

Original Paper

2,3-Dihydroxypyridine Loaded Amberlite XAD-2 (AXAD-2-DHP): Preparation, Sorption–Desorption Equilibria with Metal Ions, and Applications in Quantitative Metal Ion Enrichment from Water, Milk and Vitamin Samples

Gopalan Venkatesh, Amit Kumar Jain, and Ajai K. Singh*

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

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Abstract. 2,3-Dihydroxypyridine loaded (via –N=N– linker) Amberlite XAD-2 (AXAD-2-DHP) was prepared and characterized by elemental analyses, TGA and FT-IR spectra. It (1 g packed in a column of 1 cm diameter; surface area $135.5 \text{ m}^2 \text{ g}^{-1}$) was found to be an effective solid phase sorbent for enriching Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} and Co^{2+} at pH 3.5 to 7.0 using flow rates between $1.0\text{--}5.0 \text{ mL min}^{-1}$. For desorption (recovery 97.0–99.8%) of the metal ions, 8 to 10 mL of 2.0 mol L^{-1} HCl or 1.5 mol L^{-1} HNO_3 at a flow rate of between 2.0 and 4.0 mL min^{-1} were found most suitable. The $t_{1/2}$ (time for 50% sorption) is between 2 and 10 min when a 50 mL solution (containing a total amount of metal of 2 mg) was equilibrated with 0.5 g of resin. Sorption of all metal ions except Pb^{2+} follows the Langmuir model, whereas for Pb the data fits with the Freundlich model. The sorption capacity is between 60.7 (for Cd) and $406.7 \text{ } \mu\text{mol g}^{-1}$ (for Cu). The resin can withstand an acid concentration of $\leq 6 \text{ mol L}^{-1}$ and can be reused for thirty cycles of sorption–desorption. The preconcentration factor varies between 100 and 300. For Cd, Ni and Cu the sorption capacity of 2,3-dihydroxypyridine loaded cellulose is lower than that of the present

resin. The tolerance limits of electrolytes, humic acid, complexing agents, Ca^{2+} and Mg^{2+} in the enrichment of all metal ions are reported. The limits of detection are 3.88, 5.37, 8.72, 13.88, 4.71, 1.24, 0.59 and $0.30 \text{ } \mu\text{g L}^{-1}$ for Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} and Co^{2+} , respectively. The calibration curves for flame AAS determination were linear in the ranges 0.018–1.0, 0.067–5.0, 0.2–5.0, 0.9–20, 0.028–2.0, 0.077–5.0, 0.19–10 and $0.1\text{--}3.5 \text{ } \mu\text{g mL}^{-1}$, respectively. All the eight metal ions in river and synthetic water samples, Co in vitamin tablets and Zn in milk samples have been quantitatively enriched with Amberlite XAD-2-DHP and determined by flame atomic absorption spectrometry.

Key words: Amberlite XAD-2; 2,3-dihydroxypyridine; chelating resin; preconcentration; metal ion; determination; flame atomic absorption spectrometry.

The direct determination of metal ions at micro/trace level in environmental samples, high purity materials, biological samples and other complex matrices is possible with a limited number of expensive analytical techniques only. This is due to their low concentrations and matrix interferences. For trace/micro analysis, therefore, preconcentration and/or separation of analyte from the complex matrix make(s) the use of cheaper and commonly available analytical techniques

* Author for correspondence. E-mail: aksingh@chemistry.iitd.ac.in

such as flame AAS feasible. These preconcentration/separation steps are thus frequently used to improve the limit and selectivity of determination by common analytical techniques such as flame AAS. Several methods are known for preconcentration/separation of metal ions at trace/micro level and used according to the nature of the samples, the concentrations of the analyte, and the measurement techniques employed [1]. Ion exchange [2], coprecipitation [3–6], solvent extraction [7] and solid phase extraction (SPE) [8–19] are among the important methods but the use of the latter with chelating matrices for metal ion preconcentration has rapidly grown in the recent past and frequently been coupled with flame AAS and ICP-AES. Chelating matrices generally have ligands immobilized on surfaces such as silica gel [10, 11], cellulose [12–14] and organic co-polymers [17, 18, 21, 22]. Immobilization of small-sized ligands on commercially available co-polymer Amberlite XAD-2 has resulted in promising chelating resins [24–28] for SPE. Therefore, Amberlite XAD-2 was loaded with 2,3-dihydroxypyridine (DHP) via azo-coupler [AXAD-2-DHP] and the resulting matrix was investigated for enrichment of Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} and Co^{2+} . The results of these investigations are reported in this paper. Flame AAS methods coupled with the enrichment with AXAD-2-DHP are developed for the determination of the eight metal ions and applied to determine cobalt in vitamin samples, zinc in milk samples and all the eight metal ions in water samples. For Cd, Ni and Cu the sorption capacity of the present resin is higher than that of 2,3-dihydroxypyridine loaded cellulose. The sorption capacities of present resin are very close to that of thiosalicylic acid and tiron loaded Amberlite XAD-2, which are rated among the best resins based on Amberlite XAD-2. In comparison to silica gel and cellulose based chelating matrices, the preconcentration factors of AXAD-2-DHP are somewhat better or comparable except for iron and cobalt.

Experimental

Instruments

A flame atomic absorption spectrometer of Perkin-Elmer Instruments, Shelton, USA (www.perkin-elmer.com), model Aanalyst 100 equipped with air-acetylene flame was used for metal ion determination. The wavelengths used for monitoring Zn, Mn, Ni, Pb, Cd, Cu, Fe and Co are 213.9, 279.8, 231.1, 217.0, 228.8, 324.8, 248.8 and 240.7 nm, respectively. A Nicolet (Madison, USA, www.thermo.com) FT-IR spectrometer, model Protégé 460,

was used to record IR spectra (in KBr) in the range of 400–4000 cm^{-1} . The pH was measured with a digital pH meter (Toshniwal Instruments, Ajmer, India). Thermogravimetric analysis (TGA) was carried out on a Dupont (Wilmington, Delaware, USA, www.dupont.com) 2100 thermal analyzer, and a Perkin Elmer (Rotkreuz, Switzerland; www.perkin-elmer.com) elemental analyzer, Model 240C, was used for elemental analyses. The flow of solution through the column was controlled using a peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK). The columns of 1 cm diameter and 10 cm in length equipped with adjustable frits were obtained from Pharmacia, Bromma, Sweden (www.pharmacia.com). A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) with a speed of 200 strokes min^{-1} was used for equilibration.

Reagents

Amberlite XAD-2 (specific surface area 330 $m^2 g^{-1}$; pore diameter 90 Å and bead size, 20–60 mesh) was procured from Aldrich (Milwaukee, USA). 2,3-Dihydroxypyridine (DHP) was also obtained from Aldrich (Milwaukee, USA) and used as received. The stock solutions of metal ions ($1 g L^{-1}$) were prepared from analytical reagent-grade metal salts as described earlier [20]. The working solutions of the metal ions were made by suitable dilution of the stock solutions with doubly distilled water. 0.1 $mol L^{-1}$ HCl and NaOH, 0.1 $mol L^{-1}$ acetic acid-acetate buffer (pH 4 and 5), 0.1 $mol L^{-1}$ phosphate buffer (pH 6 and 7) and 0.1 $mol L^{-1}$ ammonium-ammonium chloride buffer (pH 8 and 9) were used to adjust the pH of the solutions, wherever suitable. Water samples from the Ganges river (Haridwar, India), Vaigai river (Tamil Nadu, India) and tap water (New Delhi, India) were collected, acidified with 2% HNO_3 , filtered and stored in glass bottles. The glassware was washed with chromic acid and soaked in 5% HNO_3 overnight and cleaned with doubly distilled water before use. The multivitamin tablets Polybion (Merck, Mumbai, India) were used for Co analysis. The milk powder analyzed was Lactogen obtained from Nestlé (New Delhi, India).

Synthesis of DHP Loaded Amberlite XAD-2 (XAD-2-DHP)

The procedure published earlier [21] was used to prepare the nitrated beads of Amberlite XAD-2 which were also reduced to amino resin by the literature method [22]. The amino resin was suspended in 200 mL of ice cold water and then diazotized with 1 $mol L^{-1}$ HCl and 1 $mol L^{-1}$ $NaNO_2$ solution at $-5^\circ C$ until the reaction mixture started to change the color of iodide paper to violet. The diazotized polymer was filtered under ice-cold conditions (diazotized polymer decomposes at room temperature) and reacted with DHP (10 g dissolved in a mixture of 400 mL water and 200 mL glacial acetic acid) at 0 to $5^\circ C$ for 24 h. The resulting brownish crimson colored beads were filtered and washed with 4 $mol L^{-1}$ HCl and doubly distilled water successively and finally air-dried. Analyses: found: C, 60.98; H, 5.10%; calc. for $C_{13}H_{11}N_3O_3 \cdot H_2O$ C, 60.23; H, 4.25%.

Recommended Procedure for Preconcentration and Determination of Metal Ions

AXAD-2-DHP (1.0 g) was first swollen for 24 h, packed in a glass column C10/10 (Pharmacia, 10 cm \times 10 mm), between frits, using the method recommended by the manufacturer [23]. The column was treated with 4 $mol dL^{-1}$ HCl or HNO_3 (50 mL) and washed with doubly distilled water until free from acid. A suitable aliquot of the

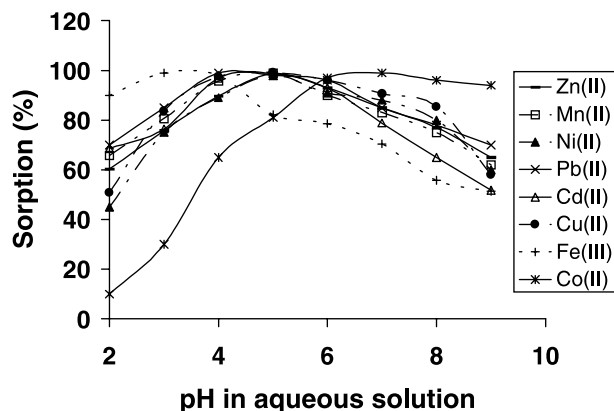


Fig. 1. Effect of pH on the sorption of metal ions on Amberlite XAD-2-DHP

sample solution containing Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} or Co^{2+} in the concentration range of 7.5 ng mL^{-1} – $1.0\text{ }\mu\text{g mL}^{-1}$ was passed through the column after adjusting its pH to the optimum value (Fig. 1) at a flow rate of $1\text{--}5\text{ mL min}^{-1}$, controlled with a peristaltic pump. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from the column with 2M HCl or HNO_3 ($10\text{--}15\text{ mL}$) passed at a flow rate of $2\text{--}5\text{ mL min}^{-1}$. The concentration of the metal ions in the eluate was determined by FAAS, standardized previously. Dilution was made with doubly distilled water before aspiration, if required. The calibration curves for FAAS determination were linear in the ranges of $0.018\text{--}1.0$, $0.067\text{--}5.0$, $0.2\text{--}5.0$, $0.9\text{--}20$, $0.028\text{--}2.0$, $0.077\text{--}5.0$, $0.19\text{--}10$ and $0.1\text{--}3.5\text{ }\mu\text{g mL}^{-1}$ for Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} and Co^{2+} , respectively.

Results and Discussion

Synthesis and Characterization of the Amberlite XAD-2 Loaded with DHP

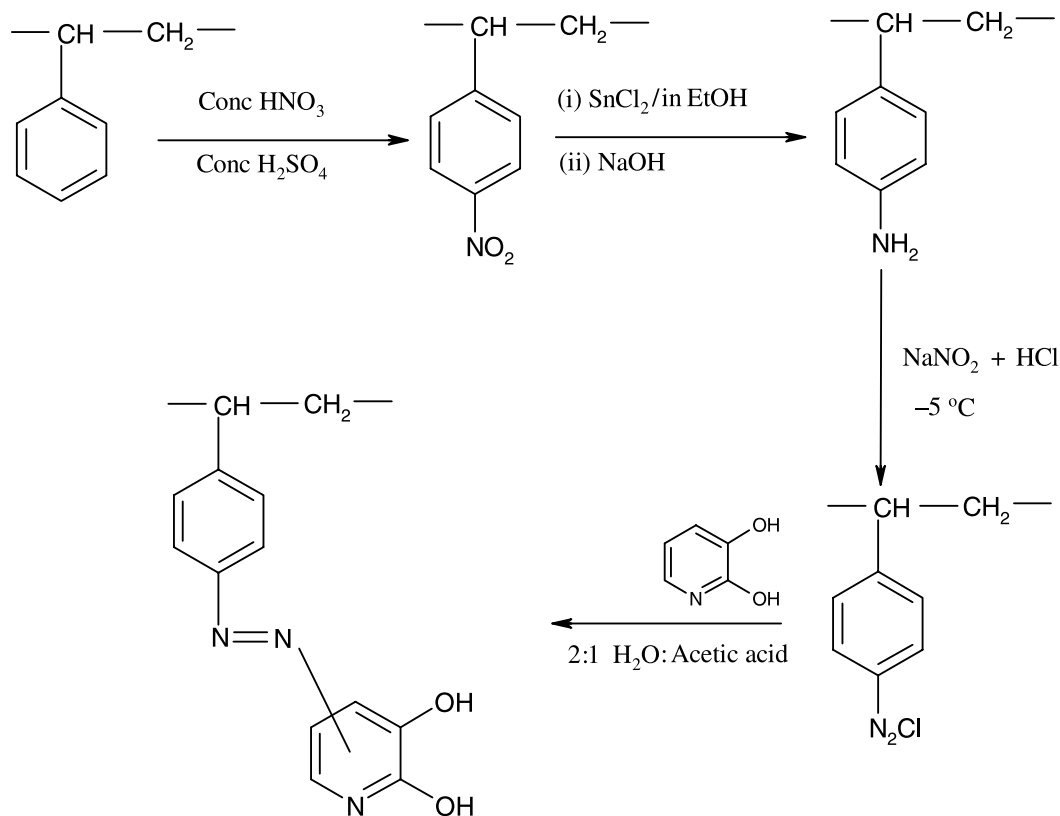
AXAD-2-DHP synthesized by the reaction given in Scheme 1 was characterized by FT-IR, TGA and elemental analyses. FT-IR spectra of nitrated Amberlite XAD-2 and AXAD-2-DHP are compared with those of free Amberlite XAD-2. The nitro derivative shows new bands at 1348 and 1525 cm^{-1} (due to $\nu(N-O)_{\text{symm}}$ ($\nu(N-O)_{\text{asymm}}$ respectively). The spectrum of AXAD-2-DHP shows additional bands (cm^{-1}) at 1271 (C–O stretching, in plane), 1448 ($-N=N-$ stretching) and 1653 (C=N stretching), which imply the immobilization of DHP on Amberlite XAD-2. The surface area of Amberlite XAD-2- NH_2 was found to be $205.5\text{ m}^2\text{ g}^{-1}$ and $135.5\text{ m}^2\text{ g}^{-1}$ for AXAD-2-DHP. The weight loss in TGA of AXAD-2-DHP occurs in two steps (6.97 and 54.62% respectively). The first is due to water present in the resin. Elemental analyses indicate that on average one DHP molecule is attached per styrene unit of Amberlite XAD-2.

Optimum Conditions for Sorption and Desorption

The multivariate approach was used to optimize the working conditions; each optimum condition was, however, checked again after standardizing the remaining ones. The optimum conditions for sorption of Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} and Co^{2+} on the column packed with the AXAD-2-DHP (pH and flow rate) and desorption (acid concentration, volume of eluent) were established by varying one of them and following the recommended column procedure. A typical optimization of pH for sorption of Cu on resin column is as follows. A set of solutions (volume: 100 mL), each containing $0.25\text{ }\mu\text{g mL}^{-1}$ of Cu, was taken. The pH of the solutions of the set was adjusted to different values in the range of $2.0\text{--}9.0$. The enrichment of the metal ion from these solutions was studied by the recommended column procedure. The pH profile for each metal ion is shown in Fig. 1. The use of $4\text{--}10\text{ mL}$ of acetate, phosphate and ammonia buffer to adjust the pH does not affect the sorption behavior. The metal ions are not significantly desorbed ($<2\%$) by distilled water; therefore chelation contributes predominantly to the retention of metal ions. The average recovery was maximum (99.8%) for Pb^{2+} and minimum (97.0%) for Co^{2+} . For five determinations of $0.25\text{ }\mu\text{g mL}^{-1}$ of each metal ion ($0.5\text{ }\mu\text{g mL}^{-1}$ for Pb) the standard deviation was between 0.009 and 0.026 , and the RSD between 1.01 and 2.58% .

Effects of Flow Rate and Eluent

The degree of metal ion sorption on a column packed with AXAD-2-DHP (1 g) was studied at various flow rates of the metal ion solution controlled with a peristaltic pump. The optimum flow rate for loading all these metal ions is between $1.0/2.0$ and $4.0/5.0\text{ mL min}^{-1}$. A flow rate $<1.0\text{ mL min}^{-1}$ was not employed to avoid a longer time of analysis. At a flow rate $>5.0\text{ mL min}^{-1}$, there was a decrease in the percentage of sorption, probably because the metal ions do not equilibrate sufficiently with the resin. The effect of the concentration of HCl or HNO_3 on the desorption of metal ions from the AXAD-2-DHP column was studied. The optimum HCl (HNO_3) concentration ranges for maximum instantaneous recovery ($>97.0\%$) are $1.5\text{--}4.0$, $2.0\text{--}4.0$, $1.5\text{--}2.5$, $0.5\text{--}2.5$ (HNO_3) $1.5\text{--}2.0$, $1.5\text{--}4.0$, $2.0\text{--}4.0$ and $1.0\text{--}4.0\text{ mol L}^{-1}$ for Zn^{2+} , Mn^{2+} , Ni^{2+} ,



Scheme 1

Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} and Co^{2+} , respectively. The efficacy of the eluent, 2 mol L^{-1} HCl, was studied by taking its different volume (1–10 mL) and applying the recommended column procedure (metal concentration $\leq 1 \mu\text{g mL}^{-1}$). It was found that 8 mL of 2 mol L^{-1} HCl was sufficient for quantitative recovery (97.0–98.0% recovery) of Cu and Co and 10 mL for Zn, Mn, Ni, Cd and Fe (98.0–99.4% recovery). For Pb, 10 mL of 1.5 mol L^{-1} HNO_3 resulted in 99.8% recovery.

Kinetics of Metal Sorption

The AXAD-2 DHP (0.5 g) was shaken with 50 mL solution containing $40 \mu\text{g mL}^{-1}$ of one of the eight metal ions for different time intervals (2, 5, 10, 15, 20, 25, 30, 35, 40 min and 5 h) under optimum conditions. The metal ions loaded onto the matrix were stripped with acid of optimum concentration and determined with FAAS. The metal ion concentration in the supernatant solution was also determined with FAAS after appropriate dilution. The variation of sorption as a function of time for all the metal ions

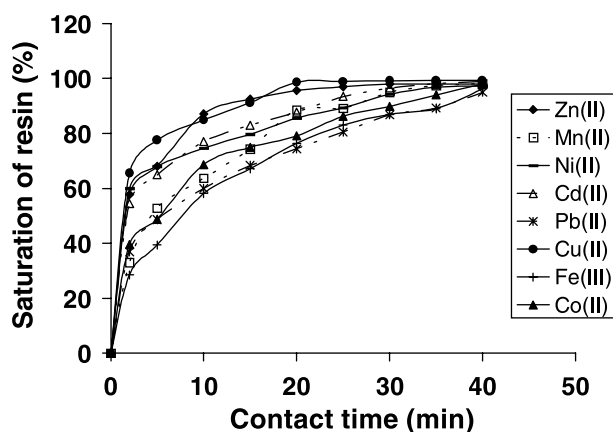


Fig. 2. Kinetics of metal ion sorption on Amberlite XAD-2-DHP

is shown in Fig. 2. Shaking for 2 min was found to be sufficient for more than 50% sorption of Zn, Ni, Pb and Cu. For more than 50% sorption of Mn ~5 min equilibration was found to be sufficient, whereas 10 min shaking was required for more than 50% sorption for Cd, Cu and Co.

Adsorption Isotherms and Feasibility of the Process

The isotherms for sorption of metal ions on AXAD-2-DHP were studied. The sorption of all metals except Pb conform to the Langmuir model (Equation (1)) which assumes uniform distribution of sorption sites and sorption energies without interactions between the sorbed molecules.

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s \cdot b} \quad (1)$$

C_s is the concentration of solution at equilibrium (mg L^{-1}) and N_f is the concentration of cations adsorbed per gram of the matrix (in mg g^{-1}). The sorption coefficient N_s is the maximum amount of solute sorbed per gram of surface (mg g^{-1}) corresponding to a condition in which all available sites are filled. The coefficient b is related primarily to the net enthalpy of sorption. Based on the linear form of the sorption isotherm, plots of C_s/N_f against C_s gave N_s values (mg g^{-1}) as 5.22, 4.03, 5.58, 4.65, 4.98, 5.77, 5.50 for Zn^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} , Fe^{3+} , Mn^{2+} and Ni^{2+} , respectively. The sorption capacity values obtained experimentally are in good agreement with these N_s values. The sorption data of Pb fit well with the Freundlich model (Equation (2)) and not with the Langmuir model.

$$\log N_f = \log A + 1/n \log C_s \quad (2)$$

The plot of $\log N_f$ against $\log C_s$ was linear. Its slope and intercept yielded the values of $1/n$ and A as 0.69 and 1.97 mg g^{-1} , respectively, which indicate sorption intensity and capacity, respectively. The numerical values of $1/n < 1$ show that sorption capacity is reduced at low equilibrium concentrations.

Sorption Capacity

The resin (1 g) was saturated with Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} or Co^{2+} ion solution

(concentration: $50 \mu\text{g mL}^{-1}$) by equilibration on a mechanical shaker under optimum conditions. The solid resin was filtered and washed with distilled water. The metal ions loaded on it were desorbed with 100 mL of $2 \text{ mol L}^{-1} \text{ HCl}/1.5 \text{ mol L}^{-1} \text{ HNO}_3$ and determined with a pre-standardized FAAS to calculate the capacity. The filtrate after removing the resin was diluted suitably (to bring the metal ion concentration in the working range) and also subjected to FAAS determination to further verify the capacity values. The sorption capacity for Cu^{2+} was found to be highest ($406.7 \mu\text{mol g}^{-1}$). For Zn^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Fe^{3+} and Co^{2+} the capacities were 175.6, 90.8, 220.1, 150.4, 65.7, 90.0 and $86.7 \mu\text{mol g}^{-1}$, respectively. The sorption capacity values found with the column method were nearly the same (variation $< 2.8\%$).

Resin Stability and Reusability

The resin is quite stable and does not show any sign of decay even after one year. The stability of AXAD-2-DHP was studied in acid ($1.0\text{--}6.0 \text{ mol L}^{-1} \text{ HCl}/\text{HNO}_3$). It was shaken with acid solutions of varying concentrations for 4 h and filtered. The solid was washed with distilled water until free from acid, then air-dried, and its sorption capacity determined as described above. The acid-treated resin was found to show a sorption capacity similar to that of untreated resin (variation $\leq 2.5\%$). Thus the present resin can withstand an acid concentration $\leq 6 \text{ mol L}^{-1}$. The chelating resin can be reused in thirty cycles of sorption-desorption (change in sorption capacity $< 2.0\%$).

Preconcentration and Recovery of Metal Ions

The enrichment factor was determined by increasing the dilution of metal ion solution while keeping the total amount of loaded metal ion fixed at $15 \mu\text{g}$ for Cu, $20 \mu\text{g}$ for Fe, Co, Mn, Zn or Cd and $25 \mu\text{g}$ for Pb or Ni

Table 1. Enrichment factors and enrichment limits of metal ions

Metal ion	Total volume (mL)	Concentration (ng mL^{-1})	Final volume (mL)	Recovery %	Preconcentration factor
Zn^{2+}	2500	8.0	10	99.16	250
Mn^{2+}	2000	10.0	10	99.33	200
Ni^{2+}	2500	10.0	10	99.60	250
Pb^{2+}	3000	8.33	10	99.46	300
Cd^{2+}	2000	10.0	10	98.16	200
Cu^{2+}	2000	7.5	8	98.00	250
Fe^{3+}	1000	20.0	10	95.00	100
Co^{2+}	1200	16.6	8	97.00	150

Table 2. Tolerance limits of electrolytes, Ca²⁺ and Mg²⁺ and organic species

Foreign species	Metal ion							
	Zn ²⁺	Mn ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Cu ²⁺	Fe ³⁺	Co ²⁺
NaNO ₃ ^a	0.70	0.25	0.008	0.22	0.005	0.007	0.30	0.05
NaCl ^a	0.015	0.01	0.008	0.003	0.003	0.10	0.08	0.01
NaBr ^a	0.014	0.04	0.012	0.001	0.001	0.50	0.05	0.01
Na ₃ PO ₄ ^a	I	I	0.07	0.006	0.002	I	0.001	0.003
Na ₂ SO ₄ ^a	0.002	0.004	0.001	0.060	0.001	0.20	0.08	0.05
NaI ^a	0.20	0.02	0.15	0.06	0.04	0.004	0.09	0.12
Humic acid ^b	10	15	12	10	13	18	20	5
Ascorbic acid ^c	0.10	0.18	1.10	0.20	0.40	0.05	0.30	0.20
Citric acid ^c	0.02	0.80	0.08	1.80	1.10	1.70	0.80	0.50
EDTA ^c	0.001	0.001	0.002	0.007	0.004	0.002	0.005	0.008
Tartaric acid ^c	0.90	0.70	1.00	1.50	0.60	0.05	0.04	0.12
Ca ²⁺ ^a	0.20	0.002	0.02	0.016	0.03	0.30	0.07	1.00
Mg ²⁺ ^a	I	0.006	0.80	0.12	0.08	0.10	0.08	1.00

^a mol L⁻¹, ^b µg mL⁻¹, ^c mmol L⁻¹ and I= Interferes.

and applying the recommended procedure. The feed volume and preconcentration factors are given in Table 1. The preconcentration factors of other chelating matrices with AXAD-2-DHP are compared in Table 5. The recoveries at the lowest concentration are also reported in Table 1. The limit of detection values (defined as (blank + 3s), where s is the standard deviation of the blank determination) are 3.88, 5.37, 8.72, 13.88, 4.71, 1.24, 0.59 and 0.30 µg L⁻¹ for Zn²⁺, Mn²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Cu²⁺, Fe³⁺ and Co²⁺, respectively, and the corresponding limit of quantification (blank + 10s) values are 4.31, 5.65, 9.38, 14.06, 5.04, 1.70, 1.36 and 0.60 µg L⁻¹, respectively.

Effects of Electrolytes and Cations

The chloride, nitrate, sulfate and phosphate ions commonly found in natural water samples have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the chelating resins to bind metal ions may be hampered resulting in the reduction of overall enrichment. Thus, the effect of NaCl, NaBr, NaNO₃, Na₂SO₄, Na₃PO₄ and NaI on the sorption efficiency of AXAD-2-DHP for Zn²⁺, Mn²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Cu²⁺, Fe³⁺ and Co²⁺ (25 µg each) was studied using the recommended procedure. The species tested for interference were added to the metal ion solution before applying the recommended procedure. The tolerance limits for electrolytes are given in Table 2. A species is considered to interfere when it lowers the recovery of metal ions by more than 3% compared to the value observed in its absence. Each reported tolerance/interference occurs

in the preconcentration and not in the determination by FAAS, as checked with the help of reagent-matched standard solutions. The tolerance limits of the electrolytes in the sorption of Cd²⁺ are somewhat low while for other metal ions the limits are reasonably good. Na₃PO₄ is tolerable only at lower concentrations (1–70 mmol L⁻¹) and shows interference in the determination of Zn²⁺ and Mn²⁺. Similarly, the effect of Ca²⁺, Mg²⁺, humic acid and some common complexing agents on the sorption efficiency of AXAD-2-DHP for the eight metal ions has also been investigated, and the tolerance limits are reported in Table 2. Ca²⁺ is tolerated with these metal ions up to a concentration range of 2.0 mmol–1.00 mol L⁻¹. Mg²⁺ interferes with the determination of Zn²⁺. It is tolerated with the rest of the metal ions in the concentration range of 6.0 mmol–1.00 mol L⁻¹. Humic acid and other organic acids can coexist with metal ions to some extent during their enrichment. In general, the tolerance limits given in Table 2 suggest that common anions, alkali and alkaline earth metal ions do not adversely affect sorption on the present resin when present in moderate amounts.

Applications of the Enrichment Method

Determination of Metal Ions in River Water Samples

AXAD-2-DHP was used to preconcentrate and determine Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺, Mn²⁺, Co²⁺, Cd²⁺ and Pb²⁺ ions in water samples collected from the river Ganges (Haridwar), the river Vaigai (Tamil Nadu) and

Table 3. Water analyses

Origin of sample	Method	Metal ion ($\mu\text{g L}^{-1}$) (RSD %)							
		Zn ²⁺	Mn ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cu ²⁺	Fe ³⁺	Co ²⁺
Vaigai river, Tamil Nadu	direct	3.3 (3.7)	6.0 (7.6)	3.2 (3.9)	3.6 (8.9)	10.3 (5.4)	43.9 (0.7)	66.1 (0.6)	11.0 (4.9)
	S.A.	3.2 (4.0)	5.9 (2.5)	3.1 (4.6)	3.5 (4.2)	10.2 (4.8)	43.6 (1.2)	66.8 (0.8)	11.3 (2.8)
Ganges river, Haridwar	direct	4.9 (4.8)	3.3 (6.3)	4.7 (2.7)	2.6 (5.5)	4.5 (4.5)	26.4 (0.9)	55.4 (0.4)	19.5 (1.0)
	S.A.	5.0 (4.0)	3.3 (3.7)	4.9 (5.1)	2.7 (4.6)	4.6 (5.4)	26.8 (0.8)	54.8 (0.4)	19.2 (1.3)
Tap water, New Delhi	direct	20.2 (1.0)	27.6 (0.9)	4.3 (4.8)	3.1 (4.6)	10.5 (1.9)	6.4 (6.6)	30.3 (1.0)	8.7 (4.4)
	S.A.	19.9 (1.2)	27.5 (0.4)	4.2 (5.1)	3.0 (4.4)	10.4 (1.4)	6.7 (3.5)	30.5 (0.8)	8.9 (2.6)

Direct Recommended procedure is directly applied, *SA* Standard addition method, RSDs for four determinations.

tap water (New Delhi). Estimation of all metal ions was made with and without (referred to as direct determination) standard addition by passing 1 L of water sample (spiked with 50–100 μg of each of the seven metal ions in case of standard addition method) through the column packed with 1.0 g of resin after adjusting the pH to an optimum value and determining the metal ion as described in the recommended procedure. The results are given in Table 3. The concentrations reported in this Table as estimated by the standard addition (SA) method are the values obtained by subtracting the amount of metal added for spiking from the total metal recovered. The closeness of results of the direct and the SA method indicates the reliability of the present results of metal analyses in water samples and the suitability of AXAD-2-DHP for metal enrichment from water samples.

Determination of Co in Pharmaceutical Samples

Solid phase extraction with AXAD-2-DHP coupled with the FAAS method of determination was applied to determine cobalt in pharmaceutical samples. Ten tablets (weighing 3.25 g) were digested in a beaker containing 25 mL of concentrated HNO_3 by slowly increasing the temperature of the mixture to 400 K. The mixture was further heated till a solid residue was obtained. It was allowed to cool and dissolved in 20 mL of concentrated HNO_3 . The solution was gently evaporated on a steam bath until a residue was left again. It was mixed with 50 mL of distilled water, and concentrated HNO_3 was added dropwise until a clear solution was obtained on gentle heating. The pH of the solution was adjusted to 5.5 by adding 10 mL of phosphate buffer, and the concentration of

cobalt was estimated by the recommended column using FAAS. The average (four determinations) amount of cobalt was found to be 1.99 $\mu\text{g g}^{-1}$ of tablet with an RSD of 1.34%. The reported value of cobalt in the tablet is 1.96 $\mu\text{g g}^{-1}$.

Determination of Zn in Milk Sample

A sample of powdered milk (1.0 g) was heated in a beaker containing a mixture of concentrated sulfuric acid (20 mL) and nitric acid (8 mL) till a clear solution was obtained. It was allowed to cool and most of the acid was neutralized with sodium hydroxide. The pH was adjusted to the optimum value and the volume was made up to 1 L. The solution was passed through the column packed with AXAD-2-DHP under optimum conditions. The zinc ions were eluted from the column using 25 mL of 2 mol L^{-1} HCl and determined using FAAS. The average (four determinations) amount of zinc was found to be 37.65 $\mu\text{g g}^{-1}$ of sample with an RSD of 1.38%. The reported value of zinc in the milk sample is 38.0 $\mu\text{g g}^{-1}$.

Analysis of Synthetic Water Samples

To check the validity and accuracy of the present matrix coupled with flame AAS for metal ion monitoring, the recommended procedure was applied to determine the copper and iron content in synthetic water samples (1 L) having a composition similar to certified water samples SLRS-4 (National Research Council, Ottawa, Ontario, Canada). The average of four determinations of copper and iron was found to be 1.77 and 101.5 $\mu\text{g L}^{-1}$ with RSD values of 1.17% and 2.05%, respectively. Amounts ($\mu\text{g L}^{-1}$) present in synthetic sample are: Cu, 1.81 and Fe, 103.

Comparison with Other Chelating Resins/Matrices

The sorption capacities of the AXAD-2-DHP are compared with those of other chelating resins/matrices in Table 4. The capacity of the present resin to sorb metal ions is better than many of the eight Amberlite XAD-2 based chelating resins given in Table 4. For Ni, Cd and Co, thiosalicylic loaded Amberlite XAD-2 shows only marginally better capacity values than the present one. Similarly, Tiron loaded Amberlite XAD-2 exhibits an only marginally better sorption capacity for Mn, Fe and Co in comparison to XAD-2-DHP. For Cd and Cu, the capacity of the present resin is higher than the values reported for resacetophenone loaded silica gel. For Cd the capacity of 2,3-dihydroxypyridine loaded cellulose is significantly lower than that of the present resin. The capacity is better in the case of Ni and Cu also in comparison to cellulose anchored with DHP. Recently, exceptionally high values of sorption capacities, several times that of the commonly observed values with most of the well-known chelating matrices, have been reported for Amberlite XAD-16 loaded with N-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphth-alene-1-suphonic acid [31]. These high values reported for this Amberlite XAD-16

based resin appear to be erroneous. Our resin is not an exception and shows lower sorption capacities than Amberlite XAD-16 loaded with N-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphth-alene-1-suphonic acid.

The preconcentration factors of the present chelating resin are compared with those of other chelating matrices in Table 5. For Pb the preconcentration factor of AXAD-2-DHP is higher than that of Amberlite XAD-16 loaded with N-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphthalene-1-suphonic acid. Surprisingly, the preconcentration factors for Amberlite XAD-16 loaded with N-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphthalene-1-suphonic acid are not exceptionally high as the sorption capacities. The AXAD-2-DHP gives preconcentration factors which are greater or comparable to those of the other eight Amberlite XAD-2 based chelating resins. In comparison to silica gel and cellulose-based chelating matrices, the preconcentration factors of AXAD-2-DHP are somewhat better or comparable except for iron and cobalt. Among its main attractive features are the reusability of AXAD-2-DHP, the generally acidic pH for maximum enrichment (except for cobalt), low values of relative standard deviations

Table 4. Comparison of sorption capacities ($\mu\text{mol g}^{-1}$)

Immobilized ligand	Zn	Mn	Ni	Cd	Pb	Cu	Fe	Co
<i>Support: Amberlite XAD-2</i>								
2,3-Dihydroxypyridine (present study)	176	91	220	150	65.7	407	90	87
Thiosalicylic acid [21]	47		310	198	89	214	66	106
Chromotropic acid [18, 24]	148		103	83	186	134	58	65
Pyrocatechol [18, 25]	28		53	41	105	93	74	23
o-Aminophenol [26]	45		55	30	16	53		58
Tiron [27]	170	182	215	84	60	220	100	110
Pyrogallol [17]	69	82	70	4	32	71	83	70
Quinalizarin [22]	22	17		15	26	50		28
1-(2-Pyridylazo)-2-naphthol [28]				23	7	108		
<i>XAD-7</i>								
Xylenol orange [29]	28		44	18	17	25	29	44
<i>XAD-16</i>								
N-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphth-alene-1-Suphonic acid [31]			1210	760	880	2050		780
<i>Silica gel</i>								
Resacetophenone [10]	191		254	58	67	186	273	365
8-Hydroxy quinoline [11]	177		255	92	158	448	386	205
<i>Cellulose</i>								
2,3-Dihydroxypyridine [13]	315		208	70	83	343	431	146
Pyrocatechol [12]	85		140	116	104	186	109	160
8-Hydroxyquinoline [14]	349		178	114	94	630	256	206

Table 5. Comparison of preconcentration factors (times of volume)

Immobilized ligand	Zn	Mn	Ni	Cd	Pb	Cu	Fe	Co
<i>Support: Amberlite XAD-2</i>								
2,3-DHP (present work)	250	200	250	200	300	250	100	150
Thiosalicylic acid [21]	200			200	100	200	400	180
Chromotropic acid [18, 24]	200		200	100	200	100	120	150
Pyrocatechol [18, 25]	100		200	200	200	100	80	200
o-Aminophenol [26]	40		65	50	40	50		100
Tiron [27]	180	64	150	48	25	200	80	56
Pyrogallol [17]	160	120	120	40	25	65	140	65
Quinalizarin [22]	100	65		50	50	100		40
1-(2-Pyridylazo)-2-naphthol [28]	50			50	50			
<i>XAD-7</i>								
Xylenol orange [29]	100		100	50	50	50	100	100
8-(Benzene sulfonamido quinoline) [30]	10			10				
<i>XAD-16</i>								
N-(3,4-dihydroxy)benzyl-4-Amino,3-hydroxynaphthalene-1-Suphonic acid [31]	300		333	267	234			300
<i>Silica gel</i>								
Resacetophenone [10]	150		200	250	250	250	200	300
8-Hydroxyquinoline [11]	200		200	150	250	300	300	250
<i>Cellulose</i>								
2,3-DHP [13]	200		125	200	200	250	300	100
Pyrocatechol [12]	180		75	250	200	300	300	100
8-Hydroxyquinoline [14]	250		90	250	200	300	300	100

and good tolerance towards many foreign species including electrolytes.

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