

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

By

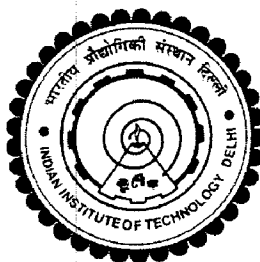
G. VENKATESH

Department of Chemistry

submitted
in fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

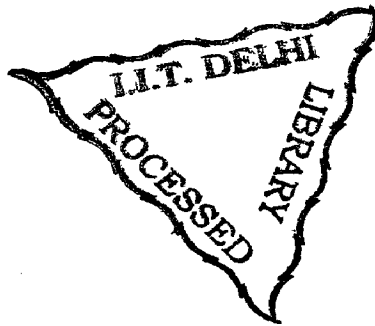
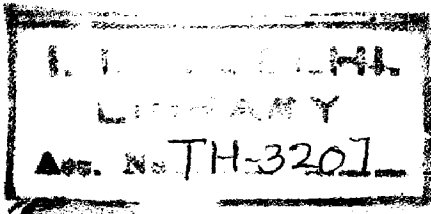
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

INDIA

SEPTEMBER, 2005



TH
S41.64
VEN-M

Dedicated to

*My Parents
&*

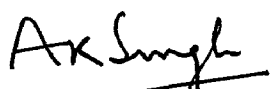
Brother

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 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. 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


~~Dr. AJAI. K. SINGH~~

Professor
Department of Chemistry
Indian Institute of Technology, Delhi
New Delhi-110 016

ACKNOWLEDGEMENT

I wish to emphasize my indebtedness to Professor Ajai K. Singh, my supervisor for his patience, valuable advice, guidance and constant encouragement throughout this work. His obsession for perfectness has always kept me on edge and has enabled me to complete my work. It wouldn't be within the power of words to describe my gratitude for him.

I would like to thank the Head, Department of Chemistry, for providing the necessary departmental facilities. I am extremely grateful to supporting staff members Mr. A. K. Aggarwal, Mrs. Shanta and Mr. Jagdish for the help they provided during the research.

I thank all my teachers who have taught throughout my academic life for raising me to this position. Especially, Late Professor. V. V. Ramachandaran, Professor. S. Meenakshi Sundaram, Professor. K. Renganathan, Professor. R. Govindarajan and Dr. R. Nagarathinam of Madura College, Madurai for their excellent guidance during my earlier days.

My sincere thanks to Mr. R. Kothandaraman (IISc, Bangalore) and Mr. J. Sankar (IIT, Kanpur) for solid state NMR and BET surface area measurements.

It is my great privilege to acknowledge invaluable help and kind co-operation of my lab colleagues, Dr. M. Kadarkaraisamy, Dr. J. Sooriyakumar, Dr. P. K. Tewari, Dr. Anupama Dutta, Dr. Vibha Lalchandani, Dr. Parbati Sengupta, Dr. Ashu Choudhry, Garima, Arun and Neetu. I am immensely thankful to Mr. Sumit Bali and Mr. P.Raghavendra Kumar for their appreciation, encouragement and extending help whenever needed.

I wish to express my appreciation and warm feelings of gratitude to all my friends, S.Vengatesan, V. Shanmugam, S. Saravanan, Francis, V.Bala Murugan, Muthulakshmi,

Kalish, Raja, Senthil Kumaran, Senthil Murugan, Mukesh, Senthil, Behera and Hanuman. They have made my stay at IIT Delhi memorable. I would also thank my seniors in different departments especially, Dr. T. Raja Gopalan, Dr. B.Bala Murugan and Dr. J. John Rajesh. I have no words to express my gratitude to Guru anna and Anitha akka for their personal affection, help and support.

Finally, I would like to thank my family members and all relatives for their love and affection, without which this work would not have been possible. I thank my brother Mr. G. Sundar, sister R. Shanthi, Brother-in-Law L. Rengarajan and kutti paiyan R. Aditya for their love and encouragement throughout my research.


G. VENKATESH

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, NaNO₃, Na₂SO₄, Na₃PO₄, 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 HNO₃ 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

$\mu\text{mol g}^{-1}$. 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 Freundlich 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 $1.0\text{--}5.0 \text{ ml min}^{-1}$ 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 $512 \mu\text{mol g}^{-1}$. 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 $1\text{--}4 \text{ ml min}^{-1}$ 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 $310 \mu\text{mol g}^{-1}$ and of AXAD-16-HIMB in the range 56 to $415 \mu\text{mol g}^{-1}$. 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 $2\text{--}4\text{ ml min}^{-1}$ 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 $425\text{ }\mu\text{mol g}^{-1}$ whereas for AXAD-16-DMABA in the range 97 to $515\text{ }\mu\text{mol g}^{-1}$. 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 $6.0\text{--}7.5$, $5.0\text{--}7.0$, $5.5\text{--}7.0$, $6.0\text{--}8.0$, $6.5\text{--}8.0$, $5.5\text{--}7.0$, $4.5\text{--}6.0$ and $6.5\text{--}7.5$ 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 $1.0\text{--}4.0\text{ ml min}^{-1}$ was found suitable for sorption and desorption. The sorption capacity of the chelating matrix is between 32 to $348\text{ }\mu\text{mol g}^{-1}$. The $t_{1/2}$ values $\leq 20\text{ min}$ 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 $4.5\text{--}5.5$. The Pd from the resin can be desorbed with 0.1 M HCl containing 3.0% thiourea. A flow rate of $1.0\text{--}4.0\text{ ml min}^{-1}$ was found suitable for sorption, whereas for desorption $2.0\text{--}5.0\text{ ml min}^{-1}$ flow rate was optimum. The sorption

capacity of the chelating matrix is $192 \mu\text{mol g}^{-1}$. 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.

TABLE OF CONTENTS

	Contents	Page No.
1.	Certificate	i
2	Acknowledgement	ii
3	Abstract	iv
4	List of Figures	xv

CHAPTER 1 INTRODUCTION

1.1	Introduction	1
1.2	Macromolecular Chelators	1
1.3	Silica gel based Chelating Matrices	4
1.4	Chelating Resins based on Amberlite Series Resins	16
1.4.1	Amberlite XAD-2	17
1.4.2	Amberlite XAD-4	25
1.4.3	Amberlite XAD-7	28
1.4.4	Amberlite XAD-16	31
1.5	Cellulose based Macromolecular Chelators	31
1.6	Present Work and its Scope	37
1.7	References	40

CHAPTER 2 EXPERIMENTAL

A	Materials and Methods	53
2.1	Instrumentation	53
2.2	Reagents and Solutions	55
2.3	Column Preparations	58

2.4	Flow Rate Control	58
2.5	Statistical Evaluation of Data	58
B	Designing and Characterization of Macromolecular Chelators	59
2.6	Synthesis and Characterization of Functionalized Silica gel	59
2.6.1	Preparation of Aminopropyl Silica gel	60
2.6.2	Preparation of Chloropropyl Silica gel	60
2.6.3	Anchoring of Chelating Ligands on Silica gel	61
2.7	Characterization of Functionalized Silica gel	61
2.8	Synthesis and Characterization of Functionalized Amberlite XAD-2 and 16	72
2.9	Amberlite XAD-2/16 based Chelating Resins: Synthesis and Characterization	72
2.9.1	Synthesis and Characterization of DMABA	72
2.9.2	Synthesis and Characterization of HIMB	73
2.9.3	Nitration of Amberlite XAD-2/16	81
2.9.4	Synthesis of Amino Resin	81
2.9.5	Diazotization of Amino Resin	81
2.9.6	Synthesis of Amberlite XAD-2/16 immobilized with 2,3-Dihydroxypyridine (DHP)	82
2.9.7	Synthesis of Amberlite XAD-2/16 immobilized with 4- {[2-Hydroxyphenyl)-imino]methyl}-1,2-benzenediol (HIMB)	82
2.9.8	Synthesis of Amberlite XAD-2/16 immobilized with 2- {[1-(3,4-Hydroxyphenyl)-methylidene]amino}-benzoic acid (DMABA)	84
2.10	Characterization of Resins	84
2.11	References	97

CHAPTER 3

METAL ION EXTRACTION WITH 2,3-DIHYDROXYPYRIDINE(DHP) IMMOBILIZED AMBERLITE XAD-2/16

3.1	Experimental	99
3.1.1	Recommended Procedure for Preconcentration and Determination of Metal Ions	100
3.2	Results and Discussion	102
3.2.1	Effect of pH	102
3.2.2	Effect of Flow Rate and Eluent	102
3.2.3	Breakthrough Elution Volume	109
3.2.4	Kinetics of Metal Sorption	112
3.2.5	Effects of Electrolytes and Cations	115
3.2.6	Adsorption Isotherms and Feasibility of the Process	115
3.2.7	Sorption Capacity	120
3.2.8	Resin Stability and Reusability	120
3.2.9	Preconcentration and Recovery of Metal Ions	121
3.3	Application of the Method	124
3.3.1	Determination of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) in Water Samples	124
3.3.2	Determination of Co in Pharmaceutical Samples	127
3.3.3	Determination of Zn in Milk Sample	127
3.3.4	Analysis of Synthetic Water Samples	128
3.3.5	Analysis of Palladium in Synthetic Materials	128
3.4	Comparison with other Preconcentrating Matrices	129
3.5	Conclusions	132
3.6	References	135

CHAPTER 4

METAL ION EXTRACTION WITH 4-[(2-HYDROXYPHENYL) IMINO] METHYL}-1,2-BENZENEDIOL (HIMB) IMMOBILIZED AMBERLITE XAD-2/16

4.1	Experimental	138
4.1.1	Recommended Procedure for Preconcentration and Determination of Metal Ions	139
4.2	Results and Discussion	140
4.2.1	Effect of pH	140
4.2.2	Effect of Flow Rate	141
4.2.3	Kinetics of Metal Sorption	148
4.2.4	Effects of Electrolytes and Cations	148
4.2.5	Sorption Capacity	151
4.2.6	Resin Stability and Reusability	155
4.2.7	Preconcentration and Recovery of Metal Ions	155
4.3	Application of the Method	158
4.3.1	Determination of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) in Water Samples	158
4.3.2	Determination of Co in Pharmaceutical Samples	161
4.3.3	Determination of Zn in Milk Sample	161
4.3.4	Analysis of Synthetic Water Samples	162
4.4	Comparison with other Preconcentrating Matrices	162
4.5	Conclusions	166
4.6	References	167

CHAPTER 5

METAL ION EXTARCTIONWITH 2-{{1-(3,4-DIHYDROXYPHENYL) METHYLIDENE}AMINO}-BENZOICACID (DMABA) IMMOBILIZED AMBERLITE XAD-2/16

5.1 Experimental 170

5.1.1	Recommended Procedure for Preconcentration and Determination of Metal Ions	171
5.2	Results and Discussion	173
5.2.1	Effect of pH	173
5.2.2	Effect of Flow Rate and Eluent	173
5.2.3	Breakthrough Elution Volume	180
5.2.4	Kinetics of Metal Sorption	183
5.2.5	Effects of Electrolytes and Cations	186
5.2.6	Sorption Capacity	186
5.2.7	Resin Stability and Reusability	190
5.2.8	Preconcentration and Recovery of Metal Ions	191
5.3	Application of the Method	194
5.3.1	Determination of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) in Water Samples	194
5.3.2	Determination of Co in Pharmaceutical Samples	197
5.3.3	Determination of Zn in Milk Sample.	197
5.3.4	Analysis of Synthetic Water Samples	198
5.3.5	Analysis of Palladium in Synthetic Materials	198
5.4	Comparison with other Preconcentrating Matrices	199
5.5	Conclusions	202
5.6	References	204

CHAPTER 6 **METAL ION EXTRACTION WITH 3,4-DIHYDROXY BENZALDEHYDE (DHB) AND IMINODIACETIC ACID IMMOBILIZED SILICA GEL**

6A.1	Experimental	207
6A.1.1	Recommended Procedure for Preconcentration and Determination of Metal Ions	208
6A.2	Results and Discussion	209

6A.2.1	Effect of pH	209
6A.2.2	Effect of Flow Rate	210
6A.2.3	Acid Concentration for Desorption	214
6A.2.4	Breakthrough Volume for Elution	214
6A.2.5	Kinetics of Metal Sorption	216
6A.2.6	Sorption Capacity	216
6A.2.7	Effects of Electrolytes and Cations	218
6A.2.8	Adsorption Isotherms and Feasibility of the Sorption Process	220
6A.2.9	Stability of the Matrix	226
6A.2.10	Reusability of the Matrix	226
6A.2.11	Preconcentration and Recovery of Metal Ions	227
6A.2.12	Limit of Detection and Quantification	227
6A.3	Application of the Method	229
6A.3.1	Determination of Zn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) in Water Samples	229
6A.3.2	Determination of Co in Pharmaceutical Samples	229
6A.3.3	Determination of Zn in Milk Sample	231
6A.3.4	Analysis of Synthetic Water Samples	231
6A.3.5	Analysis of Palladium in Synthetic Materials	232
6A.4	Comparison with other Preconcentrating Matrices	232
6A.5	Conclusions	236
6B.1	Experimental	238
6B.1.1	Recommended Procedure for Preconcentration and Determination of Metal Ions	239
6B.2	Results and Discussion	240
6B.2.1	Effect of pH	240

6B.2.2	Effect of Flow Rate	241
6B.2.3	Acid Concentration for Desorption	241
6B.2.4	Breakthrough Volume for Elution	242
6B.2.5	Kinetics of Metal Sorption	242
6B.2.6	Sorption Capacity	247
6B.2.7	Adsorption Isotherms and Feasibility of the Sorption Process	247
6B.2.8	Effects of Electrolytes and Cations	249
6B.2.9	Stability of the Matrix	249
6B.2.10	Reusability of the Matrix	250
6B.2.11	Preconcentration and Recovery of Metal Ions	250
6B.2.12	Limit of Detection and Quantification	252
6B.3	Application of the Method	252
6B.3.1	Analysis of Palladium in Synthetic Materials	252
6B.4	Conclusions	252
6B.5	References	254
SUMMARY		256
CURRICULUM VITAE		262