or chemical modification. Chelating resins prepared by chemical linkage exhibit better resistance to the leaching of the ligands. High selectivity may be attributed to their function as chelate formation, ion exchange, and physical adsorption.

The tridentate N-heterocyclic azo ligand containing N atoms, 1-(2-pyridylazo)-2-naphthol (PAN), has shown excellent complexing ability for heavy and transition metal ions, and its analytical applications in the spectrophotometric determination of the metals are well established.[9−13] It forms complexes with most metals through the ortho-hydroxyl group, the azo nitrogen nearest to the phenolic ring, and the heterocyclic nitrogen group.[14] Moreover, the hydroxyl group may be expected to introduce a good hydrophilic character into the chelating resin which facilitates better exchange kinetics.[15,16] Few chelating resins[17−28] have been prepared by loading PAN on Amberlite XAD series resins (mostly by surface modification), but chemical modification of Amberlite XAD-4 (AXAD-4) with PAN has not been reported to date.

It was, therefore, thought worthwhile to prepare a chelating resin of better sorption capacity by immobilizing PAN on AXAD-4 resin through chemical modification and characterize it in a systematic manner for its use in the prenconcentration of metal ions.

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2. Experimental Section

2.1. Instruments. A Perkin-Elmer model 3100 (Waltham, MA) was used for determining metal ion concentrations by flame atomic absorption spectrometry (FAAS) with an air-acetylene flame. The wavelengths (slit widths) used for Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) were (213.9 (0.7), 240.7 (0.2), 232.0 (0.2), 324.8 (0.7), and 283.3 (0.7)) nm, respectively, while maintaining the lamp current at (15, 30, 25, 15, and 8) mA, respectively. An Elico-LI-120 (Hyderabad, India) digital pH meter was used for pH measurements. A thermostatted mechanical shaker NSW-133 (New Delhi, India) was used for carrying out equilibrium studies at 200 strokes min^{-1}. Infrared (IR) spectra were recorded on a Fourier transform-IR spectrometer from Spectro Lab-Interspec 2020 (Newbury, U.K.) using the KBr disk method. A Shimadzu TG/DTA simultaneous measuring instrument DTG-60/60H (Kyoto, Japan) was used for thermogravimetric analysis (TGA) and differential thermal analysis (DTA). CHN analysis was carried out on Carlo Erba-EA1108 (Milan, Italy) elemental analyzer in the sophisticated analytical instrument facility of the Central Drug Research Institute (Lucknow, India). A column $[(1 \times 10)\ \text{cm}^2]$, for dynamic studies, was obtained from J-SIL scientific industries (Agra, India).

2.2. Reagents and Solutions. All solutions were prepared in distilled water. Stock solutions of nitrate salts of Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) (supplied by Central Drug House (P) Ltd., New Delhi, India) at the concentration of 1000 $\text{mg}\cdot\text{L}^{-1}$ in 1 % HNO_3 were standardized by complexometric titration[29] before use. The working solutions of the metals were prepared by appropriately diluting the stock solutions. Reagents used for preparing the buffer solutions for pH adjustment were obtained from Merck (Mumbai, India). For this, solutions containing suitable amounts of sodium sulfate−sodium bisulfate for pH 2, acetic acid−ammonium acetate for pH 4−6, ammonia−ammonium chloride for pH 8−10, and sodium hydroxide−sodium biphosphate for pH 12 were prepared in distilled water. Fulvic acid powder and soluble humates containing 75 % humic acid and 10 % potassium were received as a gift from Nutri-Tech solutions (Yandina, Australia). AXAD-4 with a 20−60 mesh particle size with 725 $\text{m}^2\cdot\text{g}^{-1}$ of surface area and PAN (CAS 85−85−8) were procured from Sigma-Aldrich chemie GmbH (Steinheim, Germany). Standard reference materials (SRMs) such as vehicle exhaust particulates NIES 8, pond sediment NIES 2, chlorella NIES 3, human hair NIES 5, and tea leaves NIES 7 were obtained from the National Institute of Environmental Studies (Ibaraki, Japan). Rompin Hematite JSS (800−3) and zinc base die-casting alloy C NBS 627 were provided by the Iron and Steel Institute of Japan (Tokyo, Japan) and the National Bureau of Standards, U.S. Department of Commerce (Washington, DC), respectively. A multivitamin capsule (bearing the commercial name Maxirich) from Cipla Limited (Mumbai, India) and infant milk substitute (commercially available as Lactogen 1) obtained from Nestle India Limited (New Delhi, India) were used.

2.3. Pretreatment of Samples. 2.3.1. Natural and Sewage Water Samples. Water samples of river water (collected from the Ganga, Narora, India), canal water (collected from Kasimpur, Aligarh, India), sewage water (collected from area in the vicinity of a local nickel electroplating industry, Aligarh, India), and tap water (collected from University campus, Aligarh, India) were immediately filtered through a Millipore cellulose membrane filter (0.45 μm pore size), acidified to pH 2 ± 0.01 with HNO_3, and stored in precleaned polyethylene bottles. The bottles were cleaned by soaking in an alkaline detergent and then 4 $\text{mol}\cdot\text{L}^{-1}$ HCl, finally treated with 2 $\text{mol}\cdot\text{L}^{-1}$ HF and 0.5 $\text{mol}\cdot\text{L}^{-1}$ HNO_3, and rinsed with triply distilled water between each step.

2.3.2. Digestion of Environmental, Biological, and Alloy Standard Reference Materials (SRMs). To dissolve the environmental SRMs, 0.5 g of the sample was dissolved by adding 10 mL of concentrated nitric acid (15.5 $\text{mol}\cdot\text{L}^{-1}$), 10 mL of concentrated perchloric acid (12.2 $\text{mol}\cdot\text{L}^{-1}$), and 2 mL of concentrated hydrofluoric acid (22.4 $\text{mol}\cdot\text{L}^{-1}$) in a 100 mL Teflon beaker. The solution was evaporated to near dryness, redissolved in a minimum volume of 2 % HCl, filtered, and made up to a 50 mL volume in a calibrated flask.

The sample solutions of biological SRMs were prepared as proposed by the International Atomic Energy Agency.[30] A 0.05 g (0.6 g for *Chlorella*) of each of the samples was agitated with 25 mL of acetone, and then washed three times with distilled water and with 25 mL of acetone. The contact time of the cleaning medium with the sample was 10 min. The samples were finally dried for 16 h at (100 ± 0.2) °C following which each of the samples was dissolved in (10 to 20) mL of concentrated nitric acid. After the addition of 0.5 mL of 30 % H_2O_2, the solution was boiled to dryness. The residue obtained was dissolved in a minimum amount of 2 % HCl and made up to a 50 mL volume in a calibrated flask.

The solution of standard alloy was prepared by taking 0.025 g of the sample into a beaker and dissolving in (10 to 50) mL of aqua regia. The solution was boiled to near dryness. Finally the residue was dissolved in a minimum volume of 2 % HCl and filtered through a Whatman filter paper no.1. The residue was washed with two 5 mL portions of hot 2 % HCl. The aqueous layer was evaporated to dryness. The residue was redissolved in 5 mL of 2 % HCl and made up to 50 mL with distilled water.

2.3.3. Digestion of Multivitamin Formulation and Infant Milk Substitute (IMS). Five multivitamin capsules (5.64 g) were taken into a beaker containing 25 mL of concentrated HNO_3 and digested by slowly increasing the temperature of the mixture to (120 ± 0.2) °C until a solid residue was obtained. It was cooled, redissolved with 20 mL of concentrated HNO_3, and gently evaporated on a steam bath until a residue was left again. It was subsequently mixed with 10 mL of distilled water, and concentrated HNO_3 was then added dropwise until a clear solution was obtained on gentle heating and made up to 50 mL with distilled water.

A powdered IMS sample (0.2 g) was heated in a beaker containing a mixture of concentrated H_2SO_4 (20 mL) and HNO_3 (10 mL) until a clear solution was obtained. It was allowed to cool, and most of the acid was neutralized with NaOH. The total volume was made up to 50 mL and kept as stock.

2.4. Functionalization of Amberlite XAD-4 Resin. An amount of 5 g of air-dried AXAD-4 resin was pretreated with an ethanol−hydrochloric acid−water (2:1:1) solution overnight and subsequently rinsed with triply distilled water until the pH of the supernatant water became neutral so that it was free from any impurities. The resin beads were then subjected to modification by initially nitrating and then subsequently reducing to the amino compound (by refluxing for 12 h in a reducing mixture containing 40 g of $SnCl_2$, 45 mL of concentrated HCl, and 50 mL of ethanol). The amino compound was washed thoroughly with 2 $\text{mol}\cdot\text{L}^{-1}$ NaOH and then with 4 mol L^{-1} HCl in order to remove the excess $SnCl_2$. The product was diazotized according to the recommended procedure.[31] After amination, the subsequent steps were carried out at a temperature of (0 to 5 ± 0.2) °C in order to prevent the degradation of the intermediates. The diazotized product was rapidly filtered off, washed with cold distilled water until free from acid, and then subjected to a coupling reaction by treating it with a solution of PAN (2.5 g) in 10 % NaOH mixed with ethanol at a temperature as low as (0 to 5 ± 0.2) °C over a period of 24 h. The dark purple resin was filtered off and thoroughly washed with 2 $\text{mol}\cdot\text{L}^{-1}$ HCl and distilled water until free from alkali and acid. Finally, the resin was dried at (50 ± 0.2) °C and kept over fused $CaCl_2$ in a desiccator for further use.

2.5. Characterization of the Functionalized Resin. The resin was characterized by its elemental analysis and IR spectral data. The thermal and chemical stabilities and water regain capacity of the resin were also determined.

2.5.1. Thermal and Chemical Stability. The thermal stability of the resin was studied by TGA and DTA analysis. To check the applicability of the resin, it was also kept at a constant temperature of (200 ± 0.2) °C for 24 h and then the metal sorption capacity was determined by the recommended batch method. Resistance to chemical changes was tested by soaking the resin in 25 mL of acid [(1 to 10) $\text{mol}\cdot\text{L}^{-1}$ of HCl or HNO_3] and alkaline solution [(1 to 5) $\text{mol}\cdot\text{L}^{-1}$ of NaOH] for 48 h and subsequent washing. The sorption capacity was later determined by the recommended batch method.

2.5.2. Water Regain Value and Hydrogen Ion Capacity. The rate of metal ion phase transfer is governed by the extent of hydrophilicity of the polymeric matrix. Water regain is defined as the amount of water absorbed by 1.0 g of polymer. A batch method was employed for this experiment. The dried resin was stirred in doubly distilled water for 48 h, and then filtered off by suction, dried in air, weighed, dried again at (100 ± 0.2) °C overnight, and reweighed. The water regain value was calculated as

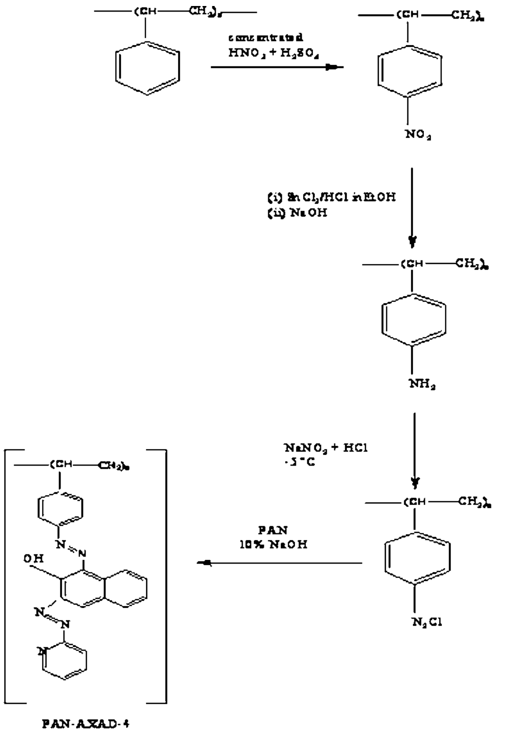
$$W = (m_\text{w} - m_\text{d})/m_\text{d}$$

where m_w is the weight of the air-dried polymer after filtration by suction and m_d is the weight of the resin after drying at (100 ± 0.2) °C overnight. For overall hydrogen ion capacity,[4] an accurately weighed (0.5 g) resin was first treated with 4.0 $\text{mol}\cdot\text{L}^{-1}$ HCl and then filtered off, washed with distilled water to make it free from acid, and dried at (100 ± 0.2) °C for (5 to 6) h. The acidic form of the resin was equilibrated (following the batch method) with 20.0 mL of 0.1 $\text{mol}\cdot\text{L}^{-1}$ NaOH solution for 6 h at room temperature while stirring, and then the excess alkali was estimated with 0.1 $\text{mol}\cdot\text{L}^{-1}$ hydrochloric acid solution. For the evaluation of the contribution of the hydroxyl hydrogen ion to the overall hydrogen ion capacity, another sample of the resin in the acid form was equilibrated with $NaHCO_3$ solution in place of NaOH.

2.6. Recommended Procedure for Sorption and Desorption Studies of Metal Ions. 2.6.1. Batch "Static" Method. A weighed amount of the synthesized resin was equilibrated[31] with a suitable volume of metal solutions of appropriate concentration maintained at constant pH for 2 h. The resin was filtered, and the sorbed metal ions were desorbed by shaking with 4 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 and subsequently analyzed by FAAS.

2.6.2. Column "Dynamic" Method. A sample of modified resin was soaked in water for 24 h and then poured into a glass column. The resin bed in the column was further buffered with 5 mL of the appropriate buffer system. A solution of metal ions of optimum concentration was passed through the column[31] at an optimum flow rate of 4.0 $\text{mL}\cdot\text{min}^{-1}$ after being adjusted to a suitable pH with suitable buffers. After the sorption operation, recovery experiments were performed. For this purpose, the column was washed with water, and then 5 mL of 4 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 was made to percolate through the bed of loaded resin whereby the sorbed metal ions get eluted. The eluents were collected in 5 mL for the subsequent determination by FAAS. The required flow rate was maintained by adjusting the pressure of the glass-made suction apparatus (J-SIL Scientific Industries) that is attached to the column.

Scheme 1. Synthesis of PAN-AXAD-4



3. Results and Discussion

3.1. Synthesis and Characteristics of Resin. In order to study the extent of product formation, elemental analysis was carried out at each stage of the reaction scheme (Scheme 1). The nitrogen content of the nitrated resin and the subsequent reduced product was found to be 9.38 % (6.71 $\text{mmol}\cdot\text{g}^{-1}$) and 11.76 % (8.40 $\text{mmol}\cdot\text{g}^{-1}$), respectively. Elemental analysis of PAN-AXAD-4 gave C 69.50 %, H 4.79 %, and N 17.59 % which are in agreement with calculated values for $C_{23}H_{17}N_5O\cdot H_2O$ as % C 69.52, % H 4.78, and % N 17.63. The presence of 12.59 mmol of nitrogen in the final product may suggest the incorporation of 2.52 mmol of PAN in 1.0 g of resin. Since each PAN group contains one replaceable hydrogen ion as a hydroxyl group, the expected hydrogen ion capacity would therefore be 2.52 $\text{mmol}\cdot\text{g}^{-1}$ of resin. Experimentally, the hydrogen ion capacity (± standard deviation, $n = 3$) due to this hydroxyl group was found to be [2.55 (± 0.03)] $\text{mmol}\cdot\text{g}^{-1}$ which further supports the amount of PAN incorporated. The overall hydrogen ion capacity of [3.96 (± 0.11)] $\text{mmol}\cdot\text{g}^{-1}$ of resin may include the contribution of the pyridinic nitrogen and azo-nitrogen besides the hydroxyl group of PAN.

In the thermogravimetric analysis of PAN-AXAD-4, an early weight loss of 4.84 % up to 151 °C could be seen. This initial step corresponds to the endothermic peak in the DTA curve which may be attributed to the loss of sorbed water molecules. The above result implies that each monomeric unit of the functionalized resin consists of at least one H_2O molecule. The synthesized resin was found to retain 98 % of the metal ion capacity up to 200 °C. The sorption capacity of the resin starts decreasing after 200 °C which may be due to the loss of the PAN moiety which is responsible for the retention of metal ions. This loss may have been caused by the degradation of the moiety as supported by the exothermic peak at 254 °C corresponding to the weight loss of 4.38 %.

The resin was found to be stable up to 8 $\mathrm{mol \cdot L^{-1}}$ acids and 5 $\mathrm{mol \cdot L^{-1}}$ NaOH with no significant loss of metal ion capacity (< 3 %). This high chemical stability may be ascribed to its preparation by a chemical method that imparts resistance to leaching of the incorporated chelating ligand.

The chelating resins were characterized by employing Fourier transform infrared spectrometry (FTIR). In the IR spectrum of PAN-AXAD-4, peaks at 3438.46 $\mathrm{cm^{-1}}$, 3025.51 $\mathrm{cm^{-1}}$, 2925.92 $\mathrm{cm^{-1}}$, 2858.67 $\mathrm{cm^{-1}}$, 1702.51 $\mathrm{cm^{-1}}$, 1612.59 $\mathrm{cm^{-1}}$, and 1502.21 $\mathrm{cm^{-1}}$ correspond to the stretching frequencies of OH (H_2O), CH, OH (phenolic), $=$CH, N$=$N (azo spacer), N$=$N (pyridinic side), and C$-$O, respectively. The presence of two azo groups reaffirms the incorporation of PAN into the Amberlite XAD-4 resin. The peak at 1702.51 $\mathrm{cm^{-1}}$ which corresponds to the bridging azo group did not appear in the IR spectra of PAN. The IR studies of the metal ions chelated resin showed a red shift in the range (5 to 15) $\mathrm{cm^{-1}}$ for $-$N$=$N$-$ and $-$OH stretching frequencies indicating their role as active sites in chelation. The absence of broadening of the hydroxyl band in the spectra of the metal loaded resin proves the absence of hydrogen bonding with the participation of $-$OH groups in the coordination process.[32] It can be inferred that in the basic solution $-$OH groups of PAN on the AXAD-4 resin were ionized to $-\mathrm{O}^-$ so that the negative electron pair of $-\mathrm{O}^-$ gets coordinated with the metal ions.

The water regain capacity was found to be 11.50 (± 0.34) $\mathrm{mmol \cdot g^{-1}}$. This value reflects the high hydrophilicity of the resin which is satisfactory for column operation.

3.2. Optimum Experimental Parameters. In order to optimize the sorption of metal ions, a multivariate approach was followed to establish all the parameters. Each optimum condition was established by varying one of them and following the recommended procedure.

3.2.1. Effect of pH on Sorption Capacity. The optimum pH of metal ion uptake was determined by a static method. An excess of metal ion (50 mL, 100 $\mu\mathrm{g \cdot mL^{-1}}$) was shaken with 0.1 g of resin for 120 min. The pH of the metal ion solution was adjusted prior to equilibration over a range pH 2−10 ± 0.01 with the corresponding buffer system. Preliminary experiments showed that the maximum sorption of Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) (Figure 1) was observed in the pH range 8.0−9.2 ± 0.01. The nitrogen of the heterocyclic ring of PAN gets protonated at lower pH while the phenolic OH group dissociates in the alkaline region. Due to this fact, the reagent reacts with the metal ions under slightly alkaline conditions to form a stable complex. Hence, pH 9.2 ± 0.01 for Zn(II), Co(II), Ni(II), and Cu(II) while 8.0 ± 0.01 for Pb(II) were adjusted in all further experiments. The addition of (2 to 5) mL of buffer solution to adjust the pH did not affect the sorption of metal ions. The batch capacities of the metal ions are indicated in Table 1.

3.2.2. Kinetics of Sorption. For studying the effect of time on the sorption capacity, a 0.1 g amount of resin beads was stirred with 100 mL of solution containing one of the metal ions (20 $\mu\mathrm{g \cdot mL^{-1}}$) at two different temperatures for (2, 5, 10, 20, 30, 40, 60, 80, 100, and 120) min at the optimum pH. The loading halftime, $t_{1/2}$, that is, the time required to reach 50 % of the total loading capacity of the resin, was evaluated from the resulting isotherm (Table 1). From the kinetics of sorption for each metal it was observed that 60 min was sufficient for the sorbent to reach the saturation level for all the metal ions. In the kinetic studies, the sorption time course curve (Figure 2) shows a double nature, that is, curved and linear. The curved portion represents film diffusion followed by intraparticle diffusion as shown by the linear portion.[33] Such double nature can be accounted for if we assume that the low initial metal ion concentration reduces the probability of diffusion of metal ions in the boundary layer. The higher distance between the lines at different temperatures suggests that the process of retention takes place through a change from a dissociated ($\mathrm{H^+}$-form) to a nondissociated species (chelated metal complex) of the resin.[33] The rate of sorption at higher temperature was found to proceed toward linearity much earlier than at lower temperature. Therefore, it can be inferred that an increase in temperature favors intraparticle diffusion. Considering the Brykina method,[4] the sorption rate constant, k, can be calculated using the following equation

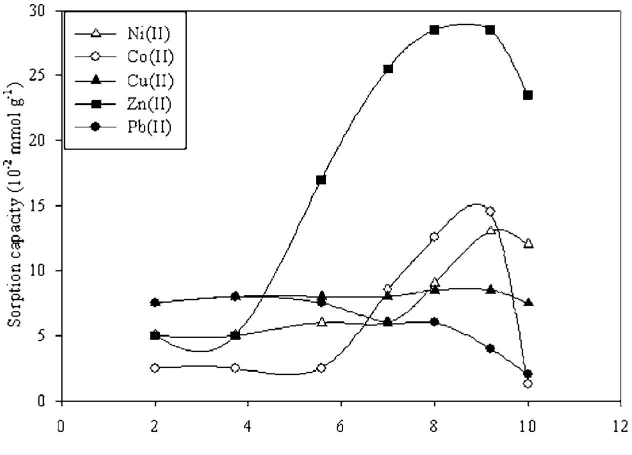


Figure 1. Dependence of sorption capacity on the pH of the solution (experimental conditions: 50 mL solution, 100 $\mu\mathrm{g \cdot mL^{-1}}$, 0.1 g resin).

$$-\ln(1 - F) = kt$$

where F is the ratio of the sorbed amount at sorption time t (Q_t) and the sorbed amount at equilibrium (Q). By putting the value of Q_t at $t_{1/2}$ in the above equation we may get the corresponding value of k for every metal ion (Table 1). The kinetic studies also showed that the temperature affected the rate constants significantly; that is, saturation was reached at a faster rate at higher temperature. This temperature effect may be a manifestation of the fact that the resin swells more completely at higher temperature, which allows metal ions to diffuse more easily into the interior of the resin, and that the sorption was an endothermic process and hence high temperature facilitates higher sorption. A plot (Figure 3) of log D versus $1/T$, where the distribution ratio (D) represents the ratio of sorption capacity and the concentration of free metal ion at the equilibrium sorption, respectively, revealed that the distribution ratio increased with the increase of temperature. This again implies that the sorption process was an endothermic process. The values of ΔH and ΔS were calculated (Table 1) using the slope and intercept from the above plots using the following relationship:

$$\log D = (-\Delta H/2.303RT) + (\Delta S/2.303R)$$

Table 1. Kinetics and Batch Capacity of Sorption of Metal Ions on PAN-AXAD-4[a]

	loading halftime $t_{1/2}$/min		rate constant $k \cdot 10^{-2}$/min $^{-1}$		batch capacity	$-\Delta H$	ΔS
metal ion	(35 ± 0.2) °C	(45 ± 0.2) °C	(35 ± 0.2) °C	(45 ± 0.2) °C	$\mathrm{mmol \cdot g^{-1}}$ ± SD[b]	$\mathrm{J \cdot mol^{-1}}$ ± SD	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ ± SD
Zn(II)	16.5	8.3	4.2	8.3	0.285 ± 0.012	75.49 ± 0.25	1249.1 ± 0.65
Co(II)	14.8	6.5	4.6	10.6	0.145 ± 0.003	68.38 ± 0.26	1144.54 ± 0.55
Ni(II)	14.5	11	4.7	6.3	0.135 ± 0.003	113.4 ± 0.28	1775.62 ± 0.72
Cu(II)	16	2.5	4.3	27.7	0.085 ± 0.003	34.03 ± 0.22	619.18 ± 0.43
Pb(II)	29.5	15	2.3	4.6	0.076 ± 0.003	13.11 ± 0.21	404.41 ± 0.36

[a] Experimental conditions: 100 mL, solution; 0.1 g, resin. [b] SD, standard deviation for $n = 3$.

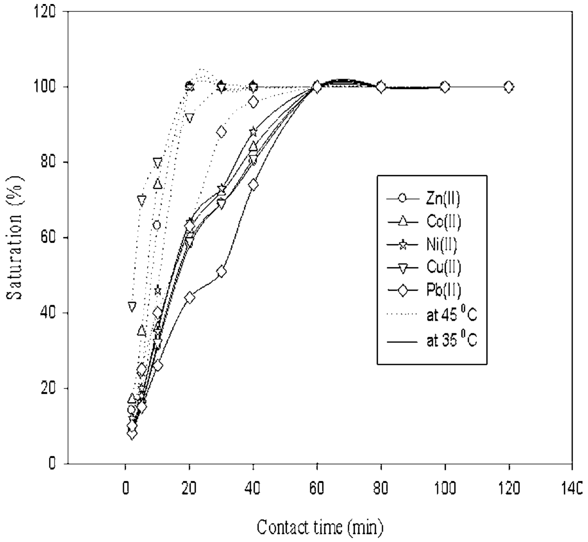


Figure 2. Rate of sorption of metal ions at different temperature (experimental conditions: 100 mL solution, 20 $\mu\mathrm{g \cdot mL^{-1}}$, 0.1 g resin).

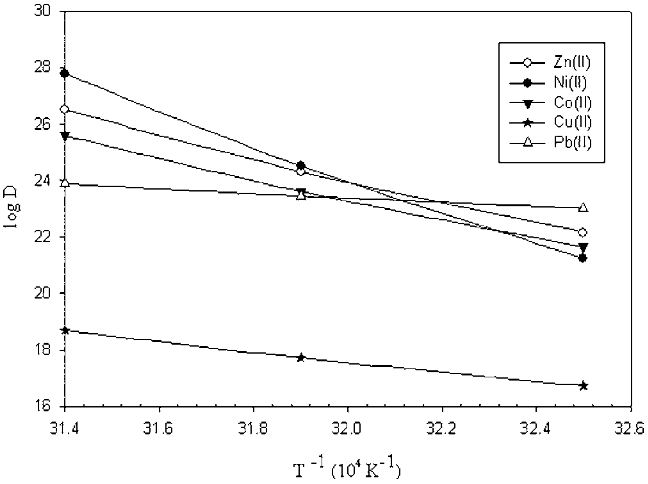


Figure 3. Influence of temperature on the distribution ratio of metal ions (experimental conditions: 100 mL solution, 20 $\mu\mathrm{g \cdot mL^{-1}}$, 0.1 g resin).

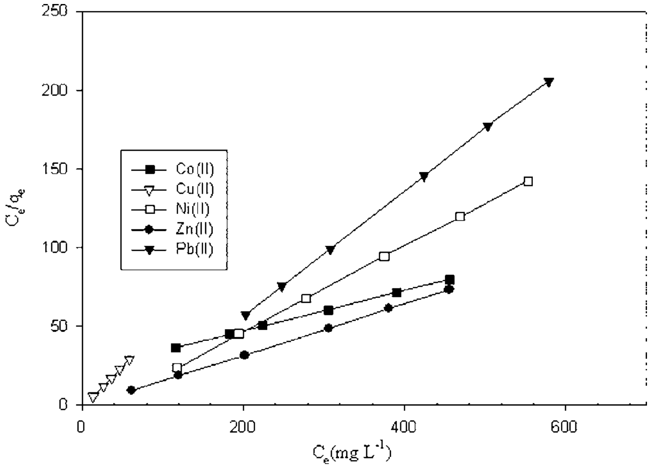


Figure 4. Langmuir sorption isotherm depicting the sorption behavior of metal ions by PAN functionalized resin (experimental conditions: 100 mL; 0.25 g resin).

3.2.3. Adsorption Isotherm. In order to determine the sorption capacity of the resin, test solutions of Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) weighing in the range (100 to 50 000) μg were taken in batches containing 0.25 g of chelated resin and recoveries were investigated. Langmuir isotherms were plotted in order to determine the resin capacity in accordance to the literature.[34] The Langmuir adsorption isotherm is described by the equation given as $q_{\mathrm{e}} = q_{\max}a_{\mathrm{L}}{}_{\mathrm{e}}/(1 + a_{\mathrm{L}}C_{\mathrm{e}})$ where q_{e} is the amount of metal sorbed per unit weight of the resin ($\mathrm{mg \cdot g^{-1}}$) at equilibrium, C_{e} is the final concentration in the solution ($\mathrm{mg \cdot L^{-1}}$), $q_{\max}$ is the maximum sorption at monolayer coverage ($\mathrm{mg \cdot g^{-1}}$), and a_{L} is the sorption equilibrium constant, which is related to the energy of sorption. A plot of $C_{\mathrm{e}}/q_{\mathrm{e}}$ versus C_{e} shows linearity, and, hence, the Langmuir constants, $q_{\max}$ and a_{L}, can be calculated from the slope and intercept of the plot. From the plots obtained for each metal, the amount of maximum total metal ($q_{\max}$) sorbed on 1.0 g of resin is calculated. The maximum sorption capacity calculated from the Langmuir isotherm (Figure 4) indicated that the resin retained Zn(II) more strongly than the other metal ions under study. The sorption capacities for Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) are much higher than other reported methods employing chemically modified AXAD-16[18] and AXAD-1180[19] and surface modified sorbents.[20−24] The higher surface area of AXAD-4 resin complemented by highly efficient incorporation of PAN may be the contributing factors for higher sorption. This fact is also supported by the high hydrophilicity of AXAD-4-PAN which facilitates better surface contacts with the metal ions in aqueous solutions.

3.2.4. Study of Interference. Various cations and anions, which are inevitably associated with heavy metals, may interfere in determination of the latter through precipitate formation, redox reactions, or competing complexation reactions. Common chemical species such as sodium citrate, sodium tartrate, sodium oxalate, humic acid, fulvic acid, $\mathrm{NO_3^-}$, $\mathrm{CO_3^{2-}}$, $\mathrm{NH_4^+}$, $\mathrm{SO_4^{2-}}$, $\mathrm{PO_4^{3-}}$, $\mathrm{Cl^-}$, $\mathrm{K^+}$, and $\mathrm{Na^+}$ were checked for any interference in the sorption of these metals. In order to determine the tolerance limit of the resin for various interfering electrolytes and metal ion species, studies were carried out using metal ion solutions (100 mL, 10 $\mu\mathrm{g \cdot L^{-1}}$) equilibrated individually with 0.1 g of resin with varying amounts of electrolyte or metal ions until interference was observed. 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. Many anions, cations, and metal complexing agents, which are inevitably associated with metal ions present at the trace level in all natural waters, were observed to show no interference in the sorption of the heavy metals up to appreciable concentrations (Table 2). A relative error of less than 5 % was considered to be within the range of experimental error. However, the

Table 2. Tolerance Limit of Foreign Species (in Binary Mixtures) on Sorption of Metal Ions[a]

	tolerance ratio [foreign species (μg·mL^{-1})/metal ion (μg·mL^{-1})]				
foreign species	Zn(II)	Co(II)	Ni(II)	Cu(II)	Pb(II)
Na^+ (NaCl)	$1.49\cdot10^{6}$	$1.41\cdot10^{6}$	$1.10\cdot10^{6}$	$9.83\cdot10^{5}$	$7.86\cdot10^{5}$
K^+ (KCl)	$1.83\cdot10^{6}$	$1.80\cdot10^{6}$	$1.36\cdot10^{6}$	$1.05\cdot10^{6}$	$1.05\cdot10^{6}$
NH_4^+ (NH_4Cl)	$1.14\cdot10^{6}$	$1.05\cdot10^{6}$	$1.18\cdot10^{6}$	$1.01\cdot10^{6}$	$1.01\cdot10^{6}$
Cl^- (NaCl)	$2.30\cdot10^{6}$	$2.18\cdot10^{6}$	$1.69\cdot10^{6}$	$1.51\cdot10^{6}$	$1.21\cdot10^{6}$
SO_4^{2-}(Na_2SO_4)	$3.04\cdot10^{6}$	$3.04\cdot10^{6}$	$3.04\cdot10^{6}$	$2.7\cdot10^{6}$	$2.7\cdot10^{6}$
NO_3^- ($NaNO_3$)	$3.65\cdot10^{6}$	$3.35\cdot10^{6}$	$3.31\cdot10^{6}$	$3.28\cdot10^{6}$	$2.91\cdot10^{6}$
PO_4^{3-} (Na_3PO_4)	$5.79\cdot10^{5}$	$4.63\cdot10^{5}$	$4.05\cdot10^{5}$	$2.89\cdot10^{5}$	$1.73\cdot10^{5}$
CO_3^{2-} (Na_2CO_3)	$1.86\cdot10^{6}$	$1.86\cdot10^{6}$	$1.86\cdot10^{6}$	$1.41\cdot10^{6}$	$1.41\cdot10^{6}$
citrate (sodium citrate)	$2.56\cdot10^{4}$	$2.56\cdot10^{4}$	$2.12\cdot10^{4}$	$1.83\cdot10^{4}$	$1.83\cdot10^{4}$
oxalate ($Na_2C_2O_4$)	$6.56\cdot10^{3}$	$6.56\cdot10^{3}$	$6.56\cdot10^{3}$	$3.94\cdot10^{3}$	$3.28\cdot10^{3}$
tartrate (NaK tartrate)	$7.07\cdot10^{3}$	$7.07\cdot10^{3}$	$6.30\cdot10^{3}$	$4.25\cdot10^{3}$	$3.54\cdot10^{3}$
fulvic acid	85	45	45	15	45
humic acid	120	85	85	25	75
CH_3COO^- (CH_3COONa)	$6.51\cdot10^{5}$	$5.64\cdot10^{5}$	$5.42\cdot10^{5}$	$4.34\cdot10^{5}$	$3.47\cdot10^{5}$
Ca^{2+} ($CaCl_2$)	$7.21\cdot10^{5}$	$6.49\cdot10^{5}$	$7.21\cdot10^{5}$	$4.32\cdot10^{5}$	$3.60\cdot10^{5}$
Mg^{2+} ($MgCl_2$)	$7.65\cdot10^{5}$	$7.65\cdot10^{5}$	$6.38\cdot10^{5}$	$5.10\cdot10^{5}$	$3.82\cdot10^{5}$

[a] Experimental conditions: 100 mL, solution; 10 μg·L^{-1}, metal ions; 0.1 g, resin.

tolerance limit for Cl^- and Na^+ does not favor the applicability of this resin in the preconcentration of seawater.

3.2.5. Effect of Flow Rate for Sorption and Elution. The effect of flow rate on the sorption was studied by varying the flow rate [(2 to 8) mL·min^{-1}] at the pH chosen for maximum sorption, keeping a constant column height. Observations indicated that metal retention on the resin was optimum at a flow rate equal to or lower than 5 mL·min^{-1}. The flow rates less than 2.0 mL·min^{-1} were not studied to avoid long analysis times. Hence, a flow rate of 4.0 mL·min^{-1} was maintained throughout the column operations. During the subsequent elution of the retained metals from the adsorbent, recovery of higher than 95 % was observed up to 3.5 mL·min^{-1}. The decrease in sorption, or exchange, with increasing flow rate is due to the decrease in equilibration time between two phases. In the elution studies, 100 % recovery of the sorbed metals from the resin could be achieved up to a flow rate of 2 mL·min^{-1}. Therefore, 2 mL·min^{-1} was used for elution studies.

3.2.6. Type of Eluting Agents and Resin Reusability Test. Elution studies were performed with different mineral acids, namely H_2SO_4, HCl, HNO_3, $HClO_4$, and organic acids such as HCOOH and CH_3COOH. The efficiency of stripping was studied by using a maximum of 5 mL, so that the preconcentration factor could be kept to a maximum, and concentrations [(0.1 to 5) mol·L^{-1}] of the mineral acids. The effect of HNO_3 concentration on elution of metal ions from the resin was studied, by carrying out the elution with (2.0 to 5.0) mol·L^{-1} HNO_3. Organic acids and $HClO_4$ were found to be unsuitable for the recovery studies. On performing the desorption studies with different mineral acids of varying concentration, 4 mol·L^{-1} HNO_3 was found to be the best eluent for 100 % stripping of the metal ions. The inefficiency of the organic acids may be due to the more stable metal chelates.

The resin was subjected to several loading and elution cycles by the dynamic method. The sorbent can be used more than 40 times in succession without any appreciable loss in the sorption efficiency. However, a reduction by 3.0 % of the sorption capacity was observed after 45 cycles of sorption and subsequent elution.

3.2.7. Preconcentration Factor and Breakthrough Capacity. The limit of preconcentration (the lowest metal ion concentration level below which the sorption becomes non-quantitative) was determined by increasing the volume of metal ion solution and keeping the total amount of loaded metal ion constant at 10 μg. It was found to be (4.0, 5.0, 5.5, 6.7, and 6.7) μg·L^{-1} with a corresponding preconcentration factor of 500, 400, 360, 300, and 300 for Zn(II), Co(II), Ni(II), Cu(II), and Pb(II), respectively. The breakthrough and total saturation volume, which correspond to the volumes at which the effluent concentration of metal ions from the column are about (3 to 5) % and 100 %, respectively, of the influent concentration, were determined by applying the recommended procedure to 2000 mL of the metal ion solution. The effluent fractions were collected in 5 mL and analyzed for the presence of the metal. The overall capacity, breakthrough capacity, and degree of column utilization were determined by a literature method.[35] The overall and breakthrough capacities calculated on the basis of total saturation and breakthrough volume (Figure 5) were found to be (0.33, 0.16, 0.15, 0.10, 0.09 and 0.22, 0.11, 0.10, 0.06, 0.06) mmol·g^{-1} for Zn(II), Co(II), Ni(II), Cu(II), Pb(II), respectively. The closeness of the breakthrough to the overall capacity and the high preconcentration factors reflect the applicability of the column technique for preconcentration. These preconcentration data reflect the superiority of PAN-AXAD-4 over sorbents used in previous work.[18−22,24−26] Such hydrophilicity of AXAD-4-PAN better facilitates contact with the metal ions which helps to attain equilibrium at a faster rate.

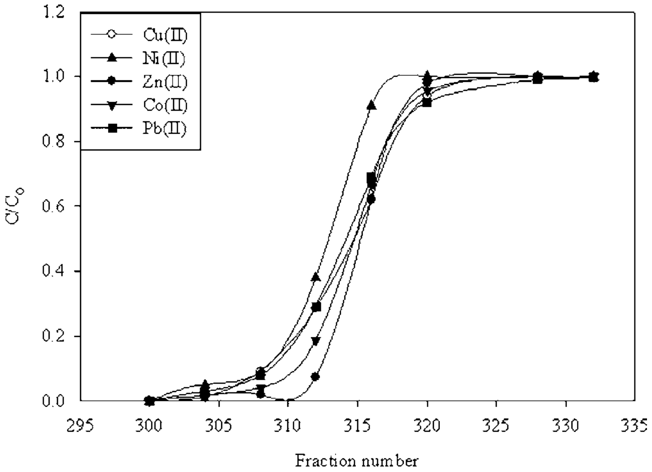


Figure 5. Breakthrough curves for sorption of metal ions: C/C_o is the concentration ratio of the effluent to influent (column parameters: sorption flow rate 4 mL·min^{-1}, 0.5 g resin).

4. Method Validation

Prior to analysis of real samples, validation of the method was performed analyzing SRMs and recoveries of trace metals

Table 3. Analysis of Standard Reference Materials for Metal Ion Contents[a]

	certified value	found by proposed method	
samples	$\mu g \cdot g^{-1}$	$\mu g \cdot g^{-1}$ (RSD)[b]	calculated student's *t*-value[c]
vehicle exhaust particulates NIES 8[d]	Co: 3.3, Cu: 67, Ni: 18.5, Pb: 219, Zn: 1040	Co: 3.26 (2.4), Cu: 66.66 (1.1), Ni: 18.32(1.1), Pb: 216.56 (2.1) Zn: 1032.68 (2.5)	1.14, 1.04, 1.99, 1.19, 1.22
pond sediment NIES 2	Zn: 343, Ni: 40, Co: 27, Cu: 210	Zn: 342.89 (1.1), Ni: 38.89 (4.1), Co: 26.80 (1.5), Cu: 206.65 (2.7)	1.84, 1.56, 1.11, 1.03
Chlorella NIES 3	Zn: 20.5, Cu: 3.5, Co: 0.87, Pb: 0.60	Zn: 19.89 (3.5), Cu: 3.42 (4.3), Co: 0.86 (1.6), Pb: 0.58 (4.8)	1.96, 1.22, 1.62, 1.61
human hair NIES 5[d]	Zn: 169, Cu: 16.3, Ni: 1.8, Pb: 6	Zn: 167.54 (1.5), Cu: 15.89 (4.5), Ni: 1.74(5.0), Pb: 5.82 (4.4)	1.28, 1.95, 1.54, 1.57
tea leaves NIES 7[d]	Zn:33, Cu: 7, Ni:6.5	Zn:31.89 (4.4), Cu: 6.76 (4.2), Ni:6.40 (3.2)	1.77, 1.89, 1.09
rompin hematite, JSS (800−3)[e]	Cu: 640, Zn: 1030, Pb: 210	Cu: 632.25 (2.2), Zn: 1018.15 (1.7) Pb: 206.56 (2.7)	1.24, 0.53, 1.38
zinc base die-casting alloy C NBS 627[f]	Cu: 1320, Pb:82, Ni: 29	Cu: 1310.45 (1.1), Pb: 80.89 (2.3), Ni: 28.32 (4.3)	1.48, 1.33, 1.25

[a] Column parameters: 4 $mL \cdot min^{-1}$, sorption flow rate; 2 $mL \cdot min^{-1}$, elution flow rate; 0.2 g, resin. [b] Relative standard deviation, $n = 5$. [c] At 95 % confidence level. [d] National Institute of Environmental Studies (nies). [e] Iron and Steel Institute of Japan (jss). [f] National Bureau of Standards (nbs).

Table 4. Preconcentration and Determination of Metal Ions in Natural Water[a]

		metal ion found by proposed method/$\mu g \cdot L^{-1}$ (RSD)[b]				
samples	method	Zn(II)	Co(II)	Ni(II)	Cu(II)	Pb(II)
canal water	direct	5.8 (2.6)	3.5 (2.4)	3.4 (2.2)	12.9 (1.9)	ND
	SA[c]	5.7 (2.1)	3.4 (2.8)	3.4 (2.6)	12.7 (1.6)	3.2 (4.3)
tap water	direct	17.4 (3.1)	6.9 (2.8)	5.5 (2.9)	10.3 (2.9)	12.7 (4.9)
	SA	16.7 (3.2)	7.0 (2.9)	5.5 (3.1)	10.2 (3.1)	12.4 (2.3)
sewage water	direct	7.4 (4.2)	5.5 (3.9)	12.3 (3.0)	8.1 (2.9)	6.0 (3.2)
	SA	7.4 (4.9)	5.4 (4.7)	12.4 (2.2)	8.1 (3.4)	6.1 (3.5)
river water	direct	4.1 (4.0)	3.1 (3.3)	3.9 (2.5)	14.0 (3.6)	ND
	SA	4.4 (2.9)	3.1 (3.8)	3.9 (2.8)	14.0 (4.1)	3.2 (3.3)

[a] Column parameters: 4 mL min^{-1}, sorption flow rate; 0.5 g, resin. [b] Relative standard deviation; $n = 3$; ND = not detected. [c] Standard additions method.

after spiking. In order to test the accuracy of the method, 50 mL of pretreated environmental (vehicle exhaust particulates and pond sediment), biological (human hair, *Chlorella* and tea leaves), and alloy (Rompin hematite and zinc base die-casting alloy C) SRM samples were analyzed by the recommended column method after adjusting to the optimum pH. The mean concentration values of the metals studied agreed with the certified values. Calculated Student's *t*-values (*t*-test) for respective metal ions were found to be less than the critical Student's *t*-value of 2.78 at the 95 % confidence level for $n = 5$ (Table 3). The results of the analysis of multivitamin capsule and IMS also favored the above fact (below critical student's *t*-value). Hence, the mean values were not statistically significant from the certified values indicating absence of bias in the present method.

Using optimum conditions, the precision of the method was evaluated. Six successive sorption and elution cycles of 10 μg each of Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) taken in 100 mL (eluted in 5 mL of 3 $mol \cdot L^{-1}$ HCl) were performed following the recommended procedure. It was found that the mean percentage recoveries of all the metal ions studied were (98.8 to 100.3) % at the 95 % confidence level. The RSD values were calculated to be below 5 %. The results of water analysis with RSD < 5 % support the applicability of the method.

A blank run was also performed applying the recommended column procedure with 100 mL of aqueous solution prepared by adding a suitable buffer (excluding metal ions) and finally eluting the same in 5 mL before subjecting it to FAAS determination. The detection limits, evaluated as three times the standard deviation(s) of the blank signal, were found to be (0.65, 0.80, 0.85, 0.95, 1.40) $\mu g \cdot L^{-1}$ for Zn(II), Co(II), Ni(II), Cu(II), and Pb(II), respectively.

5. Applications

5.1. Determination of Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) in Natural Water Samples. Applicability of the present method for preconcentration and determination of metal ions was accomplished by analyzing river, canal, sewage, and tap water. A 500 mL sample volume of each was adjusted to the optimum pH by adding 5 mL of ammonia buffer and loaded onto the column of PAN-AXAD-4. The concentrations of metal ions were determined by following the recommended method using FAAS (direct method). The metal ion determinations were also confirmed using the method of standard additions[36] from various real water (500 mL) samples which were spiked with metal ions of concentrations guided by the middle value of the preconcentration limit and maximum concentration of the working range of the calibration curve of FAAS in order to ensure complete sorption and avoid dilution of the final eluate during determination. The closeness of results of direct and SA methods (Table 4) indicates the reliability of the present method for metal analyses in water samples of various matrices without significant interference.

5.2. Determination of Zn(II) and Cu(II) in Multivitamin Capsules and Infant Powdered Food. Multivitamin capsules and IMS were subjected to preconcentration according to the recommended column procedure after their pretreatment (digested in 50 mL). The amount (student's *t* value for $n = 5$, RSD %) of Cu(II) and Zn(II) found were [394.2 (0.597, 3.8 %) and 439.7 (1.187, 1.2 %)] $\mu g \cdot g^{-1}$ and can be compared with the reported values of (398.2 and 442.5) $\mu g \cdot g^{-1}$, respectively, for multivitamin capsule while [2.8 (1.901, 4.2 %) and 35.9 (1.756, 3.9 %)] $\mu g \cdot g^{-1}$ when the reported values for IMS were (2.9 and 37.0) $\mu g \cdot g^{-1}$, respectively. The results exhibited high precision with the RSD < 5 %.

6. Conclusions

PAN-AXAD-4 resin was successfully applied to preconcentration, separation, and determination of Zn(II), Co(II), Ni(II), Cu(II), and Pb(II) by FAAS. This method has fast kinetics ($t_{1/2}$ < 30 min) which allows column preconcentration to be done within a short time interval with a sample flow rate of 3 mL min^{-1}. Compared to other PAN-functionalized polymeric support (Table 5), PAN-AXAD-4 has a greater sorption capacity and preconcentration factor (except for Pb23) and exhibits the ability to preconcentrate analytes from a smaller volume of sample even if their concentration is much less than the preconcentration limit for higher volumes. The procedure shows high tolerance to interference from various matrix ions and

Table 5. Comparison of Previous Work Using 1-(2-Pyridylazo)-2-naphthol as the Chelating Ligand

type of support	metal ions	sorption capacity mmol·g^{-1}	preconcentration factor	preconcentration limit ng·mL^{-1}	detection limit ng·mL^{-1}	ref
Chemically Modified						
present work	Zn(II), Co(II), Cu(II), Ni(II), Pb (II)	0.285, 0.145, 0.135, 0.085, 0.076	500, 400, 300, 360, 300	4.0, 5.0, 5.5, 6.7, 6.7	0.28, 0.54, 1.30, 0.42, 1.10	
Amberlite XAD-16	Ni(II), Cd(II), Co(II), Cu(II), Pb(II), Cr(III)	0.08, 0.0435, 0.0797, 0.0787, 0.0231,0.0961	200 (maximum)	10 to 20	0.161, 0.056, 0.072, 0.079, 0.121, 0.268	18
Amberlite XAD-1180	Cu(II), Ni(II), Fe(II), Pb(II), Cr(III), Cd(II), Mn(II)	0.02, 0.02, 0.02, 0.04, 0.05, 0.0033, 0.00677	100, 100, 100, 100, 80, 150, 150	20, 20, 20, 40, 50, 3.3, 6.67	0.19, 1.2, 2.7, 0.13, 4.1, 0.06, 0.13	19
Surface Modified						
Amberlite XAD-2	Cu(II), Cd(II), Pb(II)	0.108, 0.023, 0 0.007	50	25, 20, 50	5.7, 0.8, 23.2	20
Amberlite XAD-2	Ni(II)	0.00187	25	275		21
Amberlite XAD-4	Cu(II)	0.0024	296		0.06	22
Amberlite XAD-4	Pb(II)	0.00096	12 000		5.0	23
Amberlite XAD-1180	Cd(II), Ni(II)	0.047, 0.062	30, 30	20, 83	0.7, 3.1	24
Retained as Metal Chelates						
Amberlite XAD-4	Ni(II), Cd(II), Cu(II), Pb(II), Cr(II), Mn(II)		200	30, 30, 15, 15, 15, 10		25
Amberlite XAD-2000	Ni(II), Cu(II), Pb(II), Cr(II)		250	8.0		26

complexing agents. The proposed procedure is applicable for the determination of trace metals in various water resources, environmental, biological, alloy samples, and multivitamin formulations with good accuracy and precision. The reusability of the PAN-AXAD-4 resin is comparable with other work. Since the resin is prepared by chemical modification, it is found to be highly stable to acids and bases which also make its regenerability superior. The superior analytical characteristics of this resin may be attributed to the large surface area and high porosity of the nonpolar AXAD-4 resin that offers better accessibility whereby it facilitates extensive functionalization with PAN.

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