REMOVAL OF HAZARDOUS OXYANION POLLUTANTS BY LANTHANUM (III) HYDROXIDE AND LANTHANUM (III) -LOADED ION EXCHANGERS

By

YEHYA M. AHMED

Thesis Submitted to the School of Graduate Studies,
Universiti Putra Malaysia in Fulfilment of the Requirements
for the Degree of Master of Science

December 2004

DEDICATION

To:

My father's soul, my dear mother and brothers for their pray for me. My beloved wife for her unlimited sincere sacrificing, encouragement and support during my study. My beloved brave sons, I will never forget your braveness.

Abstract of the thesis presented to the Senate of Universiti Putra malaysia in
fulfilment of requirements for the degree of Master of Science

REMOVAL OF HAZARDOUS OXYANION POLLUTANTS BY LANTHANUM (III) HYDROXIDE AND LANTHANUM (III) – LOADED ION EXCHANGERS

By

YEHYA M. AHMED

December 2004

Chairman: Associate Professor Md Jelas Haron, Ph.D.

Faculty : Science

La(III) loaded poly(hydroxamic acid) chelating resin (LaPHA), lanthanum hydroxide-loaded poly(hydroxamic acid) chelating resin (LaOHPHA) and lanthanum hydroxide ($La(OH)_3$) were prepared and evaluated as sorbents for removal of As(V), As(III) and Cr(VI) from aqueous solution. LaPHA was prepared by loading lanthanum(III) onto PHA resin which was prepared by the reaction of PMA with hydroxyl amine hydrochloride in alkaline medium. LaOHPHA was prepared by treating LaPHA with ammonia solution and $La(OH)_3$ was prepared by neutralizing $LaCl_3$ solution with ammonia solution.

In order to understand the sorption characteristics of As(V), As(III) and Cr(VI) by the sorbents, batch and column studied were performed under various experimental conditions. The parameters studied were pH, contact time, isotherm study, temperature, sorbent dosage, presence of competitive anions, flow rate, sorption-desorption study and industrial wastewater treatment.

The results of batch study indicated that the sorption process was pH dependent and endothermic. Kinetic study showed that uptake of As(V) ion by all of the sorbents reached equilibrium after about 15 hours and about 10 hours for Cr(VI) by $La(OH)_3$. The maximum sorption capacity of LaPHA for As(V) at room temperature determined from the Langmuir isotherm was 14.8 mg-As/g-sorbent compared to that of LaOHPHA for As(V) which was 17.7 mg-As/g-sorbent, while the maximum sorption capacity of $La(OH)_3$ for As(V) was 133.3 mg-As/g-sorbent and for Cr(VI) was 33.1 mg-Cr/g-sorbent. The results also showed that the $La(OH)_3$ in the PHA resin (LaOHPHA) was more stable in acidic medium compared to the $La(OH)_3$. The uptake increased with increasing sorbent dosage and also increased by increasing in temperature. In the presence of competitive ions, metal uptake decreased and it was found that phosphate ion is the most effective one.

In desorption study, As(V) could be removed almost quantitatively from LaPHA and LaOHPHA by eluting with 0.4M and 0.2M NaOH solutions, respectively. The column with LaPHA could be used for not more than 3 cycles and 2 cycles for LaOHPHA. Both LaPHA and LaOHPHA resins were found effective to remove arsenic from wastewater samples from wood treatment industry. The percentages of arsenic removal from wastewater by the sorbents were higher for lower concentrations samples. More than 90% removal was obtained from the sample with the lowest arsenic concentration.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
bagi memenuhi keperluan untuk ijazah Master Sains

PENYINGKIRAN POLUTANT OKSIANION BERBAHAYA OLEH LANTHANUM (III) HIDROKSIDA DAN LANTHANUM (III) DIPEGUNKAN DALAM PENUKAR ION

Oleh

YEHYA M. AHMED

Disember 2004

Pengerusi : Professor Madya Md. Jelas Haron, Ph. D.

Fakulti : Sains

Resin pengkelat poli(asid hidroksamik) dipegunkan La(III) (LaPHA), poli(asid hidroksamik) dipegunkan $La(OH)_3$ (LaOHPHA), dan $La(OH)_3$ telah di sedikan dan dikaji keberkesanannya untuk penyingkiran ion logam As(V), As(III) dan Cr(VI) dari larutan akueus. Resin PHA telah disedikan melalui tindakbalas PMA dengan hidrosil amin hidroklorida di dalam medium berkali. LaPHA disediakan dengan tindakbalas lanthanum (III) dengan larutan ammonia.

Untuk memahami ciri-ciri erapan LaPHA, LaOHPHA dan $La(OH)_3$ terhadap As(V), As(III) dan Cr(VI), kajian kelompok dan turus telah dijalankan di bawah pelbagai keadaan eksperiment. Parameter yang dikaji pH, masa, isoterma, dos pengerap, kehadiran ion-ion saingan, kadar aliran, erapan-penyaherapan dan rawatan terhadap sample air buangan industri.

Keputusan kajian kelompok menunjukkan bahawa proses erapan dipengaruhi oleh pH dan bersifat endotermik. Kajian kinetic menunjukkan keseimbangan tindakbalas bagi erapan As(V) dan Cr(VI) masing-masing oleh diperolehi selepas 15 jam dan 10 jam. Kapasiti erapan maksimum untuk LaPHA pada suhu bilik yang ditentkan daripada isoterma Langmuir adalah 14.8 mg-As/g-pengerap berbanding oleh LaOHPHA sebanyak 17.1 mg-As/g-pengerap manakala bagi $La(OH)_3$ sebanyak 133.3 mg-As/g-pengerap dan bagi Cr(VI) sebanyak 33.1 mg-As/g-pengerap. Erapan meningkat dengan peningkatan dos pengerap. Kehadiran ion-ion saingan akan mengurangkan erapan logam dan ion fosfat adalah yang paling effective.

Dalam kajian penyaherapan, hamper semua As(V) dapat disingkikan secara kuantitatif dari LaPHA dan LaOHPHA dengan larutan pengelusi masing-masing iaitu larutan 0.4 M dan 0.2 M NaOH. Turus LaPHA dapat digunakan tidak lebih daripada 3 kali manakala turus LaOHPHA dapat digunakan tidak 2 kali sebelum kecekapan turus menurum kepada kira-kira 50%. Kedua-dua resin LaPHA dan LaOHPHA telah didapati berkesan untuk merawat air buanagan industri dari industri perawatan kayu. Peratus penyingkiran arsenic adalah bergantung kepada kepekatan asal ion arsenic dalam sample. Lebih daripada 90% arsenic telah berjaya disingkirkan dari sample air buangan dengan kepekatan arsenic paling rendah.

AKNOWLEDGMENTS

In The Name of ALLAH, The Most Merciful and Most Beneficent

Firstly, I want to send my deep appreciation, sincere gratefulness and respect to my supervisor Assoc. Prof. Dr. Md Jelas Haron for his unlimited guidance, scientific advising, encouragement and providing financial support during the period of study through the IRPA research fund and I just want to say that he not only taught me how to work but how to think and love the work that I have done.

I am also grateful to Prof. Dr. Wan Md Zin Wan Yunus for his great guidance to me as my co-advisor or through his leadership for the polymer group which had a big influence on me and gave me a real braveness for dealing with meetings and seminars.

I would like to thank all the staff at The Department of Chemistry/ Faculty of Science especially those who assisted me to complete this study, starting with Madame Choo who was very patient with me during my work at the ICP Instrument, Mr Kamal Marguna, Mr Innudin, Mr Nuruldin, Mr Abbas and to all the others I just ask them kindly to forgive me if I forgot any one.

Never forget all the GSO staff for their sincere cooperation and sympathetic behavior which I felt since my first day in UPM.

Special thanks (as a foreigner student) to Puan Aidida binti Khalid, Head of International Relations Office (IRO) and for all her staff for their real friendly and warm feelings toward the foreigner students which create a very nice environment for us at UPM.

My deep gratefulness to all my colleagues at 407 Lab. For their great encouragement especially at my early days in Malaysia while I was not so familiar with the new environment, thanks to my real friend Dr. Dedy Suhendra for his esteemed assistance, Tan Wee Chang and Shahanna both were great team mates and so close to me, Aidil, Pei Yeen, Abby, Su Fang, Wei Chee to all of you I would like to say thank you. Also thanks to my friend Mr. Lim Che Siong, Mr Ekram form Bangladesh. Thanks to Mohammad Khawalda, Ali Al-Mokarram and to Mr. Faraj Abu Ilyawi I send him my sincere Doaa' to recover soon.

At last but not least, I would like to thank Mr Salah N. Sulaiman and Madame Awatif Baa'rma for their great support for me and for my family

I certify that an Examination Committee met on 10 December 2004 to conduct the final examination of Yehya M. Ahmed on his Master of Science thesis entitled "Removal of Hazardous Oxyanion Pollutants by Lanthanum (III) Hydroxide and Lanthanum (III) Loaded Ion Exchanger" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Asmah Hj. Yahaya, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Anuar Kassim, Ph.D.
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Abdul Halim Abdullah, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd. Asri Nawi, Ph.D.
Associate Professor
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
(Independent Examiner)

GULAM RUSUL RAHMAT ALI, Ph.D.
Professor / Deputy Dean
School of Graduate Studies,
Universiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

Md. Jelas Haron, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Wan Md. Zin Wan Yunus, Ph.D.
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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 other degree at UPM or other institutions.

YEHYA M. AHMED

Date:

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

LIST OF ABBREVIATIONS

PHA	Poly (hydroxamic acid)
PMA	Poly methyl acrylate
$t_{1/2}$	Time to remove 50% of the initial concentration of the metal ion solution
Ks	Rate constant
LH	Lanthanum hydroxide
LC	Lanthanum carbonate
BLC	Basic lanthanum carbonate
U. S. EPA	United States Environmental Protection Agency
LaPHA	Lanthanum (III) loaded-poly (hydroxamic acid) resin complex
LaOHPHA	Lanthanum hydroxide loaded- poly (hydroxamic acid) resin
FTIR	Fourier transforms infrared spectroscopy
XRD	X-Ray Diffraction
CHNS	Carbon, hydrogen, nitrogen and sulphur
DVB	Divinyl benzene
d	The basal spacing
n	An integer (1, 2, 3…)
λ	Wave length A^o
θ	The angle of incidence of the x-ray beam and the atomic planes
q_e	The amount of the metal sorbed at equilibrium (mg/g).
q	The amount of the metal sorbed at time (mg/g).
t	Time of equilibrium(min)
C_e	Equilibrium concentration of the metal ion (mg/L)
Q_m	Maximum sorption capacity of the system (mg/g)
b	Constant related to the energy of the sorption (L/mg)
K_d	Distribution coefficient defined as N_e/C_e
T	Absolute temperature (K)
R	Gas constant
ΔS^o	Entropy change (J/mol K)
ΔH^o	Enthalpy change (J/mol)
ΔG^o	Free energy change (J/mol)
K_{sp}	Solubility constant

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 ION EXCHANGERS

Ion exchangers are solid and suitably insolubilized high molecular weight polyelectrolyte which can exchange their mobile ions for ions of equal charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchanger. Viewed in different light, ion exchangers can be considered high molecular weight acids or bases with a high molecular weight cation, which can exchange their hydrogen or hydroxyl ions for equally charged ions and thus are converted into high molecular weight salts.

1.1.1 Synthetic Resin Ion Exchangers

Synthetic ion exchange resins are insoluble poly electrolytes with limited moisture regain capacity. On the bases of their function, there are three types of ion exchangers, cation exchanger, anion exchanger and amphoteric ion exchanger (Dorfner, 1973). Polymerization and polycondensation in principle can be used as the synthesis routes to form the resin matrix. At the present time, polymer resins have become more important than polycondensation resins. They have a higher chemical and thermal stability. The most important starting material, which is used nearly exclusively in exchangers of the strongly acid and strongly basic types produced on a large scale, is styrene. The styrene is cross-linked with itself and with divinylbenzene into a polymeric network (Figure 1.1) (Dorfner, 1973).

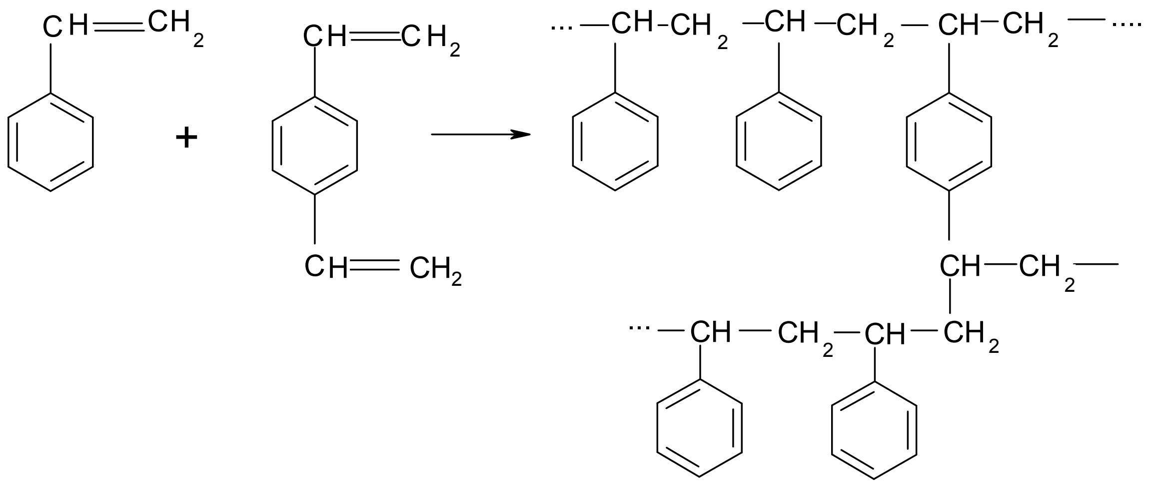

Figure 1.1: Cross-linking of styrene with divinylbenzene into a polymeric network (Dorfner, 1973).

On the other hand, matrices for weakly acid cation exchangers are formed, which is also crosslinked with divinylbenzene, from acrylic acid or methacrylic acid (Figure 1.2) (Dorfner, 1973).

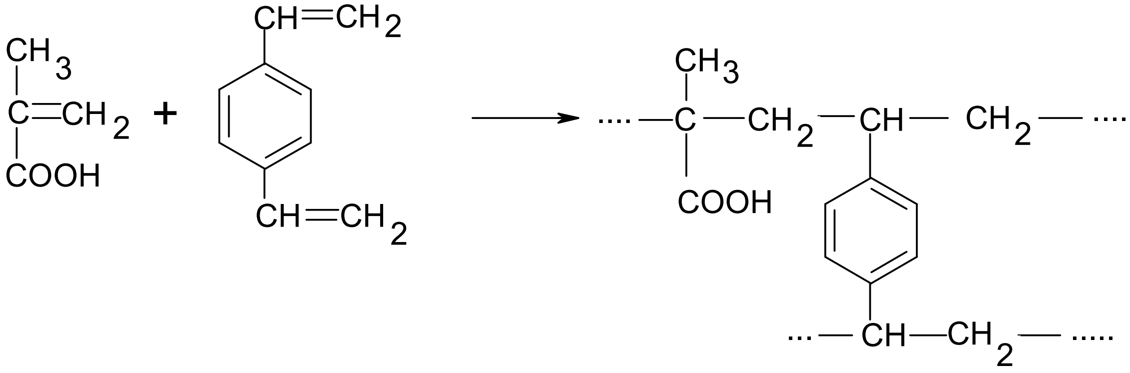

Figure 1.2: Formation of weakly acid cation exchanger from the reaction between methacrylic acid and divinylbenzene (Dorfner, 1973).

In polycondensation resins, the matrix is usually constructed from phenol and formaldehyde (Figure 1.3) (Dorfner 1973):

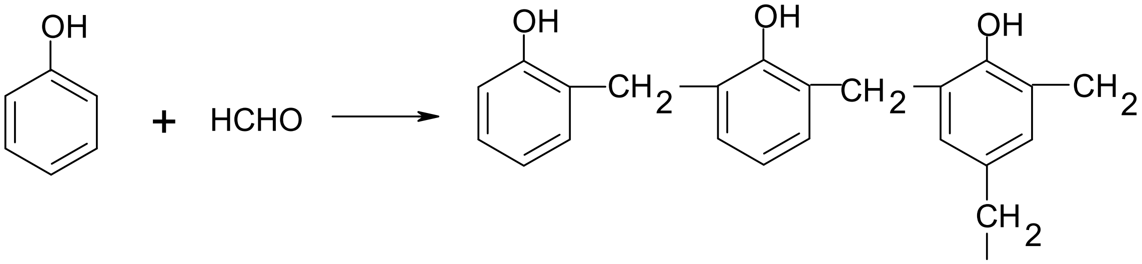

Figure 1.3: Formation of poly condensation resins from phenol and formaldehyde (Dorfner, 1973).

The properties of the exchanger depend on the nature of the phenols, the quantity of starting materials used, and their side groups (Vasilev, 1968).

1.1.2 Specific and Chelating Ion Exchangers

Specific ion exchangers are those types in which functional groups were introduced which have the properties of a specific reagent. The specificity is based on the chemical structure of the ion exchanger itself and may not be confused with the phenomenon of selectivity. Because of its specificity, an ion exchanger can sorb one ionic species to the exclusion of others under a broad range of conditions.

Specific ion exchangers include the entire group of chelating resins whose specificity is based on the chelate or complex-forming functional group. The best known commercial type is the iminodiacetate ion exchanger (Dowex A – 1), in which the iminodiacetate groups are directly attached to the styrene matrix (Figure 1.4):

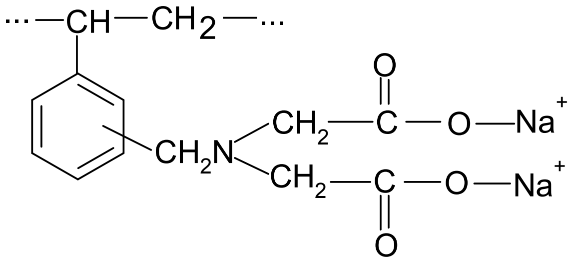

Figure 1.4: The structure of iminodiacetate chelating ion exchanger (Dowex A – 1) (Dorfner, 1973).