MACROMOLECULAR CHELATORS HAVING OXYGEN AND NITROGEN DONOR SITES: DESIGNING AND APPLICATIONS AS METAL EXTRACTANTS

By

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Department of Chemistry

submitted
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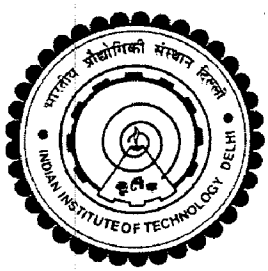
DOCTOR OF PHILOSOPHY

to the



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INDIA

SEPTEMBER, 2005

Dedicated to

My Parents

&

Brother

CERTIFICATE

This is to certify that the thesis entitled, "**MACROMOLECULAR CHELATORS HAVING OXYGEN AND NITROGEN DONOR SITES: DESIGNING AND APPLICATIONS AS METAL EXTRACTANTS**" being submitted by **Mr. G. Venkatesh** to the Indain 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. G. Venkatesh has worked under my guidance and supervision. He 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 in full to any other university or institute for award of any degree or diploma.

Date: 16. Sep. 2005

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ABSTRACT

Eight new chelating matrices have been designed using Amberlite XAD-2/16 and silica gel as support. 2,3-Dihydroxypyridine (DHP), 2-{[1-(3,4-dihydroxyphenyl)-methylidene]amino}-benzoic acid (DMABA) and 4-{[(2-hydroxyphenyl)imino]methyl}-1,2-benzenediol (HIMB) have been immobilized on Amberlite XAD-2/16 via azo linker. 3,4-Dihydroxybenzaldehyde (DHB) (via schiff's base formation) and Iminodiacetic acid (IDA) have been immobilized on Silica Gel via formation of C=N/C-N bond. These newly designed chelating matrices were characterized by ^{13}C CPMAS spectroscopy, FT-IR, TGA, elemental analyses and specific surface area measurements (BET). The IR spectra have characteristic bands of linkers as well as of the immobilized ligands. TGA curves indicate the presence of 1.0-4.0 water molecules per repeat unit of the polymer. All the eight matrices have been explored for enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), Pd(II) and Co(II). Optimum conditions were standardized. The limits up to which electrolytes NaCl, NaBr, $NaNO_3$, Na_2SO_4, Na_3PO_4, NaI, humic acid, EDTA, ascorbic acid, citric acid, sodium tartrate, Ca(II) and Mg(II) can coexist with each of the nine metal ions during their sorption on each chelating matrices without any adverse effect are reported.

The optimum pH for quantitative sorption on DHP loaded Amberlite XAD-2 (AXAD-2-DHP) is between 3.5-7.0. The 2.0 M HCl was found sufficient for quantitative recovery of all the metal ions from the resin AXAD-2-DHP except Pb and Pd which was quantitatively eluted with 1.5 M HNO_3 and 1.0 M HCl containing 3.0 % thiourea respectively. A flow rate of 1.0-5.0 ml min^{-1} was found to be suitable for sorption and 1.0-4.0 ml min^{-1} for desorption for all the metal ions. Sorption capacity is between 61 and 407

μmol g^{-1}. Sorption capacities and preconcentration factors achieved with these resin are better than many earlier reports. Sorption generally follows Langmuir model except lead system for which Fruendlich model was most plausible. The $t_{1/2}$ values are <15 min. The preconcentration factor varies between 34 and 300. The optimum pH for quantitative sorption on Amberlite XAD-16 modified with DHP (AXAD-16-DHP) was found similar to that of AXAD-2-DHP. All the metal ions can be desorbed from AXAD-16-DHP with 1.5 M HCl except Pb and Pd which was quantitatively eluted with 1.0 M HNO_3 and 1.0 M HCl containing 4.0 % thiourea. A flow rate of 1.0-5.0 ml min^{-1} was found to be optimum for both sorption and desorption for all the metal ions on AXAD-16-DHP. Sorption capacity is between 75 and 512 μmol g^{-1}. The $t_{1/2}$ values are found between 2 and 15 min. The preconcentration factor varies between 100 and 350.

The optimum pH values for quantitative sorption of all the metal ions (except Pd) on Amberlite XAD-2-HIMB resin (AXAD-2-HIMB) between 5.0 and 8.0. For Amberlite XAD-16-HIMB resin (AXAD-16-HIMB) optimum pH ranges are similar to the those of AXAD-2-HIMB. A flow rate of 1-4 ml min^{-1} was found suitable for both sorption and elution in the case of both the matrices. The 2.0 M HCl completely desorbed all metal ions from the AXAD-2-HIMB, except Pb which was eluted with 0.5 M HNO_3. In the case of AXAD-16-HIMB 1.5 M HCl completely desorbed all metal ions except Pb for which 1.0 M HNO_3 was required. The sorption capacity of AXAD-2-HIMB is between 40.0 and 310 μmol g^{-1} and of AXAD-16-HIMB in the range 56 to 415 μmol g^{-1}. The preconcentration factors are from 150 to 300 for AXAD-16-HIMB and 67 to 250 for AXAD-2-HIMB.

For Amberlite XAD-2-DMABA (AXAD-2-DMABA) the optimum pH for quantitative sorption on was found between 4.5 and 8.5 whereas for Amberlite XAD-16-DMABA (AXAD-16-DMABA) it is between 5.0 and 7.0. A flow rate of 2-4 ml min^{-1} was found suitable for both sorption as well as elution with any of the two resins. The 2.0 M HCl completely desorbed all metal ions from the two resins except Pb which was eluted with 1.0 M HNO_3 and Pd for which a mixture of 0.6 M HCl containing 5.0 % thiourea was required. The sorption capacity of AXAD-2-DMABA was in the range 65.0 to 425 μmol g^{-1} whereas for AXAD-16-DMABA in the range 97 to 515 μmol g^{-1}.The preconcentration factors are from 100 to 450 for AXAD-16-DMABA and 50 to 400 for AXAD-2-DMABA.

The sorption of Cu(II), Pb(II), Fe(III), Zn(II), Co(II), Ni(II), Pd(II) and Cd(II) on DHB immobilized silica gel was studied. The optimum pH ranges for quantitative sorption are 6.0-7.5, 5.0-7.0, 5.5-7.0, 6.0-8.0, 6.5-8.0, 5.5-7.0, 4.5-6.0 and 6.5-7.5 respectively. All the metal ions from the matrix can be desorbed with 2.0 M HCl except Pb which was quantitatively eluted with 3.0 M HNO_3 and Pd for which 2.0 M HCl containing 2.0 % thiourea was used. A flow rate of 1.0-4.0 ml min^{-1} was found suitable for sorption and desorption. The sorption capacity of the chelating matrix is between 32 to 348 μmol g^{-1}. The $t_{1/2}$ values ≤ 20 min for all the metal ions. The preconcentration factors are between 20 and 300. The sorption of Pd(II) on IDA anchored silica gel was studied. The optimum pH range for quantitative sorption is 4.5-5.5. The Pd from the resin can be desorbed with 0.1 M HCl containing 3.0 % thiourea. A flow rate of 1.0-4.0 ml min^{-1} was found suitable for sorption, whereas for desorption 2.0-5.0 ml min^{-1} flow rate was optimum. The sorption

capacity of the chelating matrix is 192 μmol g^{-1}. The $t_{1/2}$ value is 5 min and preconcentration factor 150.

Tolerance limits of foreign species are good for chelating matrices AXAD-16-DHP, AXAD-16-HIMB and AXAD-16-DMABA. The enrichments of metal ions with the eight new chelating matrices coupled with their FAAS determination have been used for water, vitamin and milk powder analysis synthetic samples corresponding to standards are also analysed.

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