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2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid immobilized Amberlite XAD-16 as metal extractant

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Abstract

2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid (DMABA) was loaded on Amberlite XAD-16 (AXAD-16) via azo linker and the resulting resin AXAD-16-DMABA explored for enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II). The optimum pH values for extraction are 6.5–7.0, 5.0–6.0, 5.5–7.5, 5.0–6.5, 6.5–8.0, 5.5–7.0, 4.0–5.0 and 6.0–7.0, respectively. The sorption capacity was found between 97 and 515 μmol g^{-1} and the preconcentration factors from 100 to 450. Tolerance limits for foreign species are reported. The kinetics of sorption is fast as $t_{1/2}$ is $\leq$5 min. The chelating resin can be reused for 50 cycles of sorption–desorption without any significant change (<1.5%) in the sorption capacity. The limit of detection values (blank +3 s) are 1.12, 1.38, 1.76, 0.67, 0.77, 2.52, 5.92 and 1.08 μg L^{-1} for Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II), respectively. The enrichment on AXAD-16-DMABA coupled with monitoring by flame atomic absorption spectrometry (FAAS) is used to determine all the metal ion ions in river and synthetic water samples, Co in vitamin tablets and Zn in milk samples.

Keywords: 2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid; Amberlite XAD-16; Metal ions; Chelating resin; Enrichment; Flame atomic absorption spectrometry; Determination

1. Introduction

The interest in ligand immobilized solid phases like silica gel, organic polymer or copolymers and cellulose continues because of their several applications, for example in solid phase metal extraction [1], designing hybrid organic–inorganic catalysts [2] and heterogenization of homogeneous catalysts [3]. The solid phase extraction of metal ions present at micro/trace level in environmental samples, high purity materials, biological samples and other complex matrices, makes possible their determination with cheap and commonly available analytical techniques, such as flame atomic absorption spectrometry (FAAS). Solid phase extraction is preferable over ion exchange and solvent extraction due its advantages like selectivity, eco-friendliness, reusability and high preconcentration factors [4]. Amberlite XAD-2 has been found to be a good support to load the chelating ligands and design chelating resins for solid phase extraction [5–15]. It has been reported recently that Amberlite XAD-16 (AXAD-16), which is chemically divinyl polystyrene copolymer (marketed by Aldrich (USA)) on ligand immobilization gives chelating resins of better sorption capacities than those of Amberlite XAD-2-based chelators [16–19]. The improvement in the sorption capacity may result due to higher surface area of Amberlite XAD-16 in comparison to that of Amberlite XAD-2 [20–21]. Thus, anchoring of a multidentate ligand 2-{[1-(3,4-dihydroxyphenyl)methylidene]amino}benzoic acid (DMABA) on Amberlite XAD-16 may result chelating resin of very high capacity. It was, therefore, thought worthwhile to design AXAD-16-DMABA and study resulting chelating resin to enrich Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II). The enrichment of these metal ions by the newly designed resin coupled with their determination by flame atomic absorption spectrometry has been applied

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to determine all eight metal ions in water samples, cobalt in vitamin tablets and zinc in milk. The details of these investigations and their results are reported in this paper.

2. Experimental

2.1. Instruments

A flame atomic absorption spectrometer of the Perkin-Elmer Instruments, Shelton, USA, model Aanalyst 100 equipped with air–acetylene flame was used for metal ion determination. The wavelengths used for monitoring Zn, Mn, Ni, Pb, Cd, Cu, Fe and Co are 213.9, 279.8, 231.1, 217.0, 228.8, 324.8, 248.8 and 240.7 nm, respectively. The calibration curves were linear in the ranges 0.02–1.00, 0.07–5.00, 0.20–5.00, 0.19–20.00, 0.28–2.00, 0.08–5.00, 0.19–20.00 and 0.10–3.50 $\mu g\,mL^{-1}$ for Zn, Mn, Ni, Pb, Cd, Cu, Fe and Co, respectively. A Nicolet (Madison, USA) FT-IR spectrometer, model Protégé 460, was used to record IR spectra (in KBr) in the range 400–4000 cm^{-1}. The pH was measured with digital pH meter (Toshniwal Instruments, Ajmer, India). Thermogravimetric analysis (TGA) was carried out on a Dupont (Wilmington, Delaware, USA) 2100 thermal analyzer and Perkin-Elmer (Rotkreuz, Switzerland) elemental analyzer, model 240C, was used for elemental analyses. The flow of solution through the column was controlled using peristaltic pump (Watson–Marlow Model 101/U/R, Falmouth, UK). The sorption and desorption studies of the metal on the chelating matrix were generally carried out on columns of 1 cm diameter (Pharmacia, Bromma, Sweden) and 10 cm in length equipped with adjustable frits. A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) with a speed of 200 strokes min^{-1} was used for batch equilibration.

2.2. Reagents

Amberlite XAD-16 (non-ionic divinyl polystyrene; specific area 800 $m^2\,g^{-1}$ and bead size, 20–60 mesh) was procured from Aldrich (Milwaukee, USA). 3,4-Dihydroxybenzaldehyde obtained from ACROS ORGANICS (New Jersey, USA) and anthranilic acid obtained from Merck India Ltd. was used as received. The stock solutions of metal ions (1000 mg L^{-1}) were prepared from analytical reagent grade metal salts as described earlier [8–11]. They were standardized [22] and working solutions of the metal ions were made by suitable dilution of the stock solutions with doubly distilled water. The 0.1 mol L^{-1} HCl and NaOH (pH 2 and 3), 0.1 mol L^{-1} acetic acid–acetate buffer (pH 4 and 5), 0.1 mol L^{-1} phosphate buffer (pH 6 and 7) and 0.1 mol L^{-1} ammonia–ammonium chloride buffer (pH 8 and 9) were used to adjust the pH of the solutions, wherever suitable. Water samples from the Ganges river (Haridwar, India) and tap water (New Delhi, India) were collected, acidified with 2% HNO_3, filtered and stored in glass bottles. The glassware were washed with chromic acid and soaked in 5% HNO_3 overnight and cleaned with doubly distilled water before use.

2.3. Synthesis of 2-{[1-(3,4-dihydroxyphenyl)methylidene]amino}benzoic acid and DMABA loaded Amberlite XAD-16 (AXAD-16-DMABA)

3,4-Dihydroxybenzaldehyde (0.138 g, 1 mmol) and anthranilic acid (0.137 g, 1 mmol) were dissolved in dry diethyl ether and the mixture was stirred at room temperature for 3 h. The solvent was removed on a rotary evaporator to get red coloured Schiff's base DMABA, which was recrystallized from ethanol. Analyses: found C, 64.22; H, 4.31; N, 5.84%; calculated for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.28; N, 5. 45%.

The procedure published [8,9] for nitration of Amberlite XAD-2 beads was used for Amberlite XAD-16 also. The nitrated Amberlite XAD-16 was also reduced to amino resin by the reported method [8,9]. The amino resin was suspended in 200 mL of ice-cold water and treated with a equimolar mixture of 1 mol L^{-1} HCl and $NaNO_2$ solution at −5 °C, until the reaction mixture started to change the colour of starch iodide paper to violet. The diazotized polymer was filtered at −5 to 0 °C to avoid its disintegration and treated with DMABA (10 g taken in a mixture of 400 mL water and 50 mL of 2% sodium hydroxide) at 0 to 5 °C for 24 h. The resulting dark brownish crimson coloured beads were filtered and washed with 4 mol L^{-1} HCl and doubly distilled water successively and finally air-dried.

Analyses: AXAD-16-DMABA: found C, 62.73; H, 5.56; N, 9.90%;

2.4. Recommended procedure for preconcentration and determination of metal ions

The column and batch methods employed for the preconcentration of metal ions are as follows.

2.4.1. Column method

Amberlite XAD-16 loaded with DMABA (1.0 g) was swollen for 24 h, packed in a glass column C10/10 (Pharmacia; 10 cm × 10 mm), between frits, using the method recommended by the manufacturer [23]. The column was treated with 4 mol L^{-1} HCl or HNO_3 (50 mL) and washed with doubly distilled water until free from acid. A suitable aliquot of the sample solution containing Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) or Co(II) in the concentration range 0.0044–1.0 $\mu g\,mL^{-1}$ (500–100 mL depending upon concentration) was passed through the column after adjusting its pH (in the range 6.5–7.0, 5.0–6.0, 5.5–7.5, 5.0–6.5, 6.5–8.0, 5.5–7.0, 4.0–5.0 and 6.0–7.0, respectively, for Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II)) at a flow rate of 1.0–5.0 mL min^{-1}, controlled with a peristaltic pump. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from the column with HCl or HNO_3 (10–25 mL) of optimum concentration