DECLARATION

I, Nimisha K. V, hereby declare that this thesis entitled “STUDIES ON SOME COMPOSITE ION EXCHANGERS AND TO INVESTIGATE THEIR ANALYTICAL IMPORTANCE” is the bona fide research work carried out by me under the supervision and guidance of Dr. C JANARDANAN, Post Graduate and Research Department of Chemistry, S. N College, Kannur. I further declare that the thesis has not previously formed the basis for the award of any other Degree or Diploma of any other similar title.

NIMISHA K. V
Acknowledgement

First and foremost, I would like to express my profound gratitude to my research guide and supervisor, Dr. C. Janardanan, for his constructive suggestions, constant encouragement, timely support and academic freedom. His valuable experience, scholarly guidance, and practical approaches have indeed been an inspiration for me.

My sincere thanks are due to Dr. Sivadasan Thirumangalath, Principal, Sree Narayana College, Kannur for providing adequate facilities for my research work. I express my thank to Dr. C. Reetha, The Head of the Department of Chemistry, Sree Narayana College, Kannur and our former HOD Dr. T. N. Sreelatha, for kindly providing us the necessary laboratory facilities.

A word of appreciation goes to the teaching and non-teaching staff of Chemistry Department of Sree Narayana College, Kannur for extending full cooperation and support during my research studies. I also express my sense of gratitude to Smt. Latha, Associate Professor, Department of English for her help and valuable suggestions.

I express my sincere gratitude to Dr. S. Sudheesh, Course Co-ordinator, Head of the Department & Dr. K. R. Haridas, Professor, School of Chemical Science, Payyannur Campus for providing all the facilities during course work period.

I am grateful to the CSIR for the financial assistance given to me in the period of my research work.

I express my sense of gratitude to all my labmates, specially Dr. Vinisha Valsaraj P, as always, they gave unselfishly of their time, energies and competence. Without their generous help and support I could not have finished this work. Also, I express my sincere gratitude to all the senior members of our research group.
I am grateful to the scientists at SAIF (STIC, CUSAT, Kochi), for providing technical facilities for the analysis of samples. I wish to thank KSCSTE, Trivandrum for the instrumental facility made available to our research centre under SARD project. I am also grateful to Dr. Shanavas, Arts College, Trivandrum, and Biogenix centre, Trivandrum for providing technical support.

I am thankful to Midas, Kannur for the excellent printing of the thesis.

I feel short words and full of emotions in thanking my grandmother and my uncle for their unconditional love, constant inspiration, blessings and good foundation with which to meet life they have provided. Special thanks go to my parents, especially my late mother, her blessings and encouragement lead me to achieve this phenomenal dream.

I express sincere gratitude to my in-laws, brothers, sisters and to all the members of family for all their support, encouragement and co-operation during the period of my research work. And special thanks go to my neighbours, especially Namiechi, Molyechi and Sneha for their love and caring of my little daughter. I am very much thankful to all my friends and my teachers for their help, caring, support and constant encouragement.

I consider myself to be fortunate enough to have a caring and understanding Husband Mr. Vijil and I express my loving thanks to him for his consideration, constant support and encouragement. Our baby Vaidehi deserves special thank for her pleasant smile, enthusiasm, patience and understanding.

I conclude this acknowledgement by thanking god for all the blessings showered upon me throughout my life.

NIMISHA K V
PREFACE

The research work done in the thesis entitled “Studies on some composite ion exchangers and to investigate their analytical importance” is compiled in eight chapters:

First chapter is a brief introduction on different aspects of ion exchange techniques. It deals with brief history of ion exchangers, properties, theory of ion exchange etc. A detailed classification of ion exchangers and details of composite ion exchangers are also given. Thorough reviews of literature covering application of composite exchangers in different field are included with a view to highlight new technological possibilities. At the end of this chapter the inspiration and main objectives of the work are elaborated.

The second chapter presents the studies on conducting polymer, polyaniline based ion exchanger. The details of materials used, preparation of reagent solutions and synthetic methods adopted were detailed here. The experimental details of physico-chemical characterizations and structural characterization of the composite ion exchangers are also included in this chapter. Detailed investigations of the results of various characterization experiments on synthesized polyaniline based composite exchangers are carried out. Separation potential and selectivity of various ion exchangers towards heavy metal ions are explained in detail. Some analytically important binary separations are achieved using the column of the exchanger and are detailed in the last part of this chapter.

In third chapter procedure adopted for the preparation of pectin based exchangers are explained. The results of ion exchange studies including ion exchange capacity, pH titration etc., have been discussed. The result of characterization of the synthesized exchangers by different techniques such as FTIR, TG, XRD etc., were explained. Applications of the synthesized exchanger in the separation of analytically important binary metal mixtures are also detailed in this chapter.

The fourth chapter covers applications of synthesized composite exchangers in waste water detoxification by sorbing toxic heavy metal ions. Details on the application of PANI-ZrMoSi exchanger for the recovery of Th(IV) metal ions and regeneration of exchanger are explained in the first part of this chapter. Kinetic, sorption and thermodynamic studies evaluated for Th(IV) ion sorption by PANI-ZrMoSi exchangers are
explained. Details of experiments and results of industrial waste water treatments carried out by different exchangers and separation and recovery of toxic metal ions from different industrial effluents using synthesized composite exchangers are explained.

Fifth chapter describes the potentiality of composite exchangers in removing toxic organic pollutants such as organic dyes phenol and antibiotic amoxicillin. Solar light driven photocatalytic degradation of different dyes carried out using synthesized composite exchangers is elucidated. The sorption potential of composite exchanger towards the pharmaceutical pollutant amoxicillin antibiotic has been utilized for their removal from aqueous solution. The study on application of PANI-CeMoSi exchanger for the removal of phenol from aqueous solution is also included.

Some biomedical applications of the composite exchangers are included in the sixth chapter. Application of composite exchanger in drug delivery field is explored by using Pc-ZrMoSi exchanger and salicylic acid as model drug. Mechanism of drug release was analysed using different kinetic models. Anti microbial activity of some synthesized ion exchangers towards \textit{E.coli} and \textit{S.aureus} was also included in this chapter.

Seventh chapter deals with some supplementary applications of synthesized ion exchangers. Details of application of ion exchangers as heterogeneous acid catalyst were illustrated using PANI-ZrWTe exchanger towards sucrose hydrolysis reaction. Also special property of photochromic behaviour Pc-ZrMoSi exchanger is discussed in second part of this chapter.

A general conclusion about the works carried out and scope of further investigations probable in this field were given in chapter 8.

References used in the text are given in serial order at the end of the thesis.

A list of research works published and papers presented by the author in seminars and conferences are given below. Research papers communicated are also included.


Poly aniline-zirconium tellurotungstate composite ion exchanger: an ecofriendly and effective solid acid catalyst for sucrose inversion, Nimisha K V and Janardanan C, accepted in *Chemistry-An Indian Journal*.


Removal of chlorobenzene and 1,4-dichlorobenzene using novel poly-o-toluidine zirconium(IV) phosphotellurite exchanger, Aparna Mohan, Nimisha K V and Janardanan (Accepted in *Resource Efficient Technologies*).

Synthesis, characterization and application of poly aniline- zirconium(IV) molybdosilicate exchanger for adsorptive recovery of Th(IV) ions from aqueous solution, Nimisha K V and Janardanan C (Communicated in *Desalination and Water Treatment*).
Synthesis, characterization of pectin-zirconium(IV) molybdosilicate composite cation exchanger and its application as drug carrier and anti bacterial agents, Nimisha K V and Janardanan C (Communicated in New Journal of Chemistry).


Adsorptive removal of amoxicillin antibiotic from aqueous solution using Pectin-Tin(IV) molybdosilicate composite cation exchanger, Nimisha K V and Janardanan C (communicated in International Journal of Chemtech Research).

Preparation and application of pectin-cerium (IV) tungstosilicate composite exchanger for the degradation of hazardous organic dyes, Nimisha K V and Janardanan C (Communicated in Journal of Industrial and Engineering Chemistry).
CONTENTS

CHAPTER 1

INTRODUCTION & LITERATURE REVIEW

1.1 Ion Exchange 1
1.2 Milestones in Ion Exchange 3
1.3 Ion exchange theory 4
  1.3.1 Crystal lattice exchange theory 4
  1.3.2 The double layer theory 4
  1.3.3 Donnan membrane theory 5
1.4 General properties of ion exchangers 5
  1.4.1 Ion exchange capacity 5
  1.4.2 Selectivity and distribution coefficient 6
  1.4.3 Ion exchange equilibrium 7
  1.4.4 Binary exchange 7
  1.4.5 Chemical stability and thermal stability 9
1.5 Classification of ion exchangers 9
  1.5.1 Organic Ion exchangers 10
    a) Strong and Weak Acid Cation Resins 11
    b) Strong and weak Base Anion Resins 11
  1.5.2 Inorganic ion exchangers 12
  1.5.3 Composite (Organic-Inorganic) ion exchangers 15
    1.5.3.1 Polymer composites 16
    1.5.3.2 Bio composites/Green composites 17
  1.5.4 Liquid ion exchangers 18
  1.5.5 Chelating ion exchangers 18
  1.5.6 Redox exchangers 19
1.6 Utility of composite ion exchangers: Literature review 19
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF POLYANILINE BASED
COMPOSITE ION EXCHANGERS AND THEIR APPLICATION IN BINARY
SEPARATION OF METAL IONS

2.1 Experimental

2.1.1 Chemicals and reagents

2.1.2 Apparatus and instruments

2.2 Synthesis

2.2.1 Synthesis of organic matrix Polyaniline

2.2.2 Synthesis of inorganic precipitate

2.2.2.1 Synthesis of Zirconium(IV) molybdosilicate

2.2.2.2 Synthesis of Cerium(IV) molybdosilicate

2.2.2.3 Synthesis of Tin(IV) molybdosilicate

2.2.2.4 Synthesis of Zirconium(IV) tungstotellurite

2.2.3 Synthesis of Polyaniline based composites exchangers

2.2.3.1 Synthesis of Polyaniline Zirconium(IV) molybdosilicate

2.2.3.2 Synthesis of Polyaniline Cerium(IV) molybdosilicate

2.2.3.3 Synthesis of Polyaniline Tin(IV) molybdosilicate

2.2.3.4 Synthesis of Polyaniline Zirconium(IV) tungstotellurite

2.3 Physico-chemical properties of composite ion exchangers

2.3.1 Determination of ion exchange capacity (IEC)

2.3.2 Chemical stability

2.3.3 Effect of temperature on IEC

2.3.4 Ion exchange capacity (IEC) for other metal ions

2.3.5 pH titration

2.3.6 Specific surface area

2.3.7 Distribution coefficient ($K_d$)

2.3.8 Quantitative separation of metal ions from binary
synthetic metal mixtures

2.4 Structural characterizations

2.4.1 Fourier Transform Infrared (FTIR) Spectroscopy
2.4.2 Thermo gravimetric analysis 39
2.4.3 X-ray Diffraction (XRD) 39
2.4.4 SEM and Energy Dispersive X-ray Spectroscopy (EDS) 40
2.4.5 High resolution Tunneling Electron Microscopy (HR TEM) 40
2.4.6 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) 40

2.5 Results and discussions 41

2.5.1 Preparation condition and ion exchange capacity of ion exchangers 41
2.5.2 Chemical stability 44
2.5.3 Effect of temperature on IEC 45
2.5.4 Ion exchange capacity (IEC) for other metal ions 46
2.5.5 pH Titration Curve 46
2.5.6 FTIR studies 49
2.5.7 Thermo Gravimetric-Differential Thermo Gravimetric Analysis 52
2.5.8 X-ray diffraction (XRD) studies 56
2.5.9 Specific Surface Area 58
2.5.10 SEM studies 59
2.5.11 Energy Dispersive X ray (EDX) spectra 62
2.5.12 Chemical composition 63
2.5.13 HR TEM studies 65
2.5.14 UV-Visible Diffuse Reflectance Spectroscopic Studies 65
2.5.15 Distribution studies in water and other electrolytes 70
2.5.16 Quantitative separation of metal ions from binary synthetic metal mixtures 75

CHAPTER 3 79 - 104
SYNTHESIS AND CHARACTERIZATION OF PECTIN BASED COMPOSITE ION EXCHANGERS AND THEIR APPLICATION IN BINARY SEPARATION OF METAL IONS

3.1 Experimental 80
3.1.1 Reagents and solutions 80
3.1.2 Apparatus and instruments 80

3.2 Synthesis 80

3.2.1 Synthesis of pectin gels 80
3.2.2 Synthesis of Inorganic precipitate 80
  3.2.2.1 Synthesis of Cerium (IV) tungstosilicate 80
  3.2.2.2 Synthesis of M(IV) molybdosilicate 81
3.2.3 Synthesis of pectin based composite exchangers 81
  3.2.3.1 Synthesis of Pectin-Cerium(IV) tungstosilicate 81
  3.2.3.2 Synthesis of Pectin-M(IV) molybdosilicate 81

3.3 Physico-chemical properties of composite ion exchangers 81

3.4 Structural characterizations 82

3.5 Results and discussions 82

  3.5.1 Preparation condition and ion exchange capacity 82
  3.5.2 Chemical stability 84
  3.5.3 Effect of temperature on IEC 84
  3.5.4 Ion exchange capacity (IEC) for other metal ions 85
  3.5.5 pH titration curve 86
  3.5.6 FTIR studies 87
  3.5.7 Thermo Gravimetric-Differential Thermo Gravimetric Analysis 88
  3.5.8 X-ray diffraction (XRD) studies 91
  3.5.9 Specific Surface Area 92
  3.5.10 SEM (Scanning Electron Microscopy) studies 92
  3.5.11 Energy Dispersive X ray (EDX) spectra 94
  3.5.12 Chemical composition and Empirical formula 95
  3.5.13 HR TEM studies 95
  3.5.14 UV-Visible Diffuse Reflectance Spectroscopic Studies 96
  3.5.15 Distribution studies in water and other electrolytes 98
  3.5.16 Quantitative separation of metal ions from binary
  synthetic metal mixtures 101
CHAPTER 4

WASTEWATER DETOXIFICATION AND ADSORPTIVE RECOVERY OF METAL IONS USING SOME SYNTHESISED COMPOSITE ION EXCHANGERS

4.1 Removal and recovery of Thorium (IV) ions using PANI-ZrMoSi exchanger

4.1.1 Experimental

4.1.1.1 Synthesis and measurements

4.1.1.2 Sorption Experiments

4.1.1.3 Effect of process parameters on sorption

4.1.1.4 Feasibility Test

4.1.1.5 Kinetic, Sorption and Thermodynamic studies

4.1.1.6 Regeneration of exchanger

4.1.2 Results and Discussions

4.1.2.1 Th(IV) loading confirmation

4.1.2.2 Effect of process parameters on sorption

4.1.2.3 Adsorption kinetics

4.1.2.4 Adsorption isotherm

4.1.2.5 Thermodynamic parameters

4.1.2.6 Test with artificial sea water

4.1.2.7 Regeneration Experiments

4.2 Industrial waste water treatment using some synthesized exchangers

4.2.1 Experimental

4.2.1.1 Sample collection and pretreatment

4.2.1.2 Column preparation

4.2.1.3 Regeneration of cation exchanger

4.2.2 Results and discussions

4.2.2.1 Separation of Cu(II) and Cd(II) using Pc-SnMoSi from metal plating and fertiliser industry waste water

4.2.2.2 Separation of Pb(II), Cu(II) and Zn(II) from textile industry effluents using Pc-CeWSi

4.2.2.3 Removal efficiency of composite exchangers towards Hg(II) and Pb(II) ions from synthetic waste water-A comparative study
CHAPTER 5

REMOVAL OF HAZARDOUS ORGANIC POLLUTANTS USING SOME SYNTHESISED COMPOSITE ION EXCHANGERS

SECTION I- STUDIES ON DYE REMOVAL

5.1 Photocatalytic degradation of dyes using Pc-CeWSi exchanger
   5.1.1 Experimental
   5.1.2 Results and discussions
      5.1.2.1 Mechanism of dye degradation
      5.1.2.2 Effect of parameters
      5.1.2.3 Kinetics of photodegradation
      5.12.4 Reusability of the catalyst

5.2 Photocatalytic degradation of MB and CV dyes using PANI-CeMoSi exchanger

5.3 Photocatalytic degradation of Rhodamine B dye using Pc-CeMoSi exchanger

SECTION II- REMOVAL STUDIES OF OTHER ORGANIC POLLUTANTS

5.4 Removal of antibiotic amoxicillin from aqueous solution using Pc-SnMoSi exchanger
   5.4.1 Experimental
   5.4.1.1 Materials
   5.4.1.2 Sorption studies
   5.4.2 Results and discussions
      5.4.2.1 Amoxicillin loading confirmation
      5.4.2.2 Sorption kinetics
      5.4.2.3 Sorption isotherm
      5.4.2.4 Mass transfer aspects of amoxicillin sorption on Pc-SnMoSi
   5.4.3 Desorption and reusability of the exchanger

5.5 Removal of phenol from aqueous solution using PANI-CeMoSi exchanger
   5.5.1 Experimental
   5.5.2 Results and discussions
   5.5.3 Regeneration of exchanger
CHAPTER 6  153 - 172

BIOMEDICAL APPLICATIONS OF SOME SYNTHESIZED COMPOSITE ION EXCHANGERS

6.1 Drug delivery applications 155
  6.1.1 Experimental 155
    6.1.1.1 Materials 155
    6.1.1.2 Preparation and characterization of drug carrier 155
    6.1.1.3 Cell viability test 156
    6.1.1.4 Drug loading studies 157
    6.1.1.5 In-vitro Drug release studies 158
  6.1.2 Results and Discussions 159
    6.1.2.2 Drug loading confirmation 159
    6.1.2.2 Cytotoxicity analysis of Pc-ZrMoSi 160
    6.1.2.3 Intercalation conditions 161
    6.1.2.4 In-vitro release studies 163
    6.1.2.5 In-vitro drug release kinetics 164
    6.1.2.6 Activity studies of SA loaded Pc-ZrMoSi exchanger 166

6.2 Antimicrobial applications 167
  6.2.1 Experimental 168
  6.2.2 Results and discussions 169

CHAPTER 7  173 - 180

STUDY OF CATALYTIC APPLICATIONS AND CHROMIC PROPERTY OF COMPOSITE ION EXCHANGERS

7.1 Composite ion exchangers as solid acid catalyst for sucrose inversion 173
  7.1.1 Experimental 174
    7.1.1.1 Reagents 174
    7.1.1.2 Catalytic Experiments 174
  7.1.2 Results and discussion 175
    7.1.2.1 Effect of pH 175
    7.1.2.2 Effect of temperature 175
7.1.2.3 Effect of concentration of sucrose
7.1.2.4 Effect of catalyst dosage
7.1.3 Reusability of the catalyst
7.2 Photochromic property of Pectin-Zirconium(IV) molybdosilicate composite exchanger
7.2.1 Results and discussions

CHAPTER 8 181 - 186
SUMMARY AND FUTURE SCOPE
8.1 Summary 181
8.2 Future scope 185

REFERENCES 187 - 204