AMBERLITE XAD-2 AND XAD-7 FUNCTIONALIZED/IMPREGENATED WITH CHELATING LIGANDS: PREPARATION AND APPLICATIONS AS METAL ION EXTRACTANTS

By

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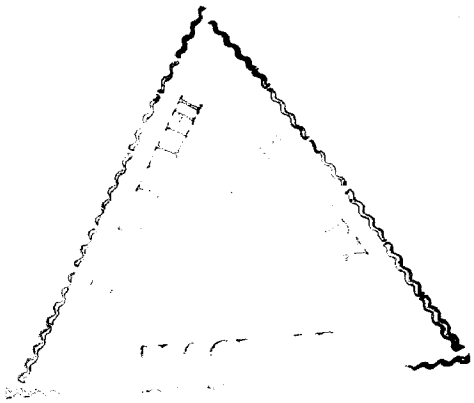

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Dedicated to

My Parents

&

Swati and Sona

CERTIFICATE

This is to certify that the thesis entitled, **"AMBERLITE XAD-2 AND XAD-7 FUNCTIONALIZED / IMPREGENATED WITH CHELATING LIGANDS: PREPARATION AND APPLICATIONS AS METAL ION EXTRACTANTS"**, being submitted by **Mr. Pankaj Kumar Tewari** 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. **Pankaj Kumar Tewari** has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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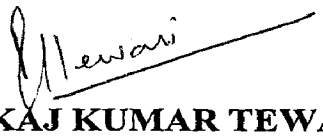

PANKAJ KUMAR TEWARI

Abstract

Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid, disodium salt dihydrate), thiosalicylic acid and pyrocatechol 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 three resins were characterized by elemental analysis, 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 1.0-1.5 molecules of water per repeat unit of polymer. Xylenol orange [*o*-cresolsulfonphthalein-3'-3"-bis(methyliminodiacetic acid sodium salt)] was also sorbed onto Amberlite XAD-7 to prepare a chelating matrix. All the four resins have been used for preconcentration of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) ions. The optimum pH values for quantitative sorption of these metal ions on chromotropic acid loaded Amberlite XAD-2 are between 3.0 and 8.0. The metal ions can be desorbed with 2 M HCl (except for Pb) or HNO_3 (recovery 96-100%). The elution breakthrough volume has been found between 5 and 10 ml of 2-4 M HCl or HNO_3. The sorption capacity of the resin is between 58.0 - 186.3 μg g^{-1} of resin. Tolerance limits for electrolytes NaCl, NaBr, $NaNO_3$, Na_2SO_4 or Na_3PO_4 and Mg(II) or Ca(II) ions (0.001-2.0 M) on the sorption of these metal ions (0.1- 0.5 μg ml^{-1}) are reported. The preconcentration factor is between 100 and 200 (metal concentration level: 5-25 μg l^{-1}) and loading half time, $t_{1/2}$ values between 2.4 and 5.8 min. The detection and quantification limits are 0.06-4.06 μg l^{-1} and 0.08-4.42 μg l^{-1} respectively.

The sorption on Amberlite XAD-2 anchored with pyrocatechol is quantitative in the pH ranges 3.0 to 7.5, whereas desorption is instantaneous with 2 M HCl (except Pb) or HNO_3. An elution volume of 6-8 ml of 2 M HCl or HNO_3 was appropriate for quantitative recovery of loaded metal ions. The sorption capacity is in the range 23.1 to 104.7 μmol g^{-1} of resin. The tolerance limits for NaCl, NaBr, $NaNO_3$, Na_2SO_4 and Na_3PO_4 in the sorption of all the seven metal ions (0.2-0.5 μg ml^{-1}) are reported. The Mg(II) and Ca(II) are tolerable with each of

them (0.2-0.5 μg ml^{-1}) upto a concentration level of 0.01 to 1.0 M. The enrichment factor has been found to be between 80 and 200. The loading half time ($t_{1/2}$) is in the range 1.4-15.5 min. The limit of detection is 0.06 - 3.80 μg l^{-1} and limit of quantification 0.08 - 4.22 μg l^{-1}.

On thiosalicylic acid (TSA) modified Amberlite XAD-2 (AXAD-2) sorption is nearly quantitative (92-98%) at pH 3.5-7.0 when flow rate is maintained between 2 and 4 ml min^{-1}. The 2 M HCl (except for Pb) or HNO_3 instantaneously elutes all the metal ions. The breakthrough volume for elution is between 4 and 10 ml of 2 M HCl or HNO_3. The sorption capacity is in the range 47.4-309.9 μmol g^{-1} whereas preconcentration factor is between 100 and 400. The tolerance limits for NaCl, NaBr, $NaNO_3$, Na_2SO_4 or Na_3PO_4 and Ca(II) or Mg(II) in the sorption of all the seven metal ions are reported. The limit of detection is in the range 0.20 - 7.87 μg l^{-1} and the limit of quantification between 0.29 and 8.64 μg l^{-1}. The loading half time $t_{1/2}$ is less than 2.0 min, except for nickel and lead for which the value is 13.2 and 4.5 min. respectively.

The optimum pH values for nearly quantitative sorption (recovery ≥ 91-100%) on Xylenol Orange coated Amberlite XAD-7 are between 4.0 and 7.0. The desorption of metal ions by 2 M HCl (except Pb) or HNO_3 is instantaneous. The elution breakthrough volumes are between 8 to 10 ml of 2 M HCl or HNO_3. The sorption capacity of the resin is between 16.9 and 44.3 μmol g^{-1}. The tolerance limits for electrolytes, NaCl, NaF, NaI, $NaNO_3$, Na_2SO_4 and Mg(II) and Ca(II) ions in the sorption of the seven metal ions are reported. Preconcentration factor is 50 to 200. The limit of detection: 0.16-2.44 μg g^{-1}. Limit of quantification: 0.26-2.76 μg g^{-1}. The $t_{1/2}$ values for sorption are found to be between 2.5 and 5.3 min. The preconcentration-coupled FAAS methods based on these four resins have been applied to determine the metal ions in river or tap water samples. The RSD values are generally less than 8% except in few cases where it is upto 24.2%. Cobalt content of pharmaceutical samples (vitamin tablets) have also been preconcentrated and determined (RSD of < 3.0 %). The simultaneous enrichment and determination of all the metal ions is possible. The performance of present resin is comparable to many commonly known chelating matrices.

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