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Characterization of a novel chelating resin of enhanced hydrophilicity and its analytical utility for preconcentration of trace metal ions

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ABSTRACT

A stable extractor of metal ions was synthesized through azo linking of p-hydroxybenzoic acid with Amberlite XAD-4 and was characterized by elemental analyses, infrared spectral and thermal studies. Its water regain value and hydrogen ion capacity were found to be 15.80 and 7.52 mmol g^{-1}, respectively. Both batch and column methods were employed to study the sorption behavior for the metal ions which were subsequently determined by flame atomic absorption spectrophotometry. The optimum pH range for Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) ions were 10.0, 8.0–9.0, 7.0, 7.0–8.0 and 7.0–8.0, respectively. The half-loading time, $t_{1/2}$, are 6.0, 8.0, 8.0, 8.0 and 4.0 min, respectively. Comparison of breakthrough and overall capacities of the metals ascertains the high degree of column utilization (>75%). The breakthrough capacities for Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) ions were found to be 0.46, 0.43, 0.42, 0.09 and 0.06 mmol g^{-1} with the corresponding preconcentration factor of 460, 460, 460, 360 and 260, respectively. The limit of preconcentration was in the range of 4.3–7.6 $\mu g\,L^{-1}$. The detection limit for Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) were found to be 0.47, 0.45, 0.50, 0.80, and 1.37 $\mu g\,L^{-1}$, respectively. The Student's *t* (*t*-test) values for the analysis of standard reference materials were found to be less than the critical Student's *t* values at 95% confidence level. The AXAD-4-HBA has been successfully applied for the analysis of natural water, multivitamin formulation, infant milk substitute, hydrogenated oil and fish.

1. Introduction

Significant accumulation of toxic metals in the environment and their persistent nature have been the subject of great concern in recent years due to their over increased use in various industries [1]. The toxicities of heavy metals may be caused by the inhibition and reduction of various enzymes, complexation with certain ligands of amino acids and substitution of essential metal ions from enzymes [2,3]. The indication of their importance relative to other potential hazards is their ranking by the U.S. Agency for Toxic Substances and Disease Registry, which lists all hazards present in the toxic waste sites according to their prevalence and severity of their toxicity. The first, second, third and sixth hazards on the list are heavy metals: lead, mercury, arsenic and cadmium, respectively [4]. Their quantification in industrial effluents, various water resources, environmental and biological samples is important, especially in the environment monitoring and assessment of occupational and environmental exposure to toxic metals.

Several analytical techniques such as anodic stripping voltammetry, atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry are available for the determination of trace metals with sufficient sensitivity for most of applications. However, the direct determination of trace metals in real matrices is difficult because of the low concentrations of the metals and strong interference from the sample matrix [5,6].

A radical way to eliminate matrix effects is a preliminary separation of macrocomponents by a relative, or absolute, preconcentration of trace metals. Preconcentration procedures allow one to decrease the detection limits while unifying the analytical schemes for materials of different nature, and simplifying the preparation of calibration samples, as well as improving the reliability of analysis. Therefore, the preconcentration and determination of trace metals in real samples have been a focus in environmental evaluation and protection study. Moreover, preconcentration and separation can lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS) [7]. FAAS has been demonstrated [7–9] to be a very effective technique in combination with preconcentration procedures. 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 require more expensive

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equipment and are usually much more sensitive to interferences from macrocomponents of various natural matrices [10]. The use of chelating resin in solid-phase extraction (SPE) as metal ion extractants has turned out to be an active area of research in the field of separation science in the recent years [11–13]. 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 regeneration of resins over many cycles with good reproducibility in the sorption characteristics are frequently quoted as an advantage [13]. It overcomes many drawbacks of solvent extraction namely the use of large volumes of carcinogenic organic solvent, emulsion formation caused by the mutual solubility between organic solvent and aqueous layer and analyte loss during multi-step extraction. The basic principle of SPE of trace element ions is the transfer of analytes from the aqueous phase to the active sites of the solid phase. Selectivity is one of the most important characteristic of sorbents [14]. From this point of view, the preferable ones are complexing sorbents, which ensure high selectivity towards heavy metals. Complexing sorbents destined for preconcentration of heavy metals are synthesized in different ways: the chemical modification of polymeric and mineral matrices (grafting of functional groups) or the non-covalent immobilization of reagents (ligands) on various supports [15–18]. The sorption by complexing sorbents is accompanied by the formation of complexes of heavy metals with functional groups of sorbents, which allows selectively extracting metals from complex solutions. Ion exchange and the reduction of metals to the lowest oxidation level are also possible during sorption. In fact, the mechanism of the interaction of metals with complexing sorbents is complicated, and depends on both the type of complex-forming groups and the sorption conditions [19–21].

Amberlite XAD resins, as the copolymer backbone for the immobilization of chelating ligands, have some physical superiority, such as porosity, uniform pore size distribution, high surface area and chemical stability towards acids, bases, and oxidizing agents, as compared to other resins. Among these adsorbents, Amberlite XAD resins (XAD-2, XAD-4, XAD-7, XAD-16, XAD-1180 and XAD-2000) are very useful for the preconcentration of metal complexes [22–25]. The use of benzoic acid derivatives (with at least one hydroxyl group) as chelating ligands have been reported in previous works [26–33], which reflect their utility in the field of preconcentration and separation of metal ions. Except a few [34], the importance of hydrophilicity has not received due attention in previous works. High hydrophilicity would lead to faster kinetics so that preconcentration of large volumes of samples of trace metal ions by column operation would require lesser time.

This paper reports on the synthesis and characterization of p-hydroxybenzoic acid modified Amberlite XAD-4 (AXAD-4-HBA) aiming to find an efficient material for the separation and preconcentration of Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) ions from an aqueous medium prior to their determination by flame atomic absorption spectrophotometry. The main objective for choosing this ligand is to bring into play the dual mechanism of accessibility and chelation by virtue of the presence of hydrophilic group (–COOH) at such a distant from the chelating site so that steric factors may not hinder the process of chelation. Several parameters influencing the recoveries of analytes, including pH of sample, sample volume, eluent volume and effect of diverse ions have been investigated in detail. An optimized procedure has been applied to the determination of trace metals in natural water samples and some standard reference samples.

2. Experimental

2.1. Instruments

A PerkinElmer model 3100 (Waltham, MA, USA), flame atomic absorption spectrometer was used for determining metal concentration. Operating parameters set for the determination of elements are given in Table 1. An ELICO (Hyderabad, India) digital pH meter (LI-120) was used for pH measurements. A thermostated mechanical shaker-NSW-133 (New Delhi, India) at 200 strokes min^{-1} was used for carrying out the equilibrium studies. Infrared (IR) spectra were recorded on a Fourier Transform-IR Spectrometer from Spectro Lab-Interspec 2020 (Newbury, UK) using KBr disc 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 Sophisticated Analytical Instrument Facility of Central Drug Research Institute (Lucknow, India). A column (1 × 10 cm), 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 Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) (supplied by Central Drug House (P) Ltd., New Delhi, India) at the concentration of 1000 mg L^{-1} in 1% HNO_3 were standardized by complexometric titration [35] before use. The working solutions of the metals were prepared by appropriately diluting the stock solutions. Buffer solutions, used for pH adjustment, were prepared with reagents 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 bi-phosphate 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). Amberlite XAD-4 resin (Sigma–Aldrich Chemie GmbH, Steinheim, Germany) was purchased as 20–60 mesh particle size (40 Å mean pore size) with 725 $\text{m}^2\,\text{g}^{-1}$ of surface area. p-Hydroxybenzoic acid (HBA) was procured from Otto Chemicals Pvt. Ltd. (Mumbai, India). Standard reference materials such as vehicle exhaust particulates NIES 8, Pond sediment NIES 2, Chlorella NIES 3, Human hair NIES 5, Tea leaves NIES 7 were obtained from the National Institute of Environmental Studies (Ibaraki, Japan),

Table 1
Operating parameters set for FAAS for the determination of elements.

Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Working range (μg)[a]	Flame composition	
					Air (L min^{-1})	Acetylene (L min^{-1})
Co(II)	240.7	0.2	30	0.25–75.0	9.5	2.3
Ni(II)	232.0	0.2	15	0.50–100.0	9.5	2.3
Cu(II)	324.8	0.7	25	0.15–50.0	9.5	2.3
Zn(II)	213.9	0.7	15	0.05–10.0	9.5	2.3
Pb(II)	283.3	0.7	8	0.5–150.0	9.5	2.3

[a] The given amount is in 5 mL of the final eluent.

Rompin hematite JSS (800-3) obtained from the Iron and Steel Institute of Japan (Tokyo, Japan) and Zinc base die-casting alloy C NBS 627 provided by the National bureau of Standards, U.S. Department of Commerce (Washington, DC, USA). A multivitamin capsule (bearing the commercial name Maxirich) was procured from Cipla Limited (Mumbai, India) and Infant milk substitute (commercially available as Lactogen 1) was obtained from Nestle India Limited (New Delhi, India). Hydrogenated oil (locally known as Vanaspati ghee) was obtained from the local market, Aligarh, India. All the reagents (HNO_3, HCl, $HClO_4$ and H_2O_2) used for wet digestion of the samples were procured from Merck (Mumbai, India).

2.3. Pretreatment of samples

2.3.1. Natural and sewage water samples

The water samples namely river water (collected from the Ganga, Narora), canal water (collected from Kasimpur, Aligarh), sewage water (collected from area in the vicinity of local nickel electroplating industry, Aligarh) and tap water (collected from University campus) were immediately filtered through Millipore cellulose membrane filter (0.45 μm pore size), acidified to pH 2 with concentrated HNO_3 (obtained from Merck, Mumbai, India), and stored in precleaned polyethylene bottles.

2.3.2. Digestion of environmental, biological and alloy standard reference materials (SRMs)

To dissolve the environmental SRMs (Vehicle exhaust particulates NIES 8 and Pond sediment NIES 2), a 0.5 g of the sample was dissolved by adding 10 mL of concentrated nitric acid (15.5 mol L^{-1}), 10 mL of concentrated perchloric acid (12.2 mol L^{-1}) and 2 mL of concentrated hydrofluoric acid (22.4 mol L^{-1}) in a 100 mL in a Teflon beaker. The solution was evaporated to near dryness, redissolved in minimum volume of 2% HCl, filtered and made up to 50 mL volume in a calibrated flask.

The sample solutions of biological SRMs (Human hair NIES 5 and Tea leaves NIES 7) were prepared as proposed by the international atomic energy agency [36]. A 50 mg (600 mg for Chlorella NIES 3) 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 °C. Then each of the samples was dissolved in 10–20 mL of concentrated nitric acid. After adding 0.5 mL of 30% H_2O_2, the solution was boiled to dryness. The residue obtained was dissolved in minimum amount of 2% HCl and made up to a 50 mL volume in a calibrated flask.

The solution of standard alloys (Rompin hematite JSS (800-3) and Zinc base die-casting alloy C NBS 627) was prepared by taking 25 mg of the sample into a beaker and dissolved in 10–50 mL of aqua regia. The solution was boiled to near dryness. Finally the residue was dissolved in 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 multi-vitamin formulation, infant milk substitute and hydrogenated oil

Five multivitamin capsules (5.64 g) were taken in a beaker containing 25 mL of concentrated HNO_3 and digested by slowly increasing the temperature of the mixture to 120 °C. The mixture was further heated till a solid residue was obtained. It was allowed to cool and then 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 subsequently mixed with 50 mL of distilled water and concentrated HNO_3 was then added dropwise until a clear solution was obtained on gentle heating.

Powdered infant milk substitute sample (200 mg) was heated in a beaker containing mixture of concentrated H_2SO_4 (20 mL) and HNO_3 (10 mL) till 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.

Hydrogenated oil (2 g) was taken in a beaker and dissolved in 15 mL of concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 50 mL with deionized water after adjusting its pH to the optimum value.

2.3.4. Digestion of fish samples

A total of 10 fishes (10.13 cm length and weighing 35.70 ± 0.60 g each), common carbs (*Cyprinus carpio*) were caught from different locations of the river Ganga (Narora, Aligarh). Fish were dissected to separate organs (flesh, gills, liver and kidney) according to FAO methods [37]. The separated organs were put in Petri dishes to dry at 120 °C until a constant weight was reached. The separated organs were placed into digestion flasks and ultrapure concentrated nitric acid and hydrogen peroxide (1:1, v/v) was added. The digestion flasks were then heated to 130 °C until all the materials were dissolved. The digest was diluted with double distilled water (50 mL) for further experiments.

2.4. Functionalization of Amberlite XAD-4 resin

An amount of 5 g of air-dried Amberlite XAD-4 resin was pretreated with an ethanol–hydrochloric acid–water (2:1:1) solution for overnight and subsequently rinsed with triply distilled water until pH of the supernatant water became neutral so that it becomes free from any impurities. The resin beads were then subjected to modification by initially nitrating and then subsequently reducing to the amino compound. The amino compound was washed thoroughly with 2 mol 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 [38]. After amination, the subsequent steps were carried out at a temperature of 0–5 °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 coupling reaction by treating it with a solution of p-hydroxybenzoic acid (2.5 g) in 10% NaOH mixed with ethanol at a temperature as low as 0–5 °C over a period of 24 h. The final product was filtered off and thoroughly washed with 2 mol L^{-1} HCl and distilled water until free from alkali and acid. Finally, the functionalized resin (henceforth abbreviated as AXAD-4-HBA) was dried at 50 °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. Elemental analysis

The extent of the coupling reaction may be interpreted from the composition of the final resin. The total nitrogen content can give a good approximation of the quantity of p-HBA incorporated. Hence, the synthesized resin was subjected to elemental (CHN) analysis.

2.5.2. 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 °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 (1–10 mol L^{-1} of HCl or HNO_3) and alkaline solution (1–5 mol L^{-1} of NaOH) for 48 h and subsequently washed. The sorption capacity was later determined by the recommended batch method.

2.5.3. 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. 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 °C overnight and reweighed. The water regain value was calculated as: $W = (m_w - m_d)/m_d$, 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 °C overnight. For overall hydrogen ion capacity, an accurately weighed (0.5 g) resin was first treated with 4.0 mol L^{-1} HC1 and then filtered off, washed with distilled water to make it free from acid and dried at 100 °C for 5–6 h. The acidic form of the resin was equilibrated with 20.0 mL of 0.1 mol L^{-1} NaOH solution for 6 h at room temperature at stirring condition and then the excess alkali was estimated with 0.1 mol L^{-1} hydrochloric acid solution. In order to evaluate the contribution of both the carboxylic and the hydroxylic hydrogen ions 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 with suitable volume of metal solution of appropriate concentration maintained at constant pH for 2 h. The resin was filtered and the sorbed metal ions were desorbed by shaking with 2 mol L^{-1} HCl 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 (1 × 10 cm). 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 at an optimum flow rates after adjusting 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 2 mol L^{-1} HCl 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.

2.6.3. Column procedure for calibration and detection limit

The standard solutions for calibration, for each metal, were prepared in 100 mL by taking suitable aliquot of metal ions and buffer solutions, and then subjected to the recommended column procedure. A blank run was also performed applying recommended column procedure with the same volume of aqueous solution prepared by adding suitable buffer (excluding metal ions) and finally eluting the same in 5 mL before subjecting it to FAAS determination.

3. Results and discussion

3.1. Synthesis and characteristics of resin

The results of elemental analyses of the dried beads of AXAD-4-HBA (C, 62.96%; H, 4.86%; N, 9.82%) agree with the values calculated by presuming the stoichiometry of its repeat unit to be $C_{15}H_{12}N_2O_3{\cdot}H_2O$ (calculated: C, 62.94%; H, 4.89%; N, 9.79%). The nitrogen content of the nitrated resin and the subsequent reduced product was found to be 10.20% (7.28 mmol g^{-1}) and 13.00% (9.28 mmol g^{-1}), respectively.

In thermogravimetric analysis, the AXAD-4-HBA resin shows an earlier weight loss of 6.6% up to 170 °C. This initial step corresponds to the endothermic peak in the DTA curve and may be attributed to the loss of sorbed water molecule. The TGA and elemental analyses together suggest that at least one water molecules per repeat unit is sorbed. The subsequent exothermic peak corresponding to the weight loss of 13.42% up to 200 °C is observed for the modified resin. Thermal analysis indicated that the synthesized resin was stable up to 200 °C, above which degradation commences.

The IR spectrum of the modified resin AXAD-4-HBA was compared with that of untreated Amberlite XAD-4. The band at 3437 cm^{-1} may be assigned to the phenolic hydroxyl group, while the other three additional bands at 1631, 2926 and 1699 cm^{-1} may be due to azo (–N=N–) besides hydroxyl (–OH) and carboxy ($>$C=O) stretching vibrations of the carboxylic acid group, respectively. The IR spectrum of the metal ion-free chelating resin was compared with those of the metal ion-saturated resin. A red shift (2–5 cm^{-1}) in the bands of the azo group and the disappearance of the phenolic hydroxyl group in the metal ion-saturated AXAD-4-HBA suggest that chelation of metal ions through –OH and –N=N–(azo) groups is probably responsible for metal sorption.

After soaking the resin in mineral acids, such as HCl, HNO_3 and H_2SO_4, it showed no loss in sorption capacity up to strength of 5 mol L^{-1}. Again, after subjecting the resin to alkaline medium constituting 5 mol L^{-1} NaOH, there was no loss in the sorption capacity. Hence, the resin exhibited high chemical stability.

The water regain capacity was found to be 15.8 mmol g^{-1}. This value reflects the high hydrophilicity of the resin which is excellent for column operation. The overall hydrogen ion capacity amounts to 7.52 mmol g^{-1} of resin, which may be due to the hydrogen ions of the carboxyl and the hydroxyl groups constituting the molecule. Theoretically, if that 3.5 mmol of the reagent constitute per gram of the resin, the hydrogen ion capacity due to the carboxylic and the hydroxyl groups should be 7.0 mmol g^{-1}, which is in close agreement with the experimental value.

3.1.1. Effect of pH on sorption capacity

Optimum pH of metal ion uptake was determined by static method. Excess of metal ion (50 mL, 100 μg mL^{-1}) was shaken with 100 mg of resin for 120 min. The pH of metal ion solution was adjusted prior to equilibration over a range pH 2–10 with the corresponding buffer system. pH > 10 was not studied to avoid metal hydroxide precipitation. Preliminary experiments showed that the maximum sorption of Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) (Fig. 1) was observed at pH ranges of 10.0, 8.0–9.0, 7.0, 7.0–8.0 and 7.0–8.0, respectively. Hence, pH 7.0 was adjusted for Cu(II), Zn(II) and Pb(II) while pH 9.0 and pH 10 were adjusted for Ni(II) and Co(II), respectively, in all further experiments. The addition of 2–5 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 2.

Table 2
Kinetics and batch capacity of sorption of metal ions on AXAD-4-HBA (experimental conditions: 100 mL solution, 100 mg of resin).

Metal ion	Loading halftime $t_{1/2}$ (min)	Rate constant k ($\times 10^{-2}$ min^{-1})	Batch capacity (mmol g^{-1})
Co(II)	6	11.5	0.60
Ni(II)	8	8.6	0.55
Cu(II)	8	8.6	0.54
Zn(II)	8	8.6	0.12
Pb(II)	4	17.3	0.08

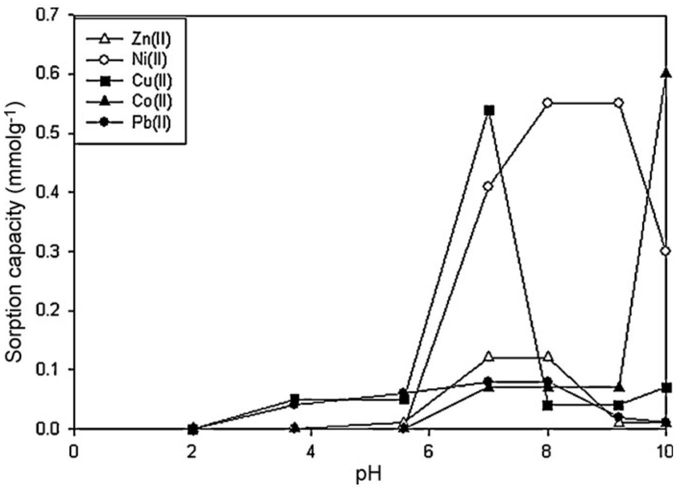

Fig. 1. Effect of sorption capacity on the pH. Experimental conditions: 50 mL solution, 100 μg mL^{-1}, 100 mg resin.

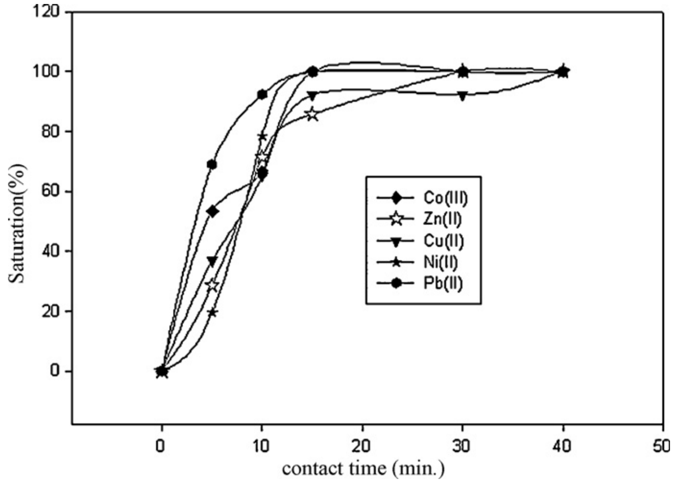

Fig. 2. Kinetic of sorption of metal ions on AXAD-4-HBA. Experimental conditions: 100 mL solution, 20 μg mL^{-1}, 100 mg resin.

3.1.2. *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 μg mL) at two different temperatures for 2, 5, 10, 20, 30,40, 60, 80, 100 and 120 min (under the optimum conditions). The loading half time needed to reach 50% of the total loading capacity was estimated from Fig. 2. The loading half time ($t_{1/2}$) values (Table 2) for all the metals are ≤8 min that reflects its superiority over previously reported methods [28,29]. The profile of metal ion uptake on these resins reflects good accessibility of the chelating sites in the resin. From the kinetics of sorption for each metal (Fig. 2), it was observed that 15–30 min was enough for the sorbent to reach the saturation level for all the metals. Considering the Brykina method [9] the sorption rate constant, k can be calculated using the following equation: $-\ln(1-F)=kt$, where $F=Q_t/Q$ and Q_t is the sorption amount at sorption time t and Q the sorption amount at equilibrium. 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 2).

3.1.3. *Effect of flow rate for sorption and elution*

The effect of flow rate on the sorption was studied by varying the flow rate 2–8 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 or lower than 5 mL min^{-1}. The flow rates less than 2.0 mL min^{-1} were not studied to avoid long analyses times. Hence, a flow rate of 4.5 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.

3.1.4. *Type of eluting agents and resin reusability test*

Recovery studies were performed with different mineral acids namely H_2SO_4, HCl and HNO_3. The efficiency of stripping was studied by using different volumes (1–10 mL) and concentrations (0.1–5.0 mol L^{-1}) of the mineral acids. Among the acids, H_2SO_4 and HNO_3 could give a maximum recovery of 90% and 95%, respectively, when a maximum of 10 mL (5.0 mol L^{-1}) each were used. When 10 mL of 2 mol L^{-1} HCl was used, almost complete desorption (recovery >99%) was observed. The efficacy of the eluent (2 mol L^{-1} HCl) was studied taking its different volumes (1–10 mL). It was found that 3–5 mL of acid was sufficient for quantitative recovery (>99%) of the metal ions from the resin. Therefore, 5 mL of 2 mol L^{-1} HCl was used for elution in all the further studies.

The resin was subjected to several loading and elution cycles by the dynamic method. The low concentration of the eluent acid prevents any leaching and thus contributes to the sustainability of the resin. The resin cartridge can be regenerated fully up to 50 cycles. Therefore, multiple use of the resin is feasible. Similar results are shown by batch method also.

3.1.5. *Study of interferences*

Various cations and anions, which are inevitably associated with heavy metals, may interfere in the latter's determination through precipitate formation, redox reactions, or competing complexation reactions. Common chemical species such as sodium citrate, sodium tartrate, sodium oxalate, humic acid, fulvic acid, $(NO_3)^{2-}$, $(CO_3)^{2-}$, $(NH_4)^{+}$, $SO_4{}^{2-}$, $PO_4{}^{2-}$, Cl^-, K^+ and Na^+ were checked for any interference in the sorption of these metals. The effect of humic substances on metal-collection was examined because both humic and fulvic acids are generally present in natural waters at μg mL^{-1} to ng mL^{-1} levels and form complexes with various heavy metals [39–41]. Very few literatures [42,43] have considered the interference of these humic substances on the preconcentration of trace metal ions from natural waters. 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 μg L^{-1}) equilibrated individually with 100 mg of resin with varying amounts of electrolyte or metal ions till 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 and cations, which are inevitably associated with metal ions present at the trace level in all natural waters, produce no interference in the sorption of the heavy metals up to appreciable concentrations (Table 3). The use of buffer solutions does not interfere in the preconcentration of metal ions. A relative error of less than 5% was considered to be within the range of experimental error.

3.1.6. *Adsorption isotherm*

For an adsorption column, the column resin (the stationary phase) is composed of microbeads. Each binding particle that is attached to the microbead can be assumed to bind in a 1:1 ratio with the solute sample sent through the column that needs to be purified or separated. At the concentration range ($1.5–10.0 \times 10^{-4}\,g\,L^{-1}$) studied for Co(II), Ni(II), Cu(II), Zn(II), and Pb(II), the data were successfully applied for the Langmuir isotherm. The Langmuir model assumes that sorption occurs on defined sites of the sorbent with no interaction between the sorbed species and that each site can accommodate only one molecule (monolayer adsorption) with the same enthalpy sorption, independent of surface coverage. Therefore, considering the surface coordination reaction below:

$$X + C_e \leftrightarrow Q_e \tag{1}$$

where X is an adsorptive site on the AXAD-4-HBA, C_e is the equilibrium concentration of metal ions in the aqueous phase ($mol\,L^{-1}$) and XC is the surface density that can also be represented as the equilibrium concentration of metal in the solid phase, Q_e ($mol\,g^{-1}$). The mass law for this reaction is:

$$b = \frac{XC}{C_e X} \tag{2}$$

where the constant b or adsorption coefficient is related to the binding energy of the solute and adsorption enthalpy. The mass balance for X can be expressed as: KS = X + XC. Therefore, at high C_e, KS represents the saturation of the AXAD-4-HBA (Q_m = KS) with a monolayer coverage of metal ions. Appropriate substitution and rearrangement of Eqs. (1) and (2) leads to the linearized form of Langmuir isotherm in equation represented by the following equation [44].

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

Here, C_e is the equilibrium concentration ($mg\,L^{-1}$), Q_e is the amount adsorbed at equilibrium ($mg\,g^{-1}$) and Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear isotherm occurs when the solute concentration needed to be purified is very small relative to the binding molecule of the solid phase. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms (Fig. 3). The values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 4. From the values of adsorption efficiency, Q_m we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. To confirm the favorability of the adsorption process, the separation factor (R_L) is calculated and presented in Table 4. The values were found to be between 0 and 1 which confirm that the ongoing adsorption process is favorable [44].

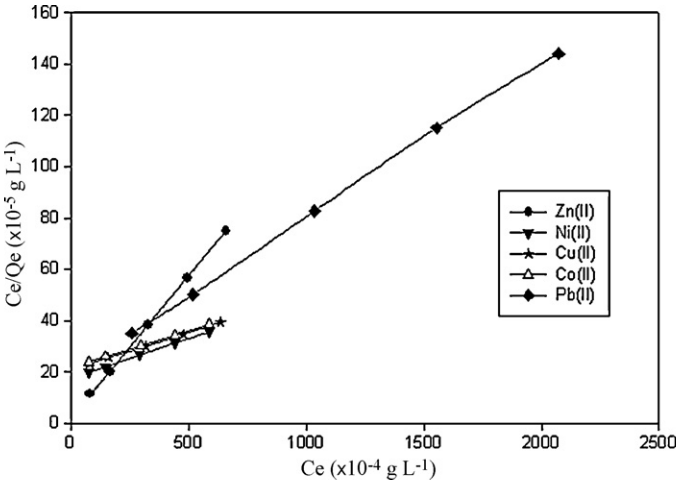

Fig. 3. Langmuir sorption isotherms depicting the sorption behaviour of metal ions onto AXAD-4-HBA. Column parameters: sorption flow rate $4.5\,mL\,min^{-1}$, 0.5 g resin.

3.1.7. *Preconcentration factor and breakthrough capacity*

The lower limit of quantitative preconcentration below which recovery becomes non-quantitative (preconcentration limit) was determined by increasing the volume of metal ion solution and keeping the total amount of loaded metal ion constant at 10 μg. The maximum preconcentration factors achieved for Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) are 460, 460, 460, 360, and 260, respectively with the corresponding preconcentration limit of 4.3, 4.3, 4.3, 5.5, and 7.6 $\mu g\,L^{-1}$, respectively. The maximum volumes of metal ion solution from which quantitative recoveries (>99%) of metal can be made into 5 mL of $2\,mol\,L^{-1}$ HCl are reported in Table 5. The breakthrough volume, which corresponds to the volume at which the effluent concentration of any chemical species from the column is about 3–5% of the influent concentration, was determined by applying the recommended procedure to 1500–2500 mL

Table 4
Langmuir isotherm constants for sorption of metal ions on AXAD-4-HBA.

Metal ions	R_L	b ($L\,mg^{-1}$)	Q_m ($mg\,g^{-1}$)	R^2	Standard deviation (n = 5)
Co(II)	0.999	0.00129	35.36	0.99993	0.07923
Ni(II)	0.999	0.00177	32.28	0.99988	0.11595
Cu(II)	0.999	0.00139	34.32	0.99992	0.09491
Zn(II)	0.999	0.05887	7.85	0.99998	0.20084
Pb(II)	0.999	0.00308	16.58	0.99993	0.61709

Table 3
Tolerance limit of foreign species (in binary mixtures) on sorption of metal ions (experimental conditions: 100 mL solution, $10\,\mu g\,L^{-1}$ of metal ion, 100 mg of resin).

Foreign species	Tolerance ratio [foreign species ($\mu g\,L^{-1}$)/metal ion ($\mu g\,L^{-1}$)]				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Pb(II)
Na^+ (NaCl)	3.32×10^6	3.32×10^6	2.32×10^6	1.83×10^5	1.83×10^5
K^+ (KCl)	3.31×10^6	3.31×10^6	2.31×10^6	1.12×10^6	1.12×10^6
NH_4^+ (NH_4Cl)	2.21×10^6	2.21×10^6	1.21×10^6	1.12×10^6	1.12×10^6
Cl^- (NaCl)	4.12×10^6	4.12×10^6	3.12×10^6	1.57×10^6	1.57×10^6
SO_4^{2-} (Na_2SO_4)	4.08×10^6	4.08×10^6	4.08×10^6	3.12×10^6	3.12×10^6
NO_3^- ($NaNO_{3)}$	4.12×10^6	4.12×10^6	4.12×10^6	3.42×10^6	3.42×10^6
PO_4^{3-} (Na_3PO_4)	6.67×10^5	6.67×10^5	6.67×10^5	3.31×10^5	3.31×10^5
CO_3^{2-} (Na_2CO_3)	2.65×10^6	2.65×10^6	2.65×10^6	1.45×10^6	1.45×10^6
Citrate (sodium citrate)	2.59×10^4	2.59×10^4	1.59×10^4	1.93×10^4	1.93×10^4
Oxalate ($Na_2C_2O_4$)	6.59×10^3	6.59×10^3	1.59×10^3	3.54×10^3	3.54×10^3
Tartrate (NaK tartrate)	7.23×10^3	7.23×10^3	2.23×10^3	2.25×10^3	2.25×10^3
Fulvic acid	83	83	20	35	35
Humic acid	145	145	45	85	75
CH_3COO^- (CH_3COONa)	7.21×10^5	7.21×10^5	2.21×10^5	3.34×10^5	3.34×10^5
Ca^{2+} ($CaCl_2$)	7.43×10^5	7.43×10^5	4.43×10^5	4.38×10^5	4.38×10^5
Mg^{2+} ($MgCl_2$)	7.83×10^5	7.83×10^5	3.83×10^5	5.10×10^5	5.10×10^5

Table 5
Preconcentration and breakthrough profiles of metal ions on p-HBA functionalized resin. Column parameters: sorption flow rate 4.5 mL min^{-1}, elution flow rate 2 mL min^{-1}, 0.5 g of resin.

Metal ions	Preconcentration studies			Breakthrough studies			
	Total volume (mL)	Preconcentration limit (μg L^{-1})	Preconcentration factor	Overall sorption capacity (mmol g^{-1})	Breakthrough capacity (mmol g^{-1})	Breakthrough volume (mL)	Degree of column utilization
Co(II)	2300	4.3	460	0.60	0.46	1950	0.77
Ni(II)	2300	4.3	460	0.55	0.43	1950	0.78
Cu(II)	2300	4.3	460	0.54	0.42	1950	0.78
Zn(II)	1800	5.5	360	0.12	0.09	1500	0.75
Pb(II)	1300	7.6	260	0.08	0.06	1200	0.75

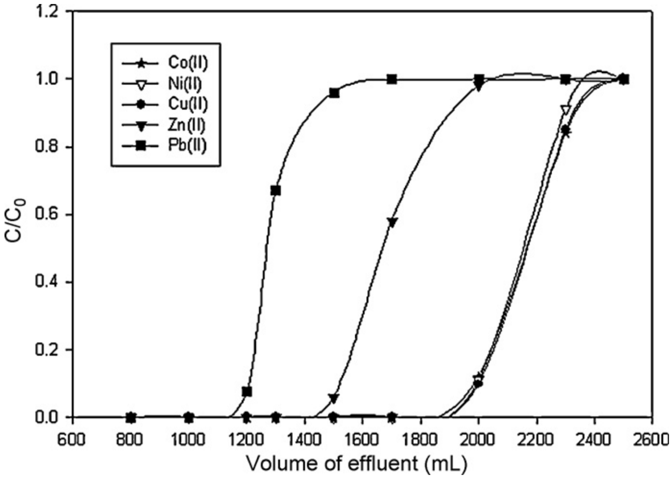

Fig. 4. Breakthrough curves for the preconcentration of metal ions. Column parameters: sorption flow rate 4.5 mL min^{-1}, 0.5 g resin.

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 the degree of utilization was determined by the literature method [45]. The total sorption capacity calculated on the basis of total saturation volume was compared with the corresponding breakthrough capacities (Fig. 4) for each metal. Since dynamic capacity gives the working capacity for column operation, therefore, the closeness of the dynamic capacity to the total sorption capacity and the high preconcentration factors (Table 5) reflect the applicability of the column technique for preconcentration. The hydrophilic character of this resin plays a major role in enhancing the preconcentration factor as it facilitates faster attainment of equilibrium between the solid and the aqueous phase.

3.2. Analytical figures of merit including precision, validation and detection limit

The quantitative recovery of the metal ions is possible from trace level as reflected by the lower limit of preconcentration for large volumes as given in Table 5. From the Langmuir isotherm, the regression coefficient (R^2) and the separation factor (R_L) were found to be $0.99 < R^2 < 1.0$ and $0 < R_L < 1.0$ for each metal suggesting the favorability of its sorption from aqueous medium.

The validity of the results was tested by standard addition method, by spiking a known amount (5 μg) of individual metal ions to the water samples. The results pertaining to the analysis of trace amount of metal ion of interest confirms the satisfactory recovery of the analytes. The close agreement of the results found by direct (applying the recommended procedure without spiking) with that found by S.A. (standard addition after spiking) method (Table 6) indicates the reliability of the present method for metal analyses in water samples of various matrices without significant interference.

The accuracy of the present method was evaluated from the results of the analysis of various SRMs including environmental, biological and alloy samples. The mean concentration values of the metals studied agreed with the certified values. Calculated Student's *t* (*t*-test) values for respective metal ions were found to be less than critical Student's *t* values (2.78, $n = 5$) at 95% confidence

Table 6
Preconcentration and determination of metal ions in natural waters collected from various locations. Experimental conditions: 100 mL solution, sorption flow rate 4.5 mL min^{-1}, elution flow rate 2 mL min^{-1}, 0.2 g resin.

Samples	Method	Metal ion found by proposed method (μg L^{-1}) ± standard deviation[a] (%recovery of the spiked amount)				
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Pb(II)
Canal water (Kasimpur)	Direct[b]	4.3 ± 0.11	4.7 ± 0.06	12.9 ± 0.15	6.2 ± 0.22	–
	S.A.[c]	4.3 ± 0.12 (100.0)	4.6 ± 0.10 (97.9)	12.9 ± 0.21 (100.0)	6.4 ± 0.15 (103.2)	2.1 ± 0.07 (100.0)
Tap water (AMU Campus, Aligarh)	Direct	6.9 ± 0.20	5.7 ± 0.1	10.3 ± 0.25	9.9 ± 0.34	8.8 ± 0.25
	S.A.	7.0 ± 0.27 (101.4)	5.7 ± 0.12 (100.0)	10.4 ± 0.36 (100.9)	9.9 ± 0.36 (100.0)	8.8 ± 0.20 (100.0)
Sewage water (Ni plating industrial area, Aligarh)	Direct	5.5 ± 0.16	12.6 ± 0.40	8.2 ± 0.25	7.7 ± 0.25	5.4 ± 0.19
	S.A.	5.6 ± 0.21 (101.8)	12.6 ± 0.35 (100.0)	8.2 ± 0.26 (100.0)	7.7 ± 0.30 (100.0)	5.5 ± 0.25 (101.8)
River water, The Ganga (Narora)	Direct	4.2 ± 0.15	4.9 ± 0.13	13.0 ± 0.42	10.1 ± 0.42	–
	S.A.	4.2 ± 0.09 (100.0)	5.0 ± 0.19 (102.0)	13.1 ± 0.42 (100.8)	10.2 ± 0.45 (100.9)	3.2 ± 0.14 (100.0)

'–' indicates not detected.
[a] Average of five determinations.
[b] Recommended procedure applied without spiking.
[c] Recommended procedure after spiking (standard addition method).

Table 7
Analysis of standard reference materials for metal ion contents. Column parameters: sorption flow rate 4.5 mL min^{-1}, elution flow rate 2 mL min^{-1}, 0.2 g of resin.

Samples	Certified value (μg g^{-1})	Found by proposed method (μg g^{-1})[a]	Calculated Student's *t* value[b]
Vehicle exhaust particulates NIES 8 [c]	Co: 3.3, Cu: 67, Ni: 18.5, Pb: 219.0, Zn: 1040	Co: 3.2 ± 0.14, Cu: 65.9 ± 1.85, Ni: 18.3 ± 0.33, Pb: 217.1 ± 3.26, Zn: 1034.9 ± 11.38	1.87, 1.34, 1.29, 1.32, 1.01
Pond sediment NIES 2	Zn: 343.0, Ni: 40.0, Co: 27, Cu: 210.0	Zn: 340.9 ± 4.09, Ni: 39.0 ± 1.25, Co: 25.9 ± 1.22, Cu: 208.6 ± 2.50	1.15, 1.75, 2.04, 1.20
Chlorella NIES 3	Zn: 20.5, Cu: 3.5, Co: 0.87, Pb: 0.60	Zn: 19.9 ± 0.84, Cu: 3.4 ± 0.14, Co: 0.9 ± 0.01, Pb: 0.6 ± 0.03	1.72, 1.73, 1.62, 1.61
Human hair NIES 5[c]	Zn: 169.0, Cu: 16.3, Ni: 1.8, Pb: 6.0	Zn: 167.9 ± 2.01, Cu: 15.9 ± 0.72, Ni: 1.7 ± 0.08, Pb: 5.8 ± 0.25	1.28, 1.95, 1.54, 1.93
Tea leaves NIES 7[c]	Zn: 33.0, Cu: 7.0, Ni: 6.5	Zn: 31.7 ± 1.43, Cu: 6.8 ± 0.29, Ni: 6.4 ± 0.16	2.05, 1.89, 1.54
Rompin hematite, JSS (800-3)[d]	Cu: 640.0, Zn: 1030.0, Pb: 210.0	Cu: 631.1 ± 11.36, Zn: 1018.0 ± 16.29, Pb: 207.4 ± 4.56	1.75, 1.65, 1.15
Zinc base die-casting alloy C NBS 627[e]	Cu: 1320.0, Pb: 82.0, Ni: 29.0	Cu: 1310.4 ± 14.41, Pb: 80.9 ± 1.86, Ni: 27.9 ± 1.31	1.48, 1.33, 1.89

[a] x ± standard deviation, $n = 5$.
[b] At 95% confidence level.
[c] National Institute of Environmental Studies (NIES).
[d] Iron and Steel Institute of Japan (JSS).
[e] National Bureau of Standards (NBS).

level (Table 7). 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 Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) taken in 100 mL (eluted in 5 mL of 2 mol L^{-1} HCl) were performed following the recommended procedure. The relative standard deviations (RSD) for the observed values were found to be below 5%.

The calibration curves were found to be linear over the concentration ranges 0.0035–0.750, 0.005–1.000, 0.0035–0.500, 0.005–0.010, and 0.0075–1.500 μg mL^{-1} for Co(II), Ni(II), Cu(II), Zn(II) and Pb(II), respectively when the standard solutions were prepared in 100 mL. The regression equations and correlation coefficients (r^2), obtained by the method of least squares, were $A = 0.0024C + 0.0008$ ($r^2 = 0.9968$), $A = 0.0595C + 0.0042$ ($r^2 = 0.9989$), $A = 0.0834C + 0.0003$ ($r^2 = 0.9979$), $A = 0.1046C + 0.0028$ ($r^2 = 0.9995$) and $A = 0.0173C + 0.0228$ ($r^2 = 0.9997$) for Co(II), Ni(II), Cu(II), Zn(II) and Pb(II), respectively, where A is the absorbance and C is the metal ion concentration (μg mL^{-1}). The linearity of the calibration curves is apparent from the correlation coefficients (r^2) which lie well above 0.99.

The detection limit evaluated as three times the standard deviation (s) of the blank signal along with the mean blank signals (absorbance) for 15 replicate measurements were found to be 0.47 (0.0007), 0.45 (0.0019), 0.50 (0.0013), 0.80 (0.0021), 1.37 (0.005) μg L^{-1} for Co(II), Ni(II), Cu(II), Zn(II) and Pb(II), respectively.

4. Applications

4.1. Determination of Co(II), Ni(II), Cu(II), Zn(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 of each of the sample volume was adjusted to optimum pH by adding appropriate buffer system and loaded on to the column of AXAD-4-HBA. The concentrations of metal ions were determined by following recommended method using FAAS (direct method). Recoveries of metal ions were ascertained by measuring the recovery of standard additions from various real water (500 mL) samples which were spiked with metal ions of concentrations guided by middle value of preconcentration limit and maximum concentration of working range of calibration curve of FAAS in order to ensure complete sorption and avoid dilution of the final eluate during determination. The concentrations reported in Table 6 as estimated by S.A. method are the values obtained by substracting the amount of metal added for spiking from the total metal recovered. It was found that the mean percentage recoveries of all the metal ions studied were 98–100% at 95% confidence level. Table 6 illustrates the results.

Table 8
Analysis of common carbs (*Cyprinus carpio*) for metal content. Experimental conditions: 50 mL solution, sorption flow rate 4.5 mL min^{-1}, 0.2 g resin.

Metal ions	Muscles (μg g^{-1})[a]	Livers (μg g^{-1})[a]	Gills (μg g^{-1})[a]
Cu(II)	0.112 ± 0.004	0.263 ± 0.009	0.523 ± 0.018
Zn(II)	1.211 ± 0.031	2.168 ± 0.048	2.784 ± 0.064
Ni(II)	0.090 ± 0.002	0.126 ± 0.002	0.110 ± 0.003
Pb(II)	0.124 ± 0.004	0.102 ± 0.003	0.179 ± 0.007

[a] X ± standard deviation.

Table 9
Determination of metal ions in multi-vitamin capsule, infant milk substitute and hydrogenated oil. Experimental conditions: 50 mL solution, sorption flow rate 4.5 mL min^{-1}, 0.2 g resin.

Samples	Reported value (μg g^{-1})	Found by proposed method (μg g^{-1}) ± standard deviation[a]
Maxirich (Cipla)	Cu: 398.2, Zn: 442.5	Cu: 395.4 ± 13.05, Zn: 438.6 ± 9.65
Lactogen 1 (Nestle)	Cu: 2.9, Zn: 37.0	Cu: 2.8 ± 0.05, Zn: 35.8 ± 1.04
Vanaspati ghee	Ni: 0.45	Ni: 0.4 ± 0.009

[a] Average of five determinations.

4.2. Analysis of metal ions in standard reference materials

The SRMs namely NIES 2, NIES 3, NIES 5, NIES 7, NIES 8, JSS (800-3) and NBS 627, after digestion by the recommended procedures, were employed for the recovery studies. Proper pH adjustment of the solutions (50 mL each) was made before performing the recommended column procedure. Table 7 illustrates the results.

4.3. Analysis of multivitamin capsules, infant powdered food, hydrogenated oil and Cyprinus carpio

Multivitamin capsules, IMS, hydrogenated oil and *Cyprinus carpio* were subjected to preconcentration according to the recommended column procedure after their pretreatment (digested in 50 mL). The results (Tables 8 and 9) show that recovery could be made with a good precision of RSD < 5%.

5. Conclusion

p-Hydroxybenzoic groups immobilized on Amberlite XAD-4 resin can easily be used to separate heavy metal ions from aqueous solutions. AXAD-4-HBA has a higher sorption capacity which is superior in comparison to 1-(2-pyridylazo)-2-naphthol [46,47], salicylic acid [32], pyrocatechol violet [48] loaded Amberlite XAD-2; 2-acetylmercaptophenyldiazo-aminoazobenzene (AMPDAA) [49] and dithiocarbamates [53] loaded Amberlite XAD-4. The relatively high chemical stability of AXAD-4-HBA in water, as well as the fast kinetics whereby heavy ions can be separated, renders this material potentially useful for analytical purposes. The rate constant is higher than most of the previously reported works [46–49,51–53]. Moreover, the use of a column preconcentration technique allows for the assessment of low trace metal concentrations, even by less sensitive determination methods such as FAAS. Preconcentration by this material (AXAD-4-HBA) from river water samples does not require any prior digestion of the samples. The preconcentration factor achieved with the present procedure is higher than that obtained with other chelating resins [28,32,46–53]. Quantitative preconcentration of analytes could be affected even in the presence of common inorganic or organic matrix components as revealed by the interference studies. The tolerance limits of the investigated foreign species are much higher than most of the reported sorbents [46–50].

References

[1] J.O. Nriagu (Ed.), Changing Metal Cycles and Human Health, Springer-Verlag, Heidelberg, 1984, p. 445.
[2] L.W. Chang, L.G. Cockerham, in: L.G. Cockerham, B.S. Shane (Eds.), Basic Environmental Toxicology, CRC Press, Florida, 1986, pp. 121–128.
[3] U. Ewers, H.W. Schlipkoter, in: E. Merian (Ed.), Metals and their Compounds in the Environment, VCH, Weinheim, 1991, p. 971.
[4] H. Hu, Harrison's Principles of Internal Medicine, vol. 2, 16th edition, McGraw-Hill, Medical Publishing Division, New York, 2005, pp. 2577.
[5] Y.H. Sung, S.D. Huang, Anal. Chim. Acta 495 (2003) 165–176.
[6] A. Sabarudin, N. Lenghor, M. Oshima, L. Hakim, T. Takayanagi, Y.H. Gao, S. Motomizu, Talanta 72 (2007) 1609–1617.
[7] J. Chen, K.C. Teo, Anal. Chim. Acta 450 (2001) 215–222.
[8] S.Q. Memon, M.I. Bhanger, S.M. Hasany, M.Y. Khuhawar, Talanta 72 (2007) 1738–1745.
[9] S. Pramanik, S. Dhara, S.S. Bhattacharyya, P. Chattopadhyay, Anal. Chim. Acta 556 (2006) 430–437.
[10] K. Pyrzynska, M. Trojanowicz, Crit. Rev. Anal. Chem. 29 (1999) 313–321.
[11] C.J. Kantipuly, S. Katragadda, A. Chow, H.D. Gesser, Talanta 37 (1990) 491–497.
[12] S. Nabi, A. Alim, A. Islam, M. Amjad, J. Sep. Sci. 28 (2005) 2463–2467.
[13] T.P. Rao, R.S. Praveen, S. Daniel, Crit. Rev. Anal. Chem. 34 (2004) 177–193.
[14] S.K. Sahni, J. Reedijk, Coord. Chem. Rev. 59 (1984) 1–139.
[15] D. Bilba, D. Bejan, L. Tofan, Croat. Chem. Acta 71 (1998) 155–178.
[16] R.A. Beauvais, S.D. Alexandratos, React. Funct. Polym. 36 (1998) 113–123.
[17] D.J. Bartkowiak, React. Funct. Polym. 62 (2005) 115–128.
[18] J. Kramer, A. Scholten, W.L. Driessen, J. Reedijk, Inorg. Chim. Acta 315 (2001) 183–190.
[19] Y.A. Zolotov, N.M. Kuzmin, in: G. Svehla (Ed.), Wilson and Wilson's Comprehensive Analytical Chemistry, Elsevier, Amsterdam, 1990, pp. 372.
[20] A. Mizuike, Enrichment Techniques for Inorganic Trace Analysis, Springer-Verlag, 1983, p. 17.
[21] F.E. Beamish, The Analytical Chemistry of the Noble Metals, Pergamon Press, Oxford/London/Edinburgh/New York/Toronto/Paris/Frankfurt, 1966, p. 41.
[22] G. Venkatesh, A.K. Jain, A.K. Singh, Microchim. Acta 149 (2005) 213–221.
[23] P.K. Tewari, A.K. Singh, Fresen. J. Anal. Chem. 367 (2000) 562–567.
[24] D. Prabhakaran, M.S. Subramanian, Anal. Bioanal. Chem. 379 (2004) 519–525.
[25] L. Elçi, M. Soylak, A. Uzun, E. Büyükpatır, Fresen. J. Anal. Chem. 368 (2000) 358–361.
[26] N. Ulrich, Anal. Chim. Acta 359 (1998) 245–253.
[27] A. Sabarudin, M. Oshima, T. Takayanagi, L. Hakim, K. Oshita, Y.H. Gao, S. Motomizu, Anal. Chim. Acta 581 (2007) 214–220.
[28] S.D. Çekiç, H. Filik, R. Apak, Anal. Chim. Acta 505 (2004) 15–24.
[29] R.K. Sharma, P. Panta, J. Hazard. Mater. 163 (2009) 295–301.
[30] G. Venkatesh, A.K. Singh, Talanta 71 (2007) 282–287.
[31] G. Venkatesh, A.K. Singh, Talanta 67 (2005) 187–194.
[32] R. Saxena, A.K. Singh, D.P.S. Rathore, Analyst 120 (1995) 403–405.
[33] G.R. De Castroa, I.L. de Alcântaraa, P.S. Roldana, D.F. Bozanob, P.M. Padilhab, A.O. Florentinob, J.C. Rochaa, Groups Mater. Res. 7 (2004) 329–334.
[34] D. Prabhakaran, M.S. Subramanian, Talanta 61 (2003) 431–437.
[35] F.J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic Acid, Van Nostrand Company, London/New York, 1958.
[36] J. Kubova, V. Hanakova, J. Medved, V. Stresko, Anal. Chim. Acta 337 (1997) 329–334.
[37] B. Dybem, FAO Fish. Tech. 212 (1983) 1–13.
[38] M. Kumar, D.P.S. Rathore, A.K. Singh, Talanta 51 (2000) 1187–1196.
[39] W.S. Gardner, P.F. Landrum, in R.F. Christman, E.T. Gjessing (Eds.), Aquatic and Terrestrial Humic Materials, Ann Arbor Science, Ann Arbor, MI, pp. 203–217.
[40] J. Buffle, R.S. Altmann, M. Filella, Anal. Chim. Acta 232 (1990) 225–237.
[41] S.D. Khattri, M.K. Singh, Indian J. Chem. Technol. 6 (1999) 112–116.
[42] M.D.G. Castro, M.D.G. Riaño, M.G. Vargas, Spectrochim. Acta B 59 (2004) 577–583.
[43] Y. Liu, Y. Guo, S. Meng, X. Chang, Microchim. Acta 158 (2007) 239–245.
[44] I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[45] F. Helfferich, Ion Exchange, McGraw Hill, New York, 1962, p. 424.
[46] P.B. Barrera, M.A. Nancy, D.L. Cristina, B.B. Adela, Microchim. Acta 142 (2003) 101–108.
[47] S.L.C. Ferreira, C.F. Brito, A.F. Dantas, N.M.L. Araujo, A.C.S. Costa, Talanta 48 (1999) 1173–1177.
[48] V.A. Lemos, D.G.D. Silva, A.L.D. Carvalho, D.A. Santana, G.S. Novaes, A.S. Passos, Microchem. J. 84 (2006) 14–21.
[49] Y. Liu, Y. Guo, X. Chang, S. Meng, D. Yang, B. Din, Microchim. Acta 149 (2005) 95–101.
[50] M. Tuzen, I. Narin, M. Soylak, L. Elci, Anal. Lett. 37 (2005) 473–489.
[51] S. Tokalioglu, S. Kartal, Microchim. Acta 162 (2008) 87–92.
[52] P.K. Tewari, A.K. Singh, Talanta 56 (2002) 735–744.
[53] A. Ramesh, K.R. Mohan, K. Seshaiah, Talanta 57 (2002) 243–252.