AMBERLITE XAD-2 FUNCTIONALIZED WITH PHENOLIC LIGANDS AS METAL ION EXTRACTANTS

BY

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DEPARTMENT OF CHEMISTRY

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...dedicated to my ***parents, wife,***

and

extremely loving daughters,
Shivangi and Himangi.

CERTIFICATE

This is to certify that the thesis entitled **"AMBERLITE XAD-2 FUNCTIONALIZED WITH PHENOLIC LIGANDS AS METAL ION EXTRACTANTS,"** being submitted by **Mr. MANJEET KUMAR**, to the Indian Institute of Technology, Delhi, for the award of the degree of **'Doctor of Philosophy' in Chemistry**, is a record of bonafide research work carried out by him. **Mr. MANJEET KUMAR** has worked under our guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

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Abstract

o-Aminophenol, tiron (1,2-dihydroxybenzene-3,5-disulphonic acid disodium salt), pyrogallol (1,2,3-trihydroxybenzene) and quinalizarin (1,2,5,8-tetra-hydroxy anthraquinone) have been immobilized (through -N=N- coupler) on Amberlite XAD-2 after its nitration, reduction (of NO_2 group) and diazotization (of NH_2 group). All the four resins were characterized by elemental analyses, TGA and IR spectroscopy. Their IR spectra show a characteristic band for azo group apart from some of the bands of the ligands immobilized. TGA curves indicate the presence of 0.5-2.0 molecules of water per repeat unit of polymer. All the four resins have been studied for preconcentration of Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II), Mn(II), Fe(III) and UO_2(II) ions, using flame AAS for their monitoring except uranium which is monitored fluorimetrically.

The optimum pH values for quantitative sorption of six metal ions viz., Cu(II), Cd(II), Co(II), Ni(II), Pb(II) and Zn(II) on Amberlite XAD-2 anchored with *o*-aminophenol are between 5.0 and 9.0. The metal ions can be desorbed with 4 M HNO_3 (recovery 96-98%, except Pb for which it is 91%). The elution breakthrough volume has been found between 10 and 25 ml of 4 M HNO_3. The sorption capacity of the resin is between 16.0-58.0 μmol g^{-1} of resin. Tolerance limits for electrolytes NaCl, NaF, $NaNO_3$, Na_2SO_4 or Na_3PO_4 and Mg(II) or Ca(II) ions on the sorption of these metal ions are reported. The preconcentration factor is between 40 and 100 (metal concentration level: 10-25 μg l^{-1}) and loading half time, $t_{1/2}$ between 8 and 18 min. The detection and quantification limits are 1.35-19.78 μg l^{-1} and 2.82-31.96 μg l^{-1}, respectively.

The sorption on tiron functionalized Amberlite XAD-2 is quantitative for the nine metal ions mentioned above in the pH ranges 4.0 to 7.5, and desorption (recovery 95-99%, except Pb for which it is 91%) is instantaneous with 3-4 M HNO_3 / 2-4 M HCl (except Pb). An elution volume of 10-25 ml (40 ml for Pb) of 4 M HNO_3 was appropriate for quantitative recovery of loaded metal ions. The sorption capacity is in the range 32.4 to 220.3 μmol g^{-1} of resin. The tolerance limits for NaCl, NaF, $NaNO_3$, Na_2SO_4 and Na_3PO_4 in the sorption of all the nine metal ions are reported. The Mg(II) and Ca(II) are tolerable with each of them upto a concentration level of 2-30 mmol l^{-1}. The enrichment factor has been found to be between 25 and 200 (metal concentration level: 3-25 μg l^{-1}). The loading half time ($t_{1/2}$) is in the range 2.8-4.0 min. The limit of detection is 0.40-19.43 μg l^{-1} and limit of quantification 0.62-30.0 μg l^{-1}.

On pyrogallol modified Amberlite XAD-2 sorption of the nine metals is quantitative [recovery 95-99%, except for Mn (93%) and Pb (90%)] at pH 5.0-8.0, when flow rate is maintained between 2 and 2.5 ml min^{-1}. The 4 M HNO_3 / HCl (except Pb) instantaneously elutes all the metal ions. The breakthrough volume for elution is between 10 and 25 ml (40 ml for Pb) of 4 M HNO_3. The sorption capacity is in the range 18.9-82.1 μmol g^{-1} whereas preconcentration factor is between 25 and 160 (metal concentration level: 3-25 μg l^{-1}). The tolerance limits for NaCl, NaF, $NaNO_3$, Na_2SO_4 or Na_3PO_4 and Ca(II) or Mg(II) in the sorption of all the nine metal ions are reported. The limit of detection is in the range 0.45-19.96 μg l^{-1} and the limit of quantification between 0.57 and 31.72 μg l^{-1}. The loading half time $t_{1/2}$ is less than 3.5 min., for all the nine metals.

For nearly quantitative sorption (recovery ≥ 91-98%) on Amberlite XAD-2 immobilized with quinalizarin, the optimum pH values for Cu(II), Cd(II), Co(II),

Pb(II), Zn(II), Mn(II) and UO_2(II) are between 5.0 and 7.0. The desorption of metal ions by 4 M HNO_3 is instantaneous. The elution breakthrough volumes are between 10 to 25 ml of 4 M HNO_3. The sorption capacity of the resin is between 9.2 and 49.6 μmol g^{-1}. The tolerance limits for electrolytes, NaCl, NaF, $NaNO_3$, Na_2SO_4 or Na_3PO_4 and Mg(II) or Ca(II) ions in the sorption of the seven metal ions are reported. Preconcentration factor is 40 to 100 (metal concentration level: 3-25 μg l^{-1}). The limit of detection is 0.85-11.51 μg g^{-1} and limit of quantification: 1.2-19.70 μg g^{-1}. The $t_{1/2}$ values for sorption are found to be between 5.3 and 15.0 min.

The preconcentration-coupled FAAS methods based on these four resins have been applied to determine the metal ions [except uranium] in river or well water samples. The RSD values are less than 8%. The enrichment coupled fluorimetric method based on last three resins has been applied to determine uranyl ion in well water samples (RSD < 6.3%). Cobalt content of pharmaceutical samples (vitamin tablets) have also been determined (RSD < 4.5 %) by preconcentration-coupled Flame-AAS method. The simultaneous enrichment and determination of all the metal ions is possible. The performance of all the four present resins is superior or comparable to many commonly known functionalized polymers.

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