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Use of 2-hydroxy-3-methoxybenzaldehyde functionalized amberlite xad-16 for preconcentration and determination of trace metal ions by flame atomic absorption spectrometry

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ABSTRACT

In this work, a styrene-divinylbenzene based resin has been functionalized with 2-Hydroxy-3-methoxybenzaldehyde with the objective of employing it for the preconcentration of Zn(II), Cu(II), Ni(II), Cd(II), and Pb(II) contained in trace amount in various matrices. The optimum pH range for the maximum sorption of Zn(II), Cu(II), Ni(II), Cd(II), and Pb(II) was observed at pH 5.5-9.0, with the half-loading time, $t_{1/2}$, ranging from 5 to 13.7 min. The sorption of these metal ions in presence of potentially interfering matrices (including naturally occurring chelating agents) was investigated. The synthesized resin was able to preconcentrate metal ions at concentration as low as 5.55-8.33 $\mu\text{g L}^{-1}$, thereby resulting in the preconcentration factor in range of 240-360. The results favour the applicability of this method for the simultaneous preconcentration and determination of all the metal ions constituting complex matrices. The method has been successfully applied to the determination of the heavy metals in natural waters as well as food samples.

Keywords: Amberlite XAD-16, Chelating resin, Trace metal ions, Kinetic parameter, Preconcentration

INTRODUCTION

With the growing industrialization and urbanization from the last few decades, a large amount of heavy metal has been exposed to the environment. The toxicity of these heavy metals is widely recognized due to their adverse effects upon human health. Hence monitoring of their concentration is an important task in order to sustain and preserve our ecosystem [1, 2].

Various methods have been employed for the trace determination of metal ions in different samples including flame atomic absorption spectrometry (FAAS) [3,4], electrothermal atomic absorption spectrometry (ETAAS) [5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6], inductive couple plasma atomic emission spectroscopy (ICP-AES) [7], inductively coupled plasma mass spectroscopy (ICP-MS) [8] and stripping voltammetry [9]. However, the direct determination of metal ions by these instruments still faces challenges posed by the low concentration and the associated complex matrices. Usually, a preconcentration step, as well as separation step, is required prior to metal analysis by these instruments [10]. For this purpose, numerous separation and preconcentration procedures have been developed for trace metal ion determination in various matrices.

Multidentate chelating resins with hydrophilic character are receiving widespread acclaim for their salient features like selectivity to bind metal ions over a wide pH range, high preconcentration factor and recovery, rapid phase separation, low cost, easy regeneration for multiple quantitative sorption–desorption cycles and good reproducibility in the sorption characteristics and the ability of combination with different detection techniques with on-line or off-line mode [11, 12]. The selective removal of toxic metal ions and recovery of precious metal ions in terms of environmental protection and economic consideration are of great significance. Various type of solid support, such as Amberlite XAD resins [13, 14], activated carbon [15], polyurethane foam [16], Amborsorb [17], and silica gel [18], have been used to preconcentrate trace metal ions from various media. However, the basic disadvantage of the solid sorbents is the lack of metal selectivity, which leads to high interference of other existing species with the analyte metal ion [19]. To overcome this problem, a chemical and physical modification of the sorbent surface with some organic moieties or complexing or chelating agents before the sorption procedure, is usually used. Chelating resin in which a chelating agent is bonded chemically is so stable that it can be used repeatedly. However, its sorption capacity to metal ions is not high because of the steric effect of the chelating agent [20]. Enhancement of the sorption capacity of chelating resin can be achieved by increasing the number of chelating sites on the resin as well as their accessibility. This can be obtained by using a resin which has a relatively high surface area and by selecting a chelating agent of small molecular size [21]. Among all of the solid support materials, the use of Amberlite XAD-16 resins, with its superior physical properties such as high surface area, porosity, uniform pore size distribution and chemical stability over other Amberlite XAD series resins [22, 23], has gained popularity as the polymeric support for the immobilization of chelating ligand of small molecular size. Recently, 2-Hydroxy-3-methoxybenzaldehyde (HMBA) were used as multidentate ligand which has three oxygen donor atoms, which exhibit suitable relative positions to coordinate metal ions [24].

Therefore, it was thought worthwhile to functionalize Amberlite XAD-16 via azo spacer with HMBA (2-Hydroxy-3-methoxybenzaldehyde) so as to develop a method for the preconcentration and separation of trace metal ions from matrix constituents of real samples such as environmental water, industrial effluents, multivitamin tablets, Infant milk substitute, and SRM samples.

MATERIALS AND METHODS

2.1. Instruments

A GBC 932+ (Dandenong, Australia), flame atomic absorption spectrometer (FAAS) was used for determining metal concentration. The wavelengths (slit widths) used for Zn(II), Cu(II), Ni(II), Cd(II) and Pb(II) were 213.9 (0.5), 324.8 (0.5), 232.0 (0.2), 228.8 (0.5) and 283.3 (0.5) nm (nm) respectively, while maintaining the lamp current at 5.0, 3.0, 4.0, 3.0 and 5.0 mA, respectively. An ELICO (Hyderabad, India) digital pH meter (LI-120) was used for pH measurements. A thermostated mechanical shaker (Scientific, New Delhi, India) at 200 strokes min⁻¹ was used for carrying out equilibrium studies. Infrared (IR) spectra were recorded on a FT-IR Spetrometer- Interspec 2020, (Spectro Lab.,UK) using KBr disc method. Shimadzu thermal analyzer was used for the thermogravimetric analysis (TGA) and differential thermal analysis (DTA). CHN analysis was carried out on Carlo Erba EA1108 elemental analyzer in Sophisticated Analytical Instrument Facility of Central Drug Research Institute (Lucknow, India). A column (1x 10 cm), for dynamic studies, was obtained from J-SIL Scientific industries, Agra, India.

2.2. Reagents and solutions

All solutions were prepared in doubly distilled water. Stock solutions of nitrate salts of Zn(II), Cu(II), Ni(II), Cd(II) and Pb(II) (supplied by Central Drug House (P) Ltd., New Delhi) at the concentration of 1000 µg mL⁻¹ in 1% HNO₃ were standardized by complexometric titration [25] before use. The working solutions of the metals were prepared by appropriately diluting the stock solutions. Buffer solutions were used for pH adjustment. For this, solutions containing suitable amounts of KCl–HCl for pH 2, acetic acid–ammonium acetate for pH 3.75–5.57, and ammonia–ammonium chloride for pH 8–10 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, Australia. Amberlite XAD-16 resin (Sigma-Aldrich chemie GmbH, Riedstr. 2 Steinheim, China) was purchased as 20-60 mesh particle size with 800 m² g⁻¹ of surface area. 2-Hydroxy-3-methoxybenzaldehyde was procured from Sigma-Aldrich chemie GmbH (Riedstr. 2 Steinheim, China.) Standard reference materials (SRMs) such as Vehicle exhaust particulates NIES 8, Chlorella NIES 3, Human hair NIES 5, Tea leaves NIES 7 were obtained from the National institute of Environmental Studies, Rompin hematite JSS (800-3) were provided by the Japan Steel Society and Zinc base die-casting alloy C NBS 627 provided by the National bureau of Standards. 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).

2.3. Pretreatment of samples

2.3.1. Natural and Sewage water samples

The water samples namely river water (collected from the Ganga, Banaras), 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), and then acidified to pH 2 with HNO_3 before storing in precleaned polyethylene bottles.

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

To dissolve the environmental SRMs, 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 were prepared as proposed by the international atomic energy agency [26]. A 50 mg (600 mg 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 °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 alloy 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 and infant milk substitute (IMS)

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 drop wise until a clear solution was obtained on gentle heating.

Powdered IMS 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.

2.4. Functionalization of Amberlite XAD-16 resin with HMBA

An amount of 10 g of air-dried Amberlite XAD-16 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 [27]. 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 HMBA (5 g) in 100 mL acetone at a temperature as low as 0-5 °C over a period of 24 h. The dark brown resin bead was filtered off and thoroughly washed with 2 mol L^{-1} HCl and distilled water until free from alkali and acid. Finally, the resin 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 HMBA 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 HNO₃) 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 HCl 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 the hydroxyl hydrogen ion to the overall hydrogen ion capacity, another sample of the resin in the acid form was equilibrated with NaHCO₃ solution in place of NaOH.

RESULTS AND DISCUSSION

3.1. Characterization of AXAD-16- HMBA

The data obtained from IR spectra of AXAD-16- HMBA sorbent indicated the existence of several additional bands in the modified resins compared to the untreated one. The sorbent showed four additional bands corresponding to stretching vibration of: O-H (3400 cm⁻¹), C=O (1676 cm⁻¹), C - N (1510 cm⁻¹) and -N=N - (1592 cm⁻¹). IR studies of the metal ions chelated resin showed a red shift in the range 10-25 cm⁻¹ for -C=O- 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 group in the coordination process. It can be inferred that in the basic solution -OH group of HMBA on AXAD-16 resin were ionized to -O⁻ so that the negative electron pair of -O⁻ was coordinated with the metal ions.

On elemental analysis of the modified resin, 63.4%, 5.33%, 9.21% and 15.53% of carbon, hydrogen, nitrogen and oxygen respectively was found as compared to the calculated values (68.09%) C, (4.96%) H, (9.93%) N and (17.02%) O. This data suggests the presence of at least one water molecules according to the repetitive unit, C₁₆H₁₄N₂O₃·H₂O. The chemical structure of the repetitive unit in the new resin is shown in ((Fig. 1).

In thermo gravimetric analysis of AXAD16- HMBA, an initial weight loss of 4.84% up to 170 °C, corresponding to the endothermic peak in the DTA curve, may be attributed to the loss of sorbed water molecule. The above result implies that each monomeric unit of the functionalized resin consists of at least one H₂O molecule. The following exothermic peak at 274 °C corresponds to the further weight loss of 13.72%. The synthesized resin was found to retain 90% of the metal ion capacity up to 250 °C.

Since each of the HMBA group contains one replaceable hydrogen ion as hydroxyl group, therefore, the expected hydrogen ion capacity would be 3.33 mmol g⁻¹ of resin. Experimentally, the hydrogen ion capacity due to this hydroxyl group was found to be 3.13 mmol g⁻¹, which further supports the amount of HMBA incorporated.

The water regain capacity was found to be 10.50 mmol g⁻¹. This value reflects the high hydrophilicity of the resin which is satisfactory for column operation.

3.2. Stability of the resin

The chelating polymeric resin (1 g) was shaken with 100 ml of acid ($1-6 \text{ mol L}^{-1} \text{ HCl}$) or alkaline ($0.1-2.0 \text{ mol L}^{-1} \text{ NaOH}$) solution for 4 h, filtered thereafter and washed with doubly distilled water. On investigation, after air drying, no change in its elemental composition was observed, whereby suggesting a robust and stable nature of the chelating polymer. The variation in the exchange capacity of the resin was investigated by subjecting it to several loading and elution (batch) operations. After 30 cycles, the sorption capacity of the resin varied by less than 2%, whereby suggesting the feasibility of the resin for repeated use.

4. OPTIMIZATION OF CERTAIN PHYSIO-CHEMICAL PARAMETERS

The method was optimized for various analytical parameters such as pH, sample volume, amounts of resin and type of eluent, in order to obtain quantitative recovery of metal ions on AXAD-16- HMBA column. The percentage of metals adsorbed on the column was calculated from the amounts of metal in the starting sample and those eluted from the column.

4.1. Batch 'static' method followed for sorption and desorption

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 $2 \text{ mol L}^{-1} \text{ HCl}$ and subsequently analyzed by FAAS.

4.1.1. Effect of pH on enrichment of metal ions

The influence of pH on the retentions of metal ions on the XAD-16- HMBA resin was investigated in the pH range of 2–10. For this purpose, column experiments were performed by using 100 mL of test solutions containing $100 \mu\text{g mL}^{-1}$ of each metal ions. The pH of the solutions was adjusted by using the appropriate buffer solutions given in the experimental section. The results are depicted in Fig. 2. Optimum pH for maximum sorption of Zn(II), Cu(II), Ni(II), Cd(II), and Pb(II) is 5.57, 9.0, 9.0, 5.57 and 5.57 respectively.

4.1.2. Kinetic study of metal sorption

To determine the rate of loading of metal ions on the resin, batch experiments were carried out as detailed below. The chelating resin beads (0.2 g) were stirred with 100 ml of solution containing one of the metal ions ($100 \mu\text{g mL}^{-1}$) at room temperature for 2, 5, 10, 15, 20, 30, 45, 60, 90, and 100 min. The concentration of metal ions in the supernatant solution was calculated by mass balance (in mg g^{-1} resin). The loading half time needed to reach 50% of the total loading capacity was estimated from the curve (Fig.3). The $t_{1/2}$ values were found to be 9.0, 5.0, 7.2, 13.7 and 12.2 min for Zn(II), Cu(II), Ni(II), Cd(II), and Pb(II) respectively. The profile of the uptake of these metal ions on AXAD-16- HMBA reflects the good accessibility of the chelating sites in the resin to metal ions. The sorption rate constant k can be calculated using the following equation: [28], $-\ln(1-F) = kt$, 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 1).

The dynamics of the adsorption process in terms of the order and the rate constant can be evaluated using the kinetic adsorption data. The process of the mention metal ions removal from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process such as chemical reaction, diffusion control and mass transfer. The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption operation. The kinetics of removal of such ions is explicitly explained in the literature using pseudo first-order, second-order kinetic models (23).

$$\text{Pseudo-first-order model: } \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\text{Pseudo-second-order model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where k_1 and k_2 is the rate constant of pseudo first-order and pseudo-second-order rate constant, respectively. q_e and q_t are adsorption capacity at equilibrium (mmol g^{-1}) and at anytime, respectively. The parameters obtained from the kinetics models are listed in Table 2. It is evident from Table 2 that a more precise fit of kinetics data was shown by the pseudo-second order model. The calculated q_e values are closer to the experimental data than the

calculated values of pseudo-first order model and the values of regression coefficients (R^2) are higher (0.99) than pseudo-first order kinetic model.

4.1.3. Adsorption isotherm

For an adsorption column, the column resin is composed of microbeads. Each binding particle immobilized to the micro bead can be assumed to bind in a 1:1 ratio with the solute sample passed through the column. At the concentration range (1.7×10^4 - 3.6×10^4 μg) studied for Zn(II), Cu(II), Ni(II), Cd(II), and Pb(II) the data were successfully applied for 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. The linearized form of Langmuir isotherm may be represented by the following equation (23).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

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 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. 4). The values of q_m and b were determined from slope and intercepts of the plots and are presented in Table 3. 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 as presented in Table 3. The values were found to be between 0 and 1 which confirm the favorability of the adsorption process (23).

4.1.4. Influence of the Resin Amount

The effect of amount of resin on the retention of the analyte ions on the AXAD-16- HMBA column was investigated in the range of 50–500 mg. As shown in the figure, quantitative recoveries of all the metals were obtained after 200 mg of the resin. When the resin amount was below 200 mg of resin, the recoveries did not exceed 80%. All further studies were carried out with 200 mg of resin.

4.2. 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.

4.2.1. Study of eluents for stripping of metal ions

The volume of eluent, that can completely strip the retained analytes from the AXAD-16-HMBA, plays a vital role in determining the maximum preconcentration factor. Hence, different volumes of varying concentrations of different acids (HCl, HNO_3 , H_2SO_4 , HCOOH , CH_3COOH , and HClO_4) were investigated for the complete stripping of the retained metal ions. Among these acids, 5mL of 2 mol L^{-1} HCl could accomplish the quantitative elution of metal ions from the AXAD-16- HMBA, while the other acids are ineffective for the complete elution of these ions. The higher tendency of penetration of HCl into the AXAD-16- HMBA may facilitate the diffusion of the retained metal ions into the eluent solution.

4.2.2. Influence of flow rates on the extraction and stripping of metal ions

The influence of flow rates, in the column, of the sample for sorption and stripping solutions for the recovery of metal ions from the AXAD-16- HMBA was investigated. It was found that, the percentage recovery was not affected up to a flow rate of 5 mL min^{-1} , after which the retention of metal ions starts decreasing. On the other hand, quantitative stripping of metal ions from the AXAD-16- HMBA was achieved in a flow-rate range of 1.0–3.5 mL

min⁻¹, using 5 mL of 2 mol L⁻¹ HCl as a stripping solution. At higher flow rates, larger volume of 2 mol L⁻¹ HCl was necessary for quantitative stripping of the metal ions.

4.2.3. Study of potentially interfering matrices

Since the presence of numerous cations and anions in association with the target metal ions is inevitable. Therefore, these associated matrices poses a potential threat to the quantitative determination of the target metal ions by virtue of precipitate formation, redox reactions, or competing complexation reactions. The analytical applicability of the resin in the presence of common potential interfering species (including humic and fulvic acids) was studied (29-31). Binary mixtures, containing the target metal ion (100 µg) and varying concentration of different alkali and alkaline metal ions as well as chelating agents, were subjected to the recommended procedure for assessing the efficiency of separation. 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. As illustrated in Table 4, the resin could resist the interference of various associated matrices in the quantitative sorption of the trace metal ions.

4.2.4. Preconcentration Studies

Since the prime object is to preconcentrate the trace metal ions in order to make FAAS determination of metal ions more feasible, it is worthwhile to investigate the minimum concentration ((preconcentration limit) up to which quantitative sorption and recovery can be done using recommended column procedure. It was determined by increasing the volume of metal ion solution and keeping the total amount of loaded metal ion constant at 10 µg during the recommended column procedure. The preconcentration factor was calculated as the ratio of maximum volume of solution used for preconcentration to the volume used to strip the sorbed metal ions from the column. High preconcentration factor (volume) of Zn(II), Cu(II), Ni(II), Cd(II) and Pb(II) were 360(1800), 340(1700), 300(1500), 260(1300), and 240(1200) with corresponding preconcentration limit of 5.55, 5.88, 6.66, 7.69 and 8.33 ng mL⁻¹, respectively.

5. APPLICATIONS

5.1. Determination of metal ions in natural water samples

Applicability of the present method for preconcentration and determination of metal ions was accomplished by analyzing river, 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-16- HMBA. 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. It was found that the mean percentage recoveries of all the metal ions studied were 98.6 -104.0% at 95% confidence level. Table 5 depicts the results.

5.2. Analysis of metal ions in standard reference materials, multivitamin capsules, infant powdered food, and hydrogenated oil

The SRMs namely NIES 3, NIES 5, NIES 7, NIES 8, JSS (800-3) and NBS 627, Multivitamin capsules, IMS, and hydrogenated oil were subjected to preconcentration according to the recommended column procedure after their pretreatment. Proper pH adjustment of the solutions was made prior to the experiment. The results (Table 6) show that recovery could be made with a good precision of RSD < 5.

6. ANALYTICAL FIGURES OF MERIT

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. The consistency between found and certified values of metal content demonstrated that the described method could be applied successfully for the analysis of real matrices constituting different matrix.

Using optimum conditions, the precision of the method was evaluated. Six successive sorption and elution cycles of 10 µg each of the metal ions taken in 100 mL (eluted in 5 mL of 2 mol L⁻¹ HCl) were performed following the recommended procedure. Standard deviation (SD) and RSD values were calculated to be below 2 and 5 % respectively. The results of water analysis (with RSD < 5 %) support the applicability of the method.

During the determination of metals by FAAS, the solutions for calibration curves were prepared using 10 mL of 1 mol L⁻¹ HCl spiked with each metal. As no significant blank values were obtained for any of the metals, the limit of

detection (LOD) for each metal was evaluated as (blank + 3 σ), where σ is the standard deviation for the procedural blank and were found to be 0.58, 1.08, 1.21, 0.86 and 1.72 $\mu\text{g L}^{-1}$ respectively with their corresponding LOQ (limit of quantification) as 1.83, 3.66, 3.96, 2.87 and 5.65 $\mu\text{g L}^{-1}$. The sensitivity of the resin is further affirmed by the lower limit of preconcentration for large volumes.

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 with that found by S.A. method (Table 5) indicates the reliability of the present method for metal analyses in water samples of various matrices without significant interference.

Table 1. Kinetics and batch capacity of sorption of metal ions on AXAD-16-HMBA. (experimental conditions:100 mL solution , 100 $\mu\text{g mL}^{-1}$, 0.2 g of resin)

Metal ion	Loading halftime $t_{1/2}$ (min)	Rate constant k (min^{-1}) $\times 10^{-2}$	Batch capacity (mmol g^{-1})
Zn(II)	9.0	7.6	0.425
Cu(II)	5.0	13.8	0.362
Ni(II)	7.2	9.5	0.310
Cd(II)	13.7	5.1	0.237
Pb(II)	12.2	5.6	0.155

Table 2. Kinetics parameter for sorption of different metal ions (experimental conditions:100 mL, solution; 0.2 g, resin)

Order of reactions	Parameters	Zn(II)	Cu(II)	Ni(II)	Cd(II)	Pb(II)
Pseudo-first-order model	K_1 (min^{-1})	0.269	0.185	0.153	0.142	0.137
	q_e (mmol g^{-1})	0.290	0.225	0.170	0.123	0.112
	R^2	0.9742	0.9596	0.9715	0.9467	0.9688
Pseudo-second-order model	K_2 ($\text{g}/\text{mmol}\cdot\text{min}$)	32.25	27.47	15.15	13.13	10.97
	q_e (mmol g^{-1})	0.492	0.334	0.320	0.216	0.122
	R^2	0.9998	0.9995	0.9995	0.9994	0.9996

Table 3. Langmuir isotherm constants for sorption of metal (experimental conditions:100 mL, solution; 0.2 g, resin)

Metal ions	R_L	B (L mg^{-1})	q_m (mg g^{-1})	R^2	Standard deviation (N=5)
Zn(II)	0.7946	0.5171	29.62	0.9997	0.3572
Cu(II)	0.6175	1.0431	25.79	0.9994	0.4150
Ni(II)	0.6459	0.9451	19.79	0.9996	0.1936
Cd(II)	0.4995	1.7903	30.72	0.9993	0.3404
Pb(II)	0.3489	0.8221	38.69	0.9982	0.2648

Table 4. Tolerance limit of foreign species (in binary mixtures) on sorption of metal ions (experimental conditions:100 mL solution, 100 μg of each metal ion, 0.2 g of resin)

Foreign species ($\mu\text{g mL}^{-1}$)	Tolerance limit of metal ions				
	Cu(II)	Zn(II)	Cd(II)	Ni(II)	Pb(II)
NaCl	35000	32000	35000	25000	20000
Na ₂ SO ₄	25000	20000	20000	28000	18000
NaNO ₃	38000	35000	28000	35000	25000
Na ₂ PO ₄	1000	800	300	800	250
NH ₄ Cl	35000	30000	30000	35000	20000
Sodium citrate	400	350	250	350	250
Sodium oxalate	150	100	100	150	80
Sodium potassium tartrate	200	125	100	125	80
Humic acid	64	65	88	89	97
Fulvic acid	54	56	79	91	92
CH ₃ COONa	10000	7000	5000	8000	5000
CaCl ₂	25000	22000	16000	25000	10000
MgCl ₂	30000	28000	25000	32000	20000

Table 5. Preconcentration and determination of metal ions in natural waters collected from various locations (Column parameter: 500 mL, solution; 5.0 mL min⁻¹, sorption flow rate; 2.0 mL min⁻¹, elution flow rate; 0.5g, resin).

Samples	Metal ion found by proposed method, $\mu\text{g L}^{-1} \pm \text{confidence limit}^a$ (% Recovery) ^b									
	Zn(II)		Cu(II)		Ni(II)		Cd(II)		Pb(II)	
	Added $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1}$	Added $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1}$	Added $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1}$	Added $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1}$	Added $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1}$
Tap water	0	5.50±0.39	0	6.08±0.45	0	4.58±0.52	0	NA	0	3.40±0.31
	5	10.70±0.46 (104.0)	5	11.12±0.59 (100.8)	5	9.51±0.43 (98.6)	5	5.08±0.28 (101.6)	5	8.36±0.43 (99.2)
Sewage water	0	8.33±0.67	0	10.28±0.55	0	14.55±0.30	0	4.22±0.57	0	5.92±0.46
	5	13.47±0.77 (102.8)	5	15.29±0.74 (100.2)	5	19.50±0.39 (99.0)	5	9.25±0.52 (100.6)	5	10.97±0.53 (101.0)
River water	0	13.36±0.65	0	16.40±0.56	0	9.84±0.47	0	6.20±0.54	0	7.79±0.47
	5	18.30±0.69 (98.8)	5	21.51±0.78 (102.2)	5	14.86±0.45 (100.4)	5	11.28±0.63 (101.6)	5	12.73±0.39 (98.8)

a Confidence limit, $C.L = \bar{x} \pm \frac{ts}{\sqrt{N}}$, N=3 at 95% confidence level; b % Recovery.

Table 6. Analysis of SRMs, multivitamin tablets and food samples for metal ion contents (Column parameters: 5.0 mL min⁻¹, sorption flow rate; 2.0 mL min⁻¹, elution flow rate; 0.5 g, resin).

Samples	Certified/Reported value ($\mu\text{g g}^{-1}$)	Mean found by proposed method $\mu\text{g g}^{-1}$ (RSD) ^a	Calculated Student's t value ^b
Vehicle exhaust particulates NIES 8 ^c	Cd: 1.1, Cu: 67.0, Ni: 18.5, Zn: 1040.0, Pb: 219	Cd: 1.06 (3.8), Cu:63.6(4.5), Ni:17.5 (4.6), Zn:1018.2(2.8), Pb:209.8(3.9)	2.22, 2.65, 2.77, 1.17, 2.51
Chlorella NIES 3	Zn: 20.5, Cu: 3.5, Pb: 0.6	Zn:19.6(3.8), Cu:3.4(3.0), Pb:0.58(3.1)	2.70, 2.19, 2.48
Human hair NIES 5 ^c	Zn: 169.0, Cu: 16.3, Ni: 1.8, Pb: 6	Zn:163.3(3.3), Cu:15.5(4.4), Ni:1.7(4.8), Pb:5.7(4.8)	2.36, 2.62, 2.74, 2.45
Tea leaves NIES 7 ^c	Zn:33.0, Cu: 7.0, Ni:6.5,Cd:300	Zn:31.5(4.1), Cu:6.8(3.9), Ni:6.2(4.2), Cd:288.8(3.8)	2.59, 1.68, 2.57, 2.28
Rompin hematite, JSS (800-3) ^d	Cu: 640, Zn: 1030.0, Pb: 210	Cu:625.4(2.5), Zn:1013.3(2.4), Pb:201.9(3.5)	2.08, 1.53, 2.56
Zinc base die-casting alloy C NBS 627 ^e	Cu: 1320.0, Ni: 29.0, Pb: 82, Cd:51	Cu:1301.0(2.9), Ni:27.6 (4.1), Pb:77.7(4.6), Cd:48.8 (4.2)	1.12, 2.76, 2.69, 2.40
Maxirich (Cipla)	Cu: 398.2; Zn: 442.5	Cu: 388.4 (2.7), Zn: 430.2 (2.9)	2.12, 2.20
Lactogen 1(Nestle)	Cu: 2.9; Zn: 37.0	Cu: 2.80 (3.1), Zn: 35.2 (4.2)	2.42, 2.72
Vanaspati ghee	Ni: 0.45	Ni: 0.44 (3.6)	1.41

a RSD, = Relative 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)

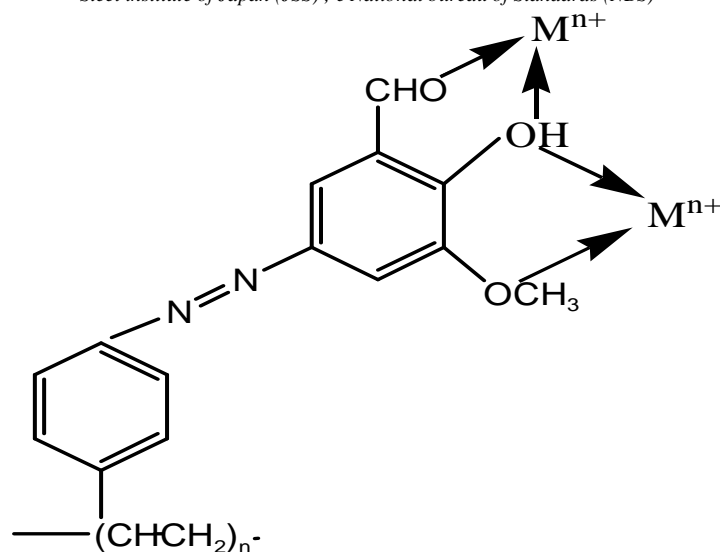


Figure 1 monomeric unit of AXAD-16-HMBA

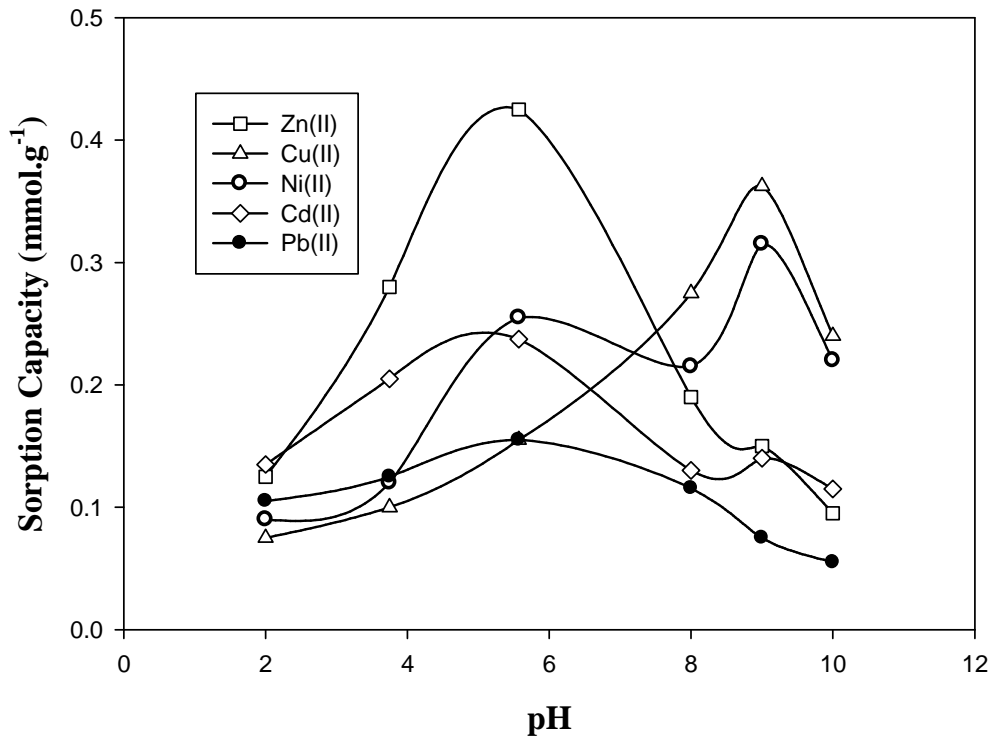


Figure 2 Effect of pH on the sorption capacity of AXAD-16-HMBA

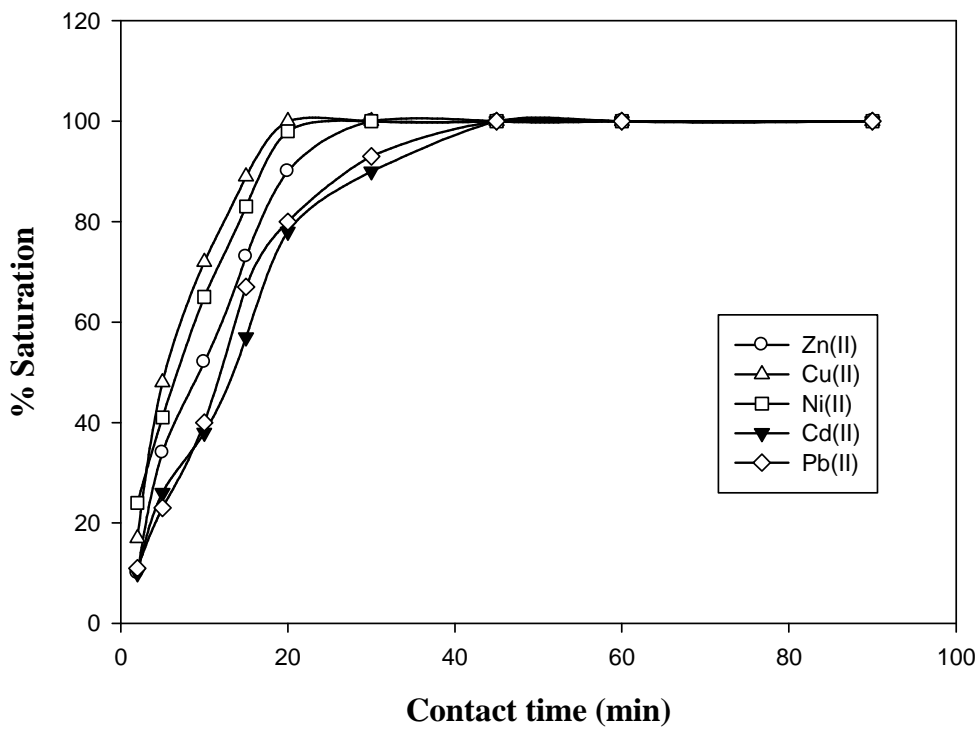


Figure 3 Kinetics of sorption of metal ions on AXAD-16-HMBA

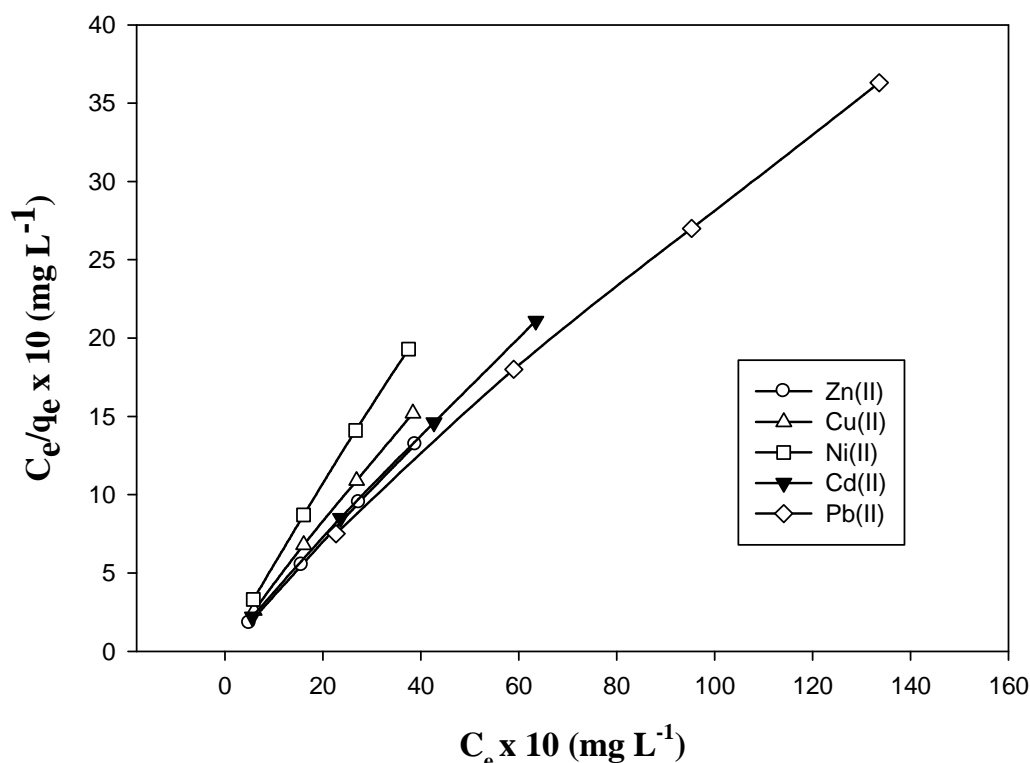


Figure 4 Langmuir sorption isotherms depicting the sorption behaviors of metal ions onto AXAD-16-HMBA

CONCLUSION

This 2-Hydroxy-3-methoxybenzaldehyde modified chelating resin coupled with FAAS offers an excellent method that facilitates the determination of trace analytes and the efficient separation of heavy metals from various matrices found in natural samples (including water resources with high salinity). Moreover, the use of a column preconcentration technique facilitates the determination of metal ions, of trace concentrations, even by less sensitive instrumental method such as FAAS. This material (AXAD-16- HMBA) does not require any prior digestion of the river water samples for the purpose of preconcentration. The use of organic solvents in the proposed method is eliminated. To our literature knowledge, no study is available on the use of Amberlite XAD-16 fixed with 2-Hydroxy-3-methoxybenzaldehyde as sorbent for the preconcentration of trace metal ions from various media.

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