



UNIVERSITI PUTRA MALAYSIA

**REMOVAL OF CHROMIUM(VI), COPPER(II) AND ARSENIC(V) FROM
AQUEOUS SOLUTION AND WASTEWATER BY ETHYLENEDIAMINE
MODIFIED RICE HULL**

TANG POH LI

FSAS 2002 20

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MODIFIED RICE HULL**

By

TANG POH LI

**Thesis Submitted to the Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for Degree of Doctor of Philosophy**

February 2002



DEDICATED TO:

My family, supervisory committee and friends,

for the support and encouragement

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirement for the degree of Doctor of Philosophy

**REMOVAL OF CHROMIUM(VI), COPPER(II) AND ARSENIC(V) FROM
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February 2002

Chairman : Prof. Dr. Lee Chnoong Kheng, Ph.D.

Faculty : Science and Environmental Studies

The potential of aminated rice hull to remove Cr(VI), Cu(II) and As(V) from aqueous solution was investigated. Amination processes enhanced the sorption capacities of rice hull with ethylenediamine being the most economical and efficient aminating agent. Chemical modification of surface functional groups of ethylenediamine modified rice hull (enRH) indicated that amine and carboxyl groups were the major sorption sites.

Both batch and column studies were performed, taking into account parameters such as pH, contact time, initial concentrations, ionic strength, particle size of sorbent, rate of agitation, presence of competitive cation and anions, use of different metal ion sources, sorbent dosage, temperature, bed depth, flow rate and sorption-desorption process.

The results of batch studies indicated that the sorption process was pH and temperature dependent. External mass transfer was not the sole rate-limiting phase and might involve chemisorption. The sorption of metal ions from single metal ion solution was in the order of $\text{Cr(VI)} > \text{Cu(II)} > \text{As(V)}$ which is consistent with the Pearson's theory on hard and soft acid base. Cr(VI) and As(V) sorptions involved electrostatic interactions while Cu(II) sorption involved complexation. Where Cu(II) was present in binary and ternary metal ion solutions, Cr(VI) and As(V) removal also involved complexation.

Column studies revealed different equilibrium states compared with batch studies. Breakthrough was bed depth, flow rate and initial concentration dependent. The presence of sulfate significantly affected the breakthrough time of Cr(VI) and Cu(II) . The relationship between service time and bed depth was linear. The predicted breakthrough curves obtained from a two-parameter mathematical model agreed well with the experimental values in Cu(II) from all systems and Cr(VI) from binary Cu(II)-Cr(VI) and ternary metal ion solutions when sulfate was absent.

Sequential columns could successfully reduce the levels of Cr(VI) and Cu(II) in the wastewater to the allowable limit for discharge into inland water. Cr(VI) and Cu(II) from dilute solution could be preconcentrated on the enRH column and thus this is useful in the analysis of trace amounts of Cr(VI) and Cu(II) in wastewater. Elution of Cr(VI) - and Cu(II) -loaded column could be carried out using 1.07 M NH_3 and 0.5 M H_2SO_4 , respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENYINGKIRAN KROMIUM(VI), KUPRUM(II) DAN ARSENIK(V)
DARIPADA LARUTAN AKUEUS DAN AIR SISA OLEH SEKAM PADI
YANG DIUBAHSUAIKAN DENGAN ETILENADIAMINA**

Oleh

TANG POH LI

Februari 2002

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Keupayaan sekam padi (NRH) yang diaminakan untuk penyingkiran Cr(VI), Cu(II) dan As(V) dari larutan akueus telah dikaji. Proses pengaminaan telah meningkatkan kapasiti erapan sekam padi. Etilenadiamina merupakan agen amina yang paling ekonomi dan berkesan. Pengubahsuaian kimia ke atas kumpulan-kumpulan berfungsi pada sekam padi terubahsuai oleh etilenadiamina (enRH) menunjukkan bahawa kumpulan amina dan karboksilik merupakan tapak erapan utama.

Kajian kelompok dan turus telah dijalankan dengan mengambilkira parameter-parameter seperti pH, masa kontak, kepekatan awal, kekuatan ion, saiz pengeras, kadar pengacauan, kehadiran kation dan anion-anion pesaing, penggunaan sumber logam berbeza, suhu, ketinggian turus, kadar aliran and edaran erapan-nyaherpan.

Kajian kelompok menunjukkan bahawa proses erapan dipengaruhi oleh pH dan suhu. Pemindahan jisim luar bukan langkah penentu kadar tunggal dan melibatkan erapan kimia. Erapan logam-logam daripada larutan logam tunggal berurutan $\text{Cr(VI)} > \text{Cu(II)} > \text{As(V)}$ selaras dengan teori Pearson mengenai asid dan bes liat dan lembut. Erapan Cr(VI) dan As(V) melibatkan interaksi elektrostatik manakala erapan Cu(II) melibatkan pembentukan kompleks. Di mana Cu(II) hadir, penyingkiran Cr(VI) dan As(V) juga melibatkan pembentukan kompleks.

Kajian turus memaparkan perbezaan di antara keadaan keseimbangan dengan kajian kelompok. Penembusan bergantung kepada tinggi turus, kadar aliran dan kepekatan awal. Kehadiran sulfat telah mempengaruhi masa penembusan Cr(VI) dan Cu(II) . Hubungan di antara masa khidmat dan tinggi turus adalah linear. Keluk penembusan ramalan menggunakan model matematik dua-parameter mematuhi nilai eksperimen bagi Cu(II) dari larutan logam tunggal dan Cr(VI) dari larutan Cu(II) - Cr(VI) dan ternari yang tidak dihadiri sulfat.

Turus berganda dapat mengurangkan Cr(VI) dan Cu(II) di dalam air sisa sehingga takat yang dibenarkan untuk disingkirkan. Cr(VI) dan Cu(II) daripada larutan cair dapat dipekatkan pada enRH dan dengan demikian berguna untuk analisis Cr(VI) dan Cu(II) yang berkepekatan rendah dalam air sisa. Elusi turus yang ditepuan oleh Cr(VI) dan Cu(II) masing-masing dilakukan dengan menggunakan 1.07 M larutan NH_3 dan 0.5 M H_2SO_4 .

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I certify that an Examination Committee met on 22nd February 2002 to conduct the final examination of Tang Poh Li on her Doctor of Philosophy of Science thesis entitled "Removal of Chromium(VI), Copper(II) and Arsenic(V) from Aqueous Solution and Wastewater by Ethylenediamine Modified Rice Hull" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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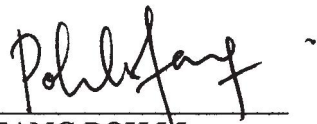


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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any degree at UPM or other institutions.


TANG POH LI

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TABLE OF CONTENTS

| | | Page |
|-----------------------------------|--------------------------------------------|-------------|
| DEDICATION | | ii |
| ABSTRACT | | iii |
| ABSTRAK | | v |
| ACKNOWLEDGEMENTS | | vii |
| APPROVAL SHEETS | | viii |
| DECLARATION FORM | | x |
| LIST OF TABLES | | xiv |
| LIST OF FIGURES | | xvii |
| LIST OF ABBREVIATIONS AND SYMBOLS | | xxviii |
| | | |
| CHAPTER | | |
| | | |
| 1 | INTRODUCTION | 1.1 |
| 1.1 | Chromium | 1.2 |
| 1.2 | Copper | 1.5 |
| 1.3 | Arsenic | 1.6 |
| 1.4 | Wood Preservative | 1.8 |
| 1.5 | Rice Hull | 1.10 |
| 1.6 | Ethylenediamine | 1.12 |
| 1.7 | Treatment of Heavy Metals | 1.13 |
| 1.7.1 | Chemical Precipitation | 1.13 |
| 1.7.2 | Adsorption | 1.15 |
| 1.7.3 | Ion Exchange | 1.16 |
| 1.7.4 | Membrane System | 1.17 |
| 1.7.5 | Biosorption | 1.18 |
| 1.8 | Significance of Study | 1.21 |
| 1.9 | Objectives of Study | 1.23 |
| | | |
| 2 | LITERATURE REVIEW | |
| 2.1 | Low-Cost Sorbent | 2.1 |
| 2.1.1 | Agricultural By-Product | 2.1 |
| 2.1.2 | Biomass | 2.4 |
| 2.1.3 | Biological Material | 2.9 |
| 2.1.4 | Industrial Waste | 2.11 |
| 2.1.5 | Mineral Waste | 2.12 |
| 2.1.6 | Soil/Clay | 2.13 |
| 2.1.7 | Natural Aquifer Material | 2.14 |
| 2.2 | Moderate Low-Cost Sorbent | 2.14 |
| 2.3 | Chemical Modification of Low-Cost Sorbents | 2.16 |
| 2.3.1 | Inorganic Acid | 2.16 |
| 2.3.2 | Base (NaOH) | 2.19 |
| 2.3.3 | Aldehyde | 2.22 |
| 2.3.4 | Amination | 2.26 |
| 2.3.5 | Sulfurisation | 2.28 |
| 2.3.6 | Phosphation | 2.31 |

| | | |
|----------|-------------------------------------------------------------------------------------------------------|------|
| 2.3.7 | Organic Acid | 2.32 |
| 2.3.8 | Dye | 2.34 |
| 2.3.9 | Immobilization of Metal Ions | 2.36 |
| 2.3.10 | Other Treatment Methods | 2.37 |
| 3 | MATERIALS AND METHODOLOGY | |
| 3.1 | Preparation of Sorbents | 3.1 |
| 3.1.1 | Preparation of Natural Rice Hull | 3.1 |
| 3.1.2 | Preparation of Aminated Rice Hull | 3.1 |
| 3.1.3 | Optimization Using Selected Aminating Agent (I) (en and TEA) and Aminating Agent (II) (CHPA and TRIS) | 3.2 |
| 3.2 | Chemical Modification of Surface Functional Groups | 3.2 |
| 3.2.1 | Esterification of Carboxylic Groups | 3.2 |
| 3.2.2 | Acetylation of Amine Groups | 3.3 |
| 3.3 | Reagents | 3.3 |
| 3.4 | Industrial Wastewater | 3.4 |
| 3.5 | Instrumental Analysis | 3.4 |
| 3.5.1 | Elemental Analyzer (C,H,N) | 3.4 |
| 3.5.2 | Fourier-transform Infrared Spectroscopy | 3.5 |
| 3.5.3 | Inductively Coupled Plasma-Atomic Emission Spectrometry | 3.5 |
| 3.5.4 | Ion Chromatography | 3.6 |
| 3.5.5 | UV-VIS Spectroscopy | 3.6 |
| 3.6 | Batch Experiments | 3.7 |
| 3.6.1 | Comparative Study on The Various Chemically Aminated Rice Hull | 3.7 |
| 3.6.2 | Effect of pH | 3.8 |
| 3.6.3 | Effect of Ionic Strength | 3.8 |
| 3.6.4 | Effect of Contact Time and Initial Concentration | 3.8 |
| 3.6.5 | Effect of Particle Size | 3.9 |
| 3.6.6 | Effect of Agitation Rate | 3.9 |
| 3.6.7 | Sorption Isotherm | 3.9 |
| 3.6.8 | Effect of Temperature | 3.10 |
| 3.6.9 | Effect of Sorbent Dosage | 3.10 |
| 3.6.10 | Effect of Anions | 3.10 |
| 3.6.11 | Effect of Counter Ions | 3.10 |
| 3.6.12 | Effect of Competitive Cations and Anions | 3.11 |
| 3.7 | Column Studies | 3.11 |
| 3.7.1 | Effect of Initial Concentration | 3.11 |
| 3.7.2 | Effect of Bed Depth | 3.12 |
| 3.7.3 | Effect of Flow Rate | 3.12 |
| 3.7.4 | Effect of Counter Ions on The Breakthrough Curve of Cu(II) | 3.12 |
| 3.7.5 | Effect of Acid Pretreatment | 3.12 |
| 3.7.6 | Sorption-Desorption Study | 3.13 |
| 3.8 | Wood Preservative Wastewater Treatment | 3.13 |
| 3.8.1 | Sorption Isotherm | 3.14 |

| | | |
|----------|---------------------------------------------------------------------------------------------------|------------|
| 3.8.2 | Comparative Study on The Breakthrough Curves of Metal Ions from Synthetic Solution and Wastewater | 3.14 |
| 3.8.3 | Effect of Bed Depth in Column Study | 3.14 |
| 3.8.4 | Effect of Flow Rate | 3.15 |
| 3.8.5 | Sequential Column for Wood Preservative Waste Treatment | 3.15 |
| 4 | RESULTS AND DISSCUSSION | |
| 4.1 | Effect of Amination Processes | 4.1 |
| 4.1.1 | Optimization of Aminating Process (I) | 4.3 |
| 4.1.2 | Optimization of Aminating Process (II) | 4.5 |
| 4.1.3 | Elemental Analysis (CHNS) on NRH and Optimized Aminated Rice Hull | 4.9 |
| 4.1.4 | Cost Analysis | 4.10 |
| 4.1.5 | Fourier-Transform Infrared Spectra | 4.11 |
| 4.2 | Chemical Modification of Functional Groups on Rice Hull | |
| 4.2.1 | Esterification of Carboxyl Groups | 4.13 |
| 4.2.2 | Acetylation of Amine Groups | 4.16 |
| 4.3 | Batch Experiments | |
| 4.3.1 | Effect of pH | 4.18 |
| 4.3.2 | Effect of Ionic Strength | 4.31 |
| 4.3.3 | Effect of Contact Time and Initial Concentration | 4.35 |
| 4.3.4 | Effect of Particle Size | 4.41 |
| 4.3.5 | Effect of Agitation Rate | 4.47 |
| 4.3.6 | Sorption Kinetics | 4.49 |
| 4.3.7 | Sorption Isotherm | 4.109 |
| 4.3.8 | Effect of Anions | 4.134 |
| 4.3.9 | Effect of Counter Ions | 4.138 |
| 4.3.10 | Effect of Competitive Cations and Anions | 4.144 |
| 4.3.11 | Effect of Sorbent Dosage | 4.151 |
| 4.3.12 | Sorption Mechanism | 4.155 |
| 4.3.13 | Effect of Temperature | 4.160 |
| 4.4 | Column Studies | 4.172 |
| 4.4.1 | Effect of Bed Depth | 4.173 |
| 4.4.2 | Bed Depth Service Time (BDST) Model | 4.194 |
| 4.4.3 | Effect of Flow Rate | 4.197 |
| 4.4.4 | Two-Parameter Mathematical Model | 4.204 |
| 4.4.5 | Effect of Initial Concentration | 4.218 |
| 4.4.6 | Sequential Column for Wood Preservative Waste Treatment | 4.234 |
| 4.4.7 | Sorption-Desorption Study | 4.235 |
| 5 | CONCLUSION | 5.1 |
| | BIBLIOGRAPHY | R.1 |
| | APENDIX | A.1 |
| | BIODATA OF THE AUTHOR | B.1 |

LIST OF TABLES

| Table | Page | |
|--------------|------------------------------------------------------------------------------------------------------------------------------------|------|
| 1.1 | Composition of rice hull | 1.11 |
| 2.1 | Sorption capacities (mmol/g) of some untreated and acid treated sorbents | 2.19 |
| 2.2 | Sorption capacities (mmol/g) of some untreated and NaOH treated sorbents | 2.22 |
| 2.3 | Sorption capacities (mmol/g) of some untreated and aldehyde treated sorbents | 2.25 |
| 2.4 | Sorption capacities (mmol/g) of some untreated and aminated sorbents | 2.28 |
| 2.5 | Sorption capacities (mmol/g) of some untreated, thiolated and xanthated low-cost sorbents | 2.30 |
| 2.6 | Sorption capacities (mmol/g) of some untreated and phosphated low-cost sorbents | 2.32 |
| 2.7 | Sorption capacities (mmol/g) of some untreated and organic acid treated low-cost sorbents | 2.33 |
| 2.8 | Reported sorption capacities (mmol/g) of some untreated and dye treated low-cost sorbents | 2.36 |
| 4.1 | Sorption efficiency (%) of metal ions by NRH and various aminated rice hull | 4.2 |
| 4.2 | Uptake of metal ions by NRH treated with TEA and en of various concentrations at 80 °C for 2 hours | 4.3 |
| 4.3 | Uptake of metal ions by NRH treated with 0.02 mole of TEA and en for 2 hours at various reaction temperatures | 4.4 |
| 4.4 | Uptake of metal ions by NRH treated with 0.02 mole of TEA and en at 80 °C for various durations | 4.5 |
| 4.5 | Uptake of metal ions by NRH treated with 1 g of aminating agents(II) and 25 mL of various NaOH concentrations at 60 °C for 2 hours | 4.6 |
| 4.6 | Uptake of metal ions by NRH treated with 1 g of aminating agents(II) and various volume of 1 M NaOH at 60 °C for 2 hours | 4.6 |

| | | |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| 4.7 | Uptake of metal ions by NRH treated with 1 g of aminating agents(II) and 15 mL of 1 M NaOH at 60 °C for various duration | 4.7 |
| 4.8 | Uptake of metal ions by NRH treated with various amount of aminating agents(II) and 15 mL of 1 M NaOH at 60 °C for 120 minutes | 4.8 |
| 4.9 | Uptake of metal ions by NRH treated with amine/NRH ratio of 1.25 and 15 mL of 1 M NaOH at various temperatures for 120 minutes | 4.9 |
| 4.10 | Amount of metal ions sorbed (mmol/g) by various optimized aminated rice hull | 4.9 |
| 4.11 | Carbon, hydrogen, nitrogen and sulfur (%) content of NRH and optimized aminated rice hull | 4.10 |
| 4.12 | Estimation on the cost of metal ions removal by CHPA-RH and enRH | 4.10 |
| 4.13 | Equilibrium pH of Cr(VI) from single and binary Cu(II)-Cr(VI) metal ion solutions at different pH _{adj} | 4.24 |
| 4.14 | The amount of Cr(VI) and Cr(III) determined after equilibrating Cr(VI) with rice hull | 4.25 |
| 4.15 | Equilibrium pH of As(V) from single, binary and ternary metal ion solutions at different pH _{adj} | 4.30 |
| 4.16 | Pseudo-first order constants for Cr(VI), Cu(II) and As(V) sorption from single, binary and ternary metal ion solutions by enRH | 4.82 |
| 4.17 | Pseudo-second order constants for Cr(VI), Cu(II) and As(V) sorption from single, binary and ternary metal ion solutions by enRH | 4.91 |
| 4.18 | Empirical parameters for predicted q_e , k and h from C_0 | 4.93 |
| 4.19 | Langmuir constants obtained from non-competitive Langmuir isotherms for Cr(VI), Cu(II) and As(V) sorption from single metal ion solution | 4.110 |
| 4.20 | Comparison of sorption capacities of enRH for Cr(VI), Cu(II) and As(V) with some other types of low-cost sorbents | 4.114 |
| 4.21 | Langmuir constants obtained from non-competitive Langmuir isotherm for Cr(VI), Cu(II) and As(V) sorption from single, binary and ternary metal ion solutions by enRH | 4.117 |

| | | |
|------|-------------------------------------------------------------------------------------------------------------------------------------|-------|
| 4.22 | Langmuir constants for Cr(VI), Cu(II) and As(V) sorption from synthetic ternary metal mixture and wastewater | 4.123 |
| 4.23 | The competitive Langmuir sorption constants for Cr(VI), Cu(II) and As(V) evaluated from the modified competitive Langmuir isotherm | 4.126 |
| 4.24 | Freundlich constants obtained from Freundlich isotherm for Cr(VI), Cu(II) and As(V) sorption from single metal ion solution by enRH | 4.131 |
| 4.25 | Equilibrium amount of Cu(II) and anions sorbed using different Cu(II) salts | 4.142 |
| 4.26 | Enthalpy and entropy for the sorption of Cr(VI), Cu(II) and As(V) from single, binary and ternary metal ion solutions by enRH | 4.169 |
| 4.27 | Gibbs free energy for the sorption of Cu(II) from single, binary and ternary metal ion solutions by enRH | 4.171 |
| 4.28 | Gibbs free energy for the sorption of Cr(VI) and As(V) from single, binary and ternary metal ion solutions by enRH | 4.171 |
| 4.29 | Utilized capacity of enRH on the sorption of Cr(VI), Cu(II) and As(V) from synthetic solutions and wastewater at various bed depths | 4.192 |
| 4.30 | Total removal percentage of metal ions from single, binary and ternary metal ion solutions at different flow rates | 4.203 |
| 4.31 | Total removal percentage of metal ions from synthetic solutions and wastewater at different initial concentrations | 4.234 |
| 4.32 | Amount of metal ions detected in the effluent treated with enRH | 4.235 |
| 4.33 | Recovery percentage of Cr(VI) in enRH using NaOH and NH ₃ of different concentrations | 4.236 |
| 4.34 | Recovery percentage of Cu(II) in enRH using HCl and H ₂ SO ₄ of different concentrations | 4.238 |

LIST OF FIGURES

| Figure | Page |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 1.1 Speciation diagram of Cr(VI) in solution as a function of pH (A: CrO_4^{2-} , B: $\text{Cr}_2\text{O}_7^{2-}$, C: HCrO_4^- , D: H_2CrO_7^- , E: H_2CrO_4) | 1.3 |
| 1.2 Speciation diagram for As(V) in solution as a function of pH | 1.7 |
| 4.1 Infrared spectra of NRH and enRH | 4.12 |
| 4.2 Effect of amination and esterification of NRH on the sorption of Cr(VI), As(V) and Cu(II) (\uparrow = uptake increased, \downarrow = uptake decreased) | 4.13 |
| 4.3 Uptakes of Cr(VI), As(V) and Cu(II) by enRH and esterified enRH (E-enRH) | 4.15 |
| 4.4 Uptakes of Cr(VI), As(V) and Cu(II) by enRH and acetylated enRH (A-enRH) | 4.17 |
| 4.5 Effect of pH on the sorption of Cu(II) from single and binary Cu(II)-Cr(VI) metal ion solutions by NRH and enRH | 4.19 |
| 4.6 Effect of pH on the sorption of Cu(II) from single, binary and ternary metal ion solutions by enRH | 4.22 |
| 4.7 Effect of pH on the sorption of Cr(VI) from single and binary Cu(II)-Cr(VI) metal ion solutions by NRH and enRH | 4.23 |
| 4.8 Effect of pH on the sorption of Cr(VI) from single, binary and ternary metal ion solutions by enRH | 4.26 |
| 4.9 Effect of pH on the sorption of As(V) from single metal ion solution by NRH and enRH | 4.28 |
| 4.10 Effect of pH on the sorption of As(V) from single, binary and ternary metal ion solutions by enRH | 4.29 |
| 4.11 Effect of ionic strength on the sorption of Cr(VI) by enRH | 4.32 |
| 4.12 Effect of ionic strength on the sorption of As(V) by enRH | 4.33 |
| 4.13 Effect of ionic strength on the sorption of Cu(II) by enRH | 4.34 |
| 4.14 Effect of contact time and initial concentration on Cr(VI) sorption from single metal ion solution by enRH | 4.36 |

| | | |
|------|--------------------------------------------------------------------------------------------------------------------------|------|
| 4.15 | Effect of contact time and initial concentration on As(V) sorption from single metal ion solution by enRH | 4.37 |
| 4.16 | Effect of contact time and initial concentration on As(V) sorption from single metal ion solution by enRH | 4.38 |
| 4.17 | Effect of contact time and initial concentration on Cr(VI) and Cu(II) sorption from binary metal mixture by enRH | 4.39 |
| 4.18 | Effect of contact time and initial concentration on As(V) and Cu(II) sorption from binary metal mixture by enRH | 4.40 |
| 4.19 | Effect of contact time and initial concentration on Cr(VI) and As(V) sorption from binary metal mixture by enRH | 4.42 |
| 4.20 | Effect of contact time and initial concentration on Cr(VI), As(V) and Cu(II) sorption from ternary metal mixture by enRH | 4.43 |
| 4.21 | Effect of particle size on Cr(VI), Cu(II) and As(V) sorption from single metal ion solution by enRH | 4.44 |
| 4.22 | Effect of particle size on Cr(VI) and Cu(II) sorption from binary metal ion solution by enRH | 4.45 |
| 4.23 | Effect of particle size on Cr(VI), Cu(II) and As(V) sorption from ternary metal ion solution by enRH | 4.46 |
| 4.24 | Effect of agitation rate on Cr(VI), Cu(II) and As(V) sorption from single metal ion solution by enRH | 4.48 |
| 4.25 | Effect of agitation rate on Cr(VI) and Cu(II) sorption from binary metal ion solution by enRH | 4.50 |
| 4.26 | Effect of agitation rate on Cr(VI), Cu(II) and As(V) sorption from ternary metal ion solution by enRH | 4.51 |
| 4.27 | Boundary layer effect on the sorption of Cr(VI) and Cu(II) from single metal ion solution by enRH | 4.53 |
| 4.28 | Boundary layer effect on the sorption of As(V) from single metal ion solution by enRH | 4.54 |
| 4.29 | Boundary layer effect on the sorption of Cr(VI) and Cu(II) from binary metal ion solution by enRH | 4.55 |
| 4.30 | Boundary layer effect on the sorption of As(V) and Cu(II) from binary metal ion solution by enRH | 4.56 |

| | | |
|------|------------------------------------------------------------------------------------------------------|------|
| 4.31 | Boundary layer effect on the sorption of As(V) and Cr(VI) from binary metal ion solution by enRH | 4.57 |
| 4.32 | Boundary layer effect on the sorption of Cr(VI) from ternary metal ion solution by enRH | 4.58 |
| 4.33 | Boundary layer effect on the sorption of Cu(II) from ternary metal ion solution by enRH | 4.59 |
| 4.34 | Boundary layer effect on the sorption of As(V) from ternary metal ion solution by enRH | 4.60 |
| 4.35 | Intraparticle diffusion of Cu(II) from single metal ion solution in enRH | 4.62 |
| 4.36 | Intraparticle diffusion of Cr(VI) and As(V) from single metal ion solution in enRH | 4.63 |
| 4.37 | Intraparticle diffusion of Cr(VI) and Cu(II) from binary metal ion solution in enRH | 4.64 |
| 4.38 | Intraparticle diffusion of Cu(II) and As(V) from binary metal ion solution in enRH | 4.65 |
| 4.39 | Intraparticle diffusion of Cr(VI) and As(V) from binary metal ion solution in enRH | 4.66 |
| 4.40 | Intraparticle diffusion of Cr(VI) and As(V) from ternary metal ion solution in enRH | 4.67 |
| 4.41 | Intraparticle diffusion of Cu(II) from ternary metal ion solution in enRH | 4.68 |
| 4.42 | Pseudo-first order kinetics for Cr(VI) sorption from single metal ion solution by enRH | 4.70 |
| 4.43 | Pseudo-first order kinetics for Cu(II) sorption from single metal ion solution by enRH | 4.71 |
| 4.44 | Pseudo-first order kinetics for As(V) sorption from single metal ion solution by enRH | 4.72 |
| 4.45 | Pseudo-first order kinetics for Cr(VI) sorption from binary Cu(II)-Cr(VI) metal ion solution by enRH | 4.73 |
| 4.46 | Pseudo-first order kinetics for Cu(II) sorption from binary Cu(II)-Cr(VI) metal ion solution by enRH | 4.74 |

| | | |
|------|------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.47 | Pseudo-first order kinetics for Cu(II) sorption from binary Cu(II)-As(V) metal ion solution by enRH | 4.75 |
| 4.48 | Pseudo-first order kinetics for As(V) sorption from binary Cu(II)-As(V) metal ion solution by enRH | 4.76 |
| 4.49 | Pseudo-first order kinetics for Cr(VI) sorption from binary Cr(VI)-As(V) metal ion solution by enRH | 4.77 |
| 4.50 | Pseudo-first order kinetics for As(V) sorption from binary Cr(VI)-As(V) metal ion solution by enRH | 4.78 |
| 4.51 | Pseudo-first order kinetics for Cu(II) sorption from ternary metal ion solution by enRH | 4.79 |
| 4.52 | Pseudo-first order kinetics for Cr(VI) sorption from ternary metal ion solution by enRH | 4.80 |
| 4.53 | Pseudo-first order kinetics for As(V) sorption from ternary metal ion solution by enRH | 4.81 |
| 4.54 | Pseudo-second order kinetics for Cr(VI) sorption from single metal ion solution by enRH | 4.84 |
| 4.55 | Pseudo-second order kinetics for Cu(II) sorption from single metal ion solution by enRH | 4.85 |
| 4.56 | Pseudo-second order kinetics for As(V) sorption from single metal ion solution by enRH | 4.86 |
| 4.57 | Pseudo-second order kinetics for Cr(VI) and Cu(II) sorption from binary metal ion solution by enRH | 4.87 |
| 4.58 | Pseudo-second order kinetics for Cu(II) and As(V) sorption from binary metal ion solution by enRH | 4.88 |
| 4.59 | Pseudo-second order kinetics for Cr(VI) and As(V) sorption from binary metal ion solution by enRH | 4.89 |
| 4.60 | Pseudo-second order kinetics for Cr(VI), Cu(II) and As(V) sorption from ternary metal ion solution by enRH | 4.90 |
| 4.61 | Comparison between the measured and pseudo-second order modeled time profiles for Cr(VI) sorption from single metal ion solution by enRH | 4.95 |
| 4.62 | Comparison between the measured and pseudo-second order modeled time profiles for Cu(II) sorption from single metal ion solution by enRH | 4.96 |

| | | |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| 4.63 | Comparison between the measured and pseudo-second order modeled time profiles for As(V) sorption from single metal ion solution by enRH | 4.97 |
| 4.64 | Comparison between the measured and pseudo-second order modeled time profiles for Cu(II) sorption from binary Cr(VI)-Cu(II) metal ion solution by enRH | 4.100 |
| 4.65 | Comparison between the measured and pseudo-second order modeled time profiles for Cr(VI) sorption from binary Cr(VI)-Cu(II) metal ion solution by enRH | 4.101 |
| 4.66 | Comparison between the measured and pseudo-second order modeled time profiles for Cu(II) sorption from binary Cu(II)-As(V) metal ion solution by enRH | 4.102 |
| 4.67 | Comparison between the measured and pseudo-second order modeled time profiles for As(V) sorption from binary Cu(II)-As(V) metal ion solution by enRH | 4.103 |
| 4.68 | Comparison between the measured and pseudo-second order modeled time profiles for Cr(VI) sorption from binary Cr(VI)-As(V) metal ion solution by enRH | 4.104 |
| 4.69 | Comparison between the measured and pseudo-second order modeled time profiles for As(V) sorption from binary Cr(VI)-As(V) metal ion solution by enRH | 4.105 |
| 4.70 | Comparison between the measured and pseudo-second order modeled time profiles for Cu(II) sorption from ternary metal ion solution by enRH | 4.106 |
| 4.71 | Comparison between the measured and pseudo-second order modeled time profiles for Cr(VI) sorption from ternary metal ion solution by enRH | 4.107 |
| 4.72 | Comparison between the measured and pseudo-second order modeled time profiles for As(V) sorption from ternary metal ion solution by enRH | 4.108 |
| 4.73 | Langmuir isotherms for the sorption of Cr(VI) from single metal ion solution by NRH and enRH | 4.111 |
| 4.74 | Langmuir isotherms for the sorption of Cu(II) from single metal ion solution by NRH and enRH | 4.112 |
| 4.75 | Langmuir isotherms for the sorption of As(V) from single metal ion solution by enRH | 4.113 |

| | | |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| 4.76 | Comparison between experimental and Langmuir model predicted sorption isotherms of Cr(VI), Cu(II) and As(V) from single metal ion solution by enRH | 4.116 |
| 4.77 | Langmuir isotherms on the sorption of Cr(VI) from single metal, binary and ternary metal ion solution enRH | 4.118 |
| 4.78 | Langmuir isotherms on the sorption of Cu(II) from single, binary and ternary metal ion solution by enRH | 4.119 |
| 4.79 | Langmuir isotherms on the sorption of As(V) from single, binary and ternary metal ion solution by enRH | 4.120 |
| 4.80 | Langmuir isotherms for Cr(VI), Cu(II) and As(V) wood preservative waste by enRH | 4.124 |
| 4.81 | Comparison of the amounts of Cr(VI) sorbed experimentally and calculated using the competitive sorption models in the binary metal ion solutions | 4.128 |
| 4.82 | Comparison of the amounts of Cu(II) sorbed experimentally and calculated using the competitive sorption models in the binary metal ion solutions | 4.129 |
| 4.83 | Comparison of the amounts of As(V) sorbed experimentally and calculated using the competitive sorption models in the binary metal ion solutions | 4.130 |
| 4.84 | Freundlich isotherms on the sorption of Cr(VI) from single metal ion solution by enRH at different pH values | 4.132 |
| 4.85 | Freundlich isotherms on the sorption of Cu(II) and As(V) from single metal ion solution by enRH | 4.133 |
| 4.86 | Comparison between experimental and Freundlich model predicted sorption isotherms of Cr(VI), Cu(II) and As(V) from single metal ion solution by enRH | 4.135 |
| 4.87 | Effect of anions on the sorption of Cr(VI) by enRH | 4.136 |
| 4.88 | Effect of anions on the sorption of As(V) by enRH | 4.137 |
| 4.89 | Uptake of Cr(VI) and sulfate at increasing sulfate concentrations | 4.139 |
| 4.90 | Uptake of As(V) and sulfate at increasing sulfate concentrations | 4.140 |
| 4.91 | Effect of counter ions on the sorption of Cr(VI) from single metal ion solution by enRH | 4.141 |

| | | |
|-------|----------------------------------------------------------------------------------------------------------------------------|-------|
| 4.92 | Effect of counter ions on the sorption of Cu(II) from single metal ion solution by enRH | 4.143 |
| 4.93 | Uptake of Cr(VI) and Cu(II) at increasing Cu(II) concentrations | 4.145 |
| 4.94 | Uptake of Cr(VI) and Cu(II) at increasing Cr(VI) concentrations | 4.146 |
| 4.95 | Uptake of Cu(II) and As(V) at increasing As(V) concentrations | 4.147 |
| 4.96 | Uptake of Cu(II) and As(V) at increasing Cu(II) concentrations | 4.148 |
| 4.97 | Uptake of Cr(VI) and As(V) at increasing Cr(VI) concentrations | 4.149 |
| 4.98 | Uptake of Cr(VI) and As(V) at increasing As(V) concentrations | 4.150 |
| 4.99 | Effect of sorbent dosage on the sorption of Cu(II) from single metal ion solution. | 4.152 |
| 4.100 | Effect of sorbent dosage on the sorption of Cr(VI) from single metal ion solution. | 4.153 |
| 4.101 | Effect of sorbent dosage on the sorption of As(V) from single metal ion solution. | 4.154 |
| 4.102 | Effect of temperature on the sorption of Cr(VI) from single, binary and ternary metal ion solution using enRH | 4.161 |
| 4.103 | Effect of temperature on the sorption of As(V) from single, binary and ternary metal ion solution using enRH | 4.162 |
| 4.104 | Effect of temperature on the sorption of Cu(II) from single, binary and ternary metal ion solution using enRH | 4.163 |
| 4.105 | van't Hoff plots for the sorption of Cr(VI) from single, binary and ternary metal ion solutions | 4.166 |
| 4.106 | van't Hoff plots for the sorption of As(V) from single, binary and ternary metal ion solutions | 4.167 |
| 4.107 | van't Hoff plots for the sorption of Cu(II) from single, binary and ternary metal ion solutions | 4.168 |
| 4.108 | Breakthrough curves of Cu(II) from single metal ion solution at different bed depths at a flow rate of 25 mL/min | 4.174 |
| 4.109 | Breakthrough curves of Cr(VI) and As(V) from single metal ion solution at different bed depths at a flow rate of 25 mL/min | 4.175 |

| | | |
|-------|----------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| 4.110 | Effect of acid pretreatment on the breakthrough curve of Cr(VI) and As(V) at a bed depth of 9.5 cm and flow rate of 25 mL/min | 4.177 |
| 4.111 | Breakthrough curves of Cr(VI) and Cu(II) from binary solution at different bed depths at a flow rate of 10 mL/min | 4.178 |
| 4.112 | Breakthrough curves of Cr(VI), Cu(II) and As(V) from ternary metal ion solution at different bed depths at a flow rate of 25 mL/min | 4.179 |
| 4.113 | Utilized capacity of enRH on the sorption of Cr(VI) from single and binary metal ion solutions of Cu(II)/Cr(VI) at different bed depths | 4.181 |
| 4.114 | Utilized capacity of enRH on the sorption of Cu(II) from single and binary metal ion solutions of Cu(II)-Cr(VI) at different bed depths | 4.182 |
| 4.115 | Utilized capacity of enRH on the sorption of Cu(II) from single and ternary metal ion solutions at different bed depths at a flow rate of 25 mL/min | 4.183 |
| 4.116 | Utilized capacity of enRH on the sorption of Cr(VI) from single and ternary metal ion solutions at different bed depths at a flow rate of 25 mL/min | 4.184 |
| 4.117 | Utilized capacity of enRH on the sorption of As(V) from single and ternary metal ion solutions at different bed depths at a flow rate of 25 mL/min | 4.185 |
| 4.118 | Breakthrough curves of Cr(VI), Cu(II) and As(V) from wood preservative waste at different bed depths at a flow rate of 25 mL/min | 4.187 |
| 4.119 | Breakthrough curves of Cr(VI) and As(V) from synthetic solution and wood preservative waste at a bed depth of 14.0 cm and flow rate of 25 mL/min | 4.188 |
| 4.120 | Breakthrough curves of Cu(II) from synthetic solution and wood preservative waste at a flow-rate of 25 mL/min and bed depth of 14.0 cm | 4.189 |
| 4.121 | Effect of counter ions on the breakthrough curve of Cu(II) at bed depth of 14.0 cm and flow rate of 10 mL/min | 4.190 |
| 4.122 | Effect of Cu(II) counter ions on the breakthrough curve of Cu(II) and Cr(VI) from binary ion solution at bed depth of 14.0 cm and flow rate of 10 mL/min | 4.191 |