REMOVAL OF HEAVY METALS FROM WASTEWATER MODEL BY USING POLYBENZOXAZINE-BASED AEROGEL AS A POLYMERIC LIGAND EXCHANGER



Tidarat Komalwanich

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2009

Thesis Title: Removal of Heavy Metals from Wastewater Model by Using

Polybenzoxazine-based Aerogel as A Polymeric Ligand

Exchanger

By: Tidarat Komalwanich

Program: Polymer Science

Thesis Advisors: Assoc. Prof. Sujitra Wongkasemjit

Dr. Thanyalak Chaisuwan

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

(Assoc. Prof. Sujitra Wongkasemjit)

(Dr. Thanyalak Chaisuwan)

Thanyalde Chaism

(Asst. Prof. Manit Nithitanakul)

(Asst. Prof. Dr. Bussarin Ksapabutr)

ABSTRACT

5072026063: Polymer Science Program

Tidarat Komalwanich: Removal Heavy Metal from Wastewater

Model by Using Polybenzoxazine-based aerogel as A Polymeric

Ligand Exchanger.

Thesis Advisors: Assoc. Prof. Sujitra Wongkasemjit, and

Dr. Thanyalak Chaisuwan 42 pp.

Keywords: Heavy metals/ Wastewater/ Polymeric ligand exchanger/ Building

block/ Binding unit/ Polybenzoxazine-based aerogel/ Metal-ligand

complexes

Heavy metals are commonly associated with water pollution; therefore, the removal of heavy metals from wastewater has become a necessity. Polymeric ligand exchangers (PLE) are a class of promising sorbents that absorbs chemicals based on their ligand characteristics rather than ionic charges. In the present study, polybenzoxazine based aerogel is chosen as the polymeric ligand exchanger. Nitrogen donor atoms in polybenzoxazine molecule are used as metal hosting sites. The removal of metal ions is in the following order: $\text{Sn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{2+}$; which is in accordance with the Irving-Williams rule. Additionally, the efficiency of the metal ion removal depends on the amount of absorbents and absorption time while the desorption process is a function of pH, type of solution, and temperature.

บทคัดย่อ

ธิดารัตน์ โกมลวานิช: การกำจัดโลหะหนักจากน้ำเสียโดยใช้ออร์กานิกแอโรเจลที่ เครียมจากพอลิเบนซอกซาซีน (Removal Heavy Metal from Wastewater Model by Using Polybenzoxazine-based aerogel as A Polymeric Ligand Exchanger) อ.ที่ปรึกษา: รอง ศาสตราจารย์ ดร.สุจิตรา วงศ์เกษมจิตต์ และ ดร. ธัญญูลักษณ์ ฉายสุวรรณ์ 42 หน้า

โลหะหนักเป็นอีกหนึ่งปัจจัยที่ทำให้เกิดมลพิษทางน้ำ ดังนั้นการกำจัดโลหะหนักออก จากน้ำเสียจึงเป็นปัญหาที่โรงงานอุตสาหกรรมจำเป็นต้องแก้ไข วัตถุประสงค์ของงานนี้คือ การศึกษาการเตรียมออร์กานิกแอโรเจลจากพอลิเบนซอกซาซีนเพื่อใช้เป็นลิแกรนสำหรับจับโลหะ หนักในน้ำเสีย จากการวิเคราะห์ผลการทดลองพบว่า แนวโน้มความสามารถในการจับโลหะหนัก ของแอโรเจลที่เตรียมได้เป็นไปตามลำดับดังนี้ ดีบุก > ทองแดง > เหล็ก > ตะกั่ว > นิเกิล > แคดเมียม > โครเมียม โดยที่โลหะหนักดังกล่าวเป็นไอออนที่มีประจุเท่ากับสองบวก การเกิด พันธะระหว่างแอโรเจลกับไอออนของโลหะในสารละลายที่ผสมเป็นเนื้อเดียวกันสามารถอธิบาย โดยใช้กฎของเออร์วิงและวิลเลียม ยิ่งไปกว่านั้น เราพบว่า ค่าการดูดซับของโลหะหนักใน สารละลายขึ้นอยู่กับปริมาณของแอโรเจลที่ใช้ในการดูดซับและเวลา สำหรับการนำแอโรเจลกลับ มาใช้อีกครั้ง โดยการกำจัดโลหะหนักที่ถูกดูดซับออกขึ้นอยู่กับสารละลาย ค่าความเป็นกรดด่าง และอุณหภูมิ

ACKNOWLEDGEMENTS

The author would like to thank Associate Professor Sujitra Wongkasemjit, her advisor, and Dr. Thanyalak Chaisuwan, her co-advisor, who not only originated this work, but also gave her continuous support, good suggestion, intensive recommendation and for the help, patience, encouragement they have shown during her one year in their research group.

She wishes to thank her thesis committee Assistant Professor Manit Nithitanakul and Assistant Professor Bussarin Ksapabutr for their suggestion and invaluable guidance.

Special thanks are to all of the Petroleum and Petrochemical College's professors who have given valuable knowledge to her at PPC and to the college staff who willingly gave support and encouragement.

She is grateful for the scholarship from the Petroleum and Petrochemical College; and the Center for Petroleum, Petrochemical, and Advanced Materials; and Ratchadapisake Sompote, Chulalongkorn University.

Her thanks are also to all her seniors and her friends for their helps, good suggestion, friendship and all the good memories.

Last, but not least, she thanks her family for giving her life, for educating her and unconditional support to pursue her interests and also for their love and encouragement.

TABLE OF CONTENTS

| | | PAGE |
|------|--|------|
| 7 | Title Page | i |
| A | Abstract (in English) | iii |
| A | Abstract (in Thai) | iv |
| P | Acknowledgements | v |
| 7 | Table of Contents | vi |
| I | List of Tables | ix |
| I | List of Figures | X |
| A | Abbreviations | xii |
| | | |
| CHAI | PTER | |
| 1 | INTRODUCTION | 1 |
| I | I LITERATURE REVIEW | 3 |
| | 2.1 Metal-ions in Wastewater | 3 |
| | 2.1.1 Removal of Toxic Metal from Wastewater | |
| | by Plant Wastes as Adsorbent | 3 |
| | 2.1.2 Removal of Toxic Metal from Wastewater | |
| | by Chitosan as Adsorbent | 4 |
| | 2.1.3 Removal of Toxic Metal from Wastewater by | |
| | Polymeric Chelating Fiber as Adsorbent | 4 |
| | 2.1.4 Removal of Toxic Metals from Wastewater by | |
| | Using Natural Zeolite Scolecite as Adsorbent | 5 |
| | 2.2 Polybenzoxazines | 6 |
| | 2.2.1 Addition of a Propargyl Group into Benzoxazine | |
| | Monomer | 7 |
| | | |

| CHAPTER | | | PAGE |
|---------|----------|---|------|
| | 2.2.2 | Addition of Allyl Group into Benzoxazine Monomer | 8 |
| | | Addition of Imide Group into Benzoxazine Monomer | 9 |
| | | Addition of Aromatic or Aliphatic Diamine into | |
| | | Benzoxazine Monomer | 10 |
| | 2.3 Poly | meric Ligand Exchangers (PLE) | 11 |
| | | Using Polymeric Ligand Exchanger for Removal | • • |
| | | of Trace Contaminants from Water | 11 |
| | 2 3 2 | Using Polymeric Ligand Exchanger for Removal | •• |
| | | of Tartaric Acid | 12 |
| | 2.3.3 | Using Polymeric Ligand Exchanger for Removal | |
| | 2.0.0 | of Arsenate from Drinking Water | 13 |
| | 2.3.4 | Using Polymeric Ligand Exchanger for Removal | 15 |
| | | of Phosphate from Reverse Osmosis (RO) | 14 |
| Ш | EXPERI | MENTAL | 15 |
| | 3.1 Mate | | 15 |
| | 3.2 Equ | ipment | 15 |
| | | Fourier Transform Infrared Spectroscopy (FT-IR) | 15 |
| | | Thermogravimetric Analysis (TGA) | 15 |
| | | Scanning Electron Microscope (SEM) | 16 |
| | | Transmission Electron Microscope (TEM) | 16 |
| | | Nuclear Magnetic Resonance (NMR) | 16 |
| | | Differential Scanning Calorimetry (DSC) | 16 |
| | | Surface Area Analyzer (SAA) | 16 |
| | | Inductively Coupled Plasma Spectrometer(ICP) | 16 |
| | | hodology | 17 |
| | | Synthesis of Organic Aerogel from Polybenzoxazine | 17 |
| | | Characteristics of Polybenzoxazine-based Aerogel | 17 |
| | | Metal Sorption Studies | 17 |

| CHAPTER | | PAGE |
|---------|--|------|
| | 3.3.4 Desorption Experiments | 18 |
| | 3.3.5 Quantitative Analysis of The Adsorbed Metal-ion on | |
| | Polybenzoxazine-based Aerogel | 18 |
| IV | REMOVAL OF HEAVY METALS FROM WASTEWATER | R BY |
| | POLYBENZOXAZINE-BASED AEROGEL | 19 |
| | 4.1 Abstract | 19 |
| | 4.2 Introduction | 20 |
| | 4.3 Experimental | 21 |
| | 4.3.1 Materials | 21 |
| | 4.3.2 Measurements | 21 |
| | 4.3.3 Methodology | 22 |
| | 4.4 Results and Discussion | 23 |
| | 4.5 Conclusions | 35 |
| | 4.6 Acknowledgements | 35 |
| | 4.7 References | 35 |
| V | CONCLUSIONS AND RECOMMENDATIONS | 38 |
| | REFERENCES | 39 |
| | CURRICULUM VITAE | 42 |

LIST OF TABLES

| TABLE | | PAGE |
|-------|--|------|
| | CHAPTER II | |
| 2.1 | Properties of various polymeric sorbents | 12 |
| 2.2 | Characteristics of DowexM-9145, its Cu(II)-bound | |
| | derivative D-Cu | 13 |
| 2.3 | Characteristics of DOW 3N, IRA 900, and IRA 958 | 14 |

LIST OF FIGURES

| FIGURE | | PAGE | |
|--------|--|------|--|
| | CHAPTER II | | |
| 2.1 | Benzoxazine polymerization | 6 | |
| 2.2 | Preparation of P-appe and B-appe | 8 | |
| 2.3 | Preparation of P-ala and B-ala | 8 | |
| 2.4 | A possible reaction at the maleimide site is the | | |
| | copolymerization of maleimide | 9 | |
| 2.5 | Preperation of polybenzoxazine precursors | 10 | |
| 2.6 | Structures of B-a and PB-a | 11 | |
| | CHAPTER IV | | |
| 4.1 | Chemical reaction of polybenzoxazine-based aerogel | | |
| | synthesis | 24 | |
| 4.2 | FTIR spectra of polybenzoxazine precursor after drying at | | |
| | 80°C (pre-cured) (a) and after heat treatment at 200°C (fully- | | |
| | cured) (b) | 25 | |
| 4.3 | ¹ H-NMR spectrum of partially cured polybenzoxazine | 26 | |
| 4.4 | DSC thermograms of benzoxazine precursor (pre-cured) (a) | | |
| | and polybenzoxazine (fully-cured) (b) | 26 | |
| 4.5 | TGA thermogram during the pyrolysis of the partially-cured | | |
| | polybenzoxazine | 27 | |
| 4.6 | SEM micrograph of polybenzoxazine-based aerogel | 27 | |
| 4.7 | TEM micrograph of polybenzoxazine-based aerogel | 28 | |
| 4.8 | The pore size distribution of polybenzoxazine-based aerogel | | |
| | particle | 28 | |
| 4.9 | The adsorption onto polybenzoxazine-based aerogel | 29 | |

| FIGURE | | PAGE |
|--------|---|------|
| 4.10 | The adsorption onto polybenzoxazine-based aerogel in single | |
| | metal solution at various weights of polybenzoxazine-based | |
| | aerogel | 29 |
| 4.11 | The adsorption onto polybenzoxazine-based aerogel in mixed | |
| | metal solutions at various weights of polybenzoxazine-based | |
| | aerogel | 31 |
| 4.12 | The adsorption onto polybenzoxazine-based aerogel in single | |
| | metal solutions at various contact times | 32 |
| 4.13 | The adsorption onto polybenzoxazine-based aerogel in mixed | |
| | metal solutions at various contact times | 33 |
| 4.14 | The desorption process of H ₂ O and 2% (w/v) NaCl at various | |
| | pHs | 34 |
| 4.15 | The desorption process 2% (w/v) NaCl at pH 4 by various | |
| | temperatures | 34 |

ABBREVIATIONS

| PBZ | polybenzoxazine-based aerogel |
|-----|-------------------------------|
| PLE | polymeric ligand exchangers |
| COD | chemical oxygen demand |
| BOD | biological chemical demand |
| TOC | total organic carbon |