

# **UNIVERSITI PUTRA MALAYSIA**

# PREPARATION AND CHARACTERIZATION OF POLY(ETHYL HYDRAZIDE) GRAFTED OIL PALM EMPTY FRUIT BUNCH FOR REMOVAL OF COPPER AND NICKEL IONS FROM AQUEOUS SOLUTIONS

# **ILI SYAZANA BINTI JOHARI**

FS 2012 59

## PREPARATION AND CHARACTERIZATION OF POLY(ETHYL HYDRAZIDE) GRAFTED OIL PALM EMPTY FRUIT BUNCH FOR REMOVAL OF COPPER AND NICKEL IONS FROM AQUEOUS SOLUTIONS



By

ILI SYAZANA BINTI JOHARI

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

November 2012

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

## PREPARATION AND CHARACTERIZATION OF POLY(ETHYL HYDRAZIDE) GRAFTED OIL PALM EMPTY FRUIT BUNCH FOR REMOVAL OF COPPER AND NICKEL IONS FROM AQUEOUS SOLUTIONS

By

### ILI SYAZANA BT JOHARI

November 2012

Chairman : Nor Azah bt Yusof, PhD

## **Faculty : Science**

Poly(ethyl hydrazide) grafted oil palm empty fruit bunch fiber (peh-g-opefb) has been successfully prepared by heating poly(methyl acrylate) grafted opefb (pma-gopefb) at 60°C for 4 hours in a solution of hydrazine hydrate (15% v/v) in ethyl alcohol. The chelating ability of peh-g-opefb was evaluated using Cu(II) and Ni(II) ions in aqueous solution. The concentration of metal was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). pH study was carried out in the pH range from pH 1 to pH 6. The results shows that the adsorption of Cu(II) is optimized at pH 5 while Ni(II) is at pH 6. Isotherm study conducted for both metal ions reveals that the adsorption follows Langmuir isotherm model with maximum adsorption capacity of 43.48 mgg<sup>-1</sup> at 25 °C and 76.92 mgg<sup>-1</sup> at 75 °C for copper ion whereas for nickel ion, the maximum adsorption capacity is 42.19 mgg<sup>-1</sup> at 25 °C and 51.02 mgg<sup>-1</sup> at 75 °C. Kinetic study shows that the adsorption of copper and nickel ion follows pseudo-second-order kinetic model. Thermodynamic study was carried out in order to determine the thermodynamic parameters Gibbs free energy,  $\Delta G^{0}$ , entropy,  $\Delta S^0$  and enthalpy value,  $\Delta H^0$  of the adsorption process. The negative values of  $\Delta G^0$  indicates that both copper and nickel adsorption onto poly(ethyl hydrazide) grafted opefb is a spontaneous process. Positive entropy,  $\Delta S^0$  indicates that the system became more disorder during bioadsorption process whereas positive enthalpy,  $\Delta H^0$  value shows that the adsorption of copper and nickel onto peh-g-opefb is an endothermic process. Selectivity study was done in mix solution of copper or nickel ions with various concentrations of interference ions including Na(I), Ca(II), Mg(II) and Cr(III). The results show that the adsorption of copper and nickel ions by peh-g-opefb was not affected by the presence of the interference ions even in high concentrations. Therefore, the peh-g-opefb is a potential and useful adsorbent which can be applied in many industries particularly related to toxic metal release. Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

## PENYEDIAAN DAN PENCIRIAN GENTIAN TANDAN KOSONG BUAH KELAPA SAWIT TERCANGKUK POLI(ETIL HIDRAZIDA) UNTUK PENYINGKIRAN ION KUPRUM DAN NIKEL DARI LARUTAN AKUEUS

Oleh

## ILI SYAZANA BT JOHARI

#### November 2012

Pengerusi : Nor Azah Bt Yusof, PhD

### Fakulti : Sains

Gentian tandan kosong buah kelapa sawit tercangkuk poli(etil hidrazida) (peh-g-opefb) telah berjaya disediakan melalui pemanasan poli(metil akrilat)-g-opefb pada suhu 60 °C selama 4 jam dengan larutan hidrazina hidrat dalam etil alcohol (15%, v/v). Keupayaan peh-g-opefb untuk mengkelat diuji dengan ion kuprum dan ion nikel dalam larutan akueus. Kepekatan ion-ion tersebut ditentukan menggunakan spektrometri pemancaran optik plasma berganding aruh (ICP-OES). Kajian pH dilakukan dalam julat pH 1 ke pH 6. Keputusan menunjukkan pH optimum penjerapan ion kuprum adalah pada pH 5 manakala ion nikel pada pH 6. Kajian isoterma yang dijalankan menunjukkan bahawa kedua-dua ion kuprum dan nikel mematuhi isoterma model Langmuir dengan jerapan maksimum bagi ion kuprum adalah 43.48 mgg<sup>-1</sup> pada suhu 25 °C dan 76.92 mgg<sup>-1</sup> pada suhu 75 °C manakala bagi ion nikel jerapan maksimum adalah 42.19 mgg<sup>-1</sup> pada suhu 25 °C dan 51.02 mgg<sup>-1</sup> pada suhu 75 °C. Kajian kinetik pula menunjukkan bahawa jerapan ion kuprum dan nikel mematuhi model kinetik tertib kedua. Kajian termodinamik dijalankan bagi menentukan parameter-parameter seperti tenaga bebas Gibbs, ΔG°, entropi, ΔS° dan entalpi, ΔH° bagi proses jerapan ion kuprum dan nikel ke atas peh-g-opefb. Nilai negatif bagi  $\Delta G^{\circ}$ , menunjukkan bahawa proses jerapan bagi kedua-dua ion adalah spontan.  $\Delta S^{\circ}$  yang bernilai positif menunjukkan sistem menjadi lebih rawak semasa proses jerapan berlaku manakala nilai  $\Delta H^{\circ}$  yang positif pula menunjukkan proses jerapan ion kuprum dan nikel yang bersifat endotermik. Kajian selektiviti telah dijalankan bagi ion kuprum atau nikel dengan mencampur ion tersebut secara berasingan dengan ion asing termasuk Na(I), Ca(II), Mg(II) dan Cr(III) dalam pelbagai kepekatan. Keputusan menunjukkan bahawa jerapan ion kuprum dan nikel tidak terjejas dengan kehadiran ion-ion asing tersebut walaupun pada kepekatan yang tinggi. Oleh yang demikian, peh-g-opefb merupakan penjerap yang berpotensi dan berguna untuk digunakan dalam pelbagai industri yang berkaitan dengan pelepasan logam toksik.

#### ACKNOWLEDGEMENTS

First and foremost, thanks to Allah, the greatest creator for His blessed and finally I have come to the end of this long journey. I would like to express my deep gratitude to Prof Dr Md Jelas Haron for his patience with guidance and constructive suggestions throughout this research. His willingness to spare his time so generously has been very much appreciated. I would also like to thank Associate Profesor Dr Nor Azah bt Yusof and Dr Siti Mariam bt Mohd Nor for their help, advice and encouragement to finish this master degree.

My appreciation also extended to my friends including Ain, Soleha, Syafiq and Zul and also the staffs Pn Rakina, Pn Maznira and Cik Hidayu for their assistance, useful advice, constructive discussion and most important for always being beside me whenever I am in vague or in vain. I am particularly grateful to have all of you as my friends.

Finally, I wish to thank my family especially to my parents Hj Johari b Zakaria and Hjh Saniah bt Ahmad for their undivided love, kindness, patience and utmost supports to me since the day I was born till now. I am so grateful to have both of you as my parents. Special thanks to my beloved husband and son, Mohd Sahrom b Yusof and Muhammad Ziyad Iman too for their patience and understanding. Both of you have inspired me and given me the strength to go through all the challenges. Last but not least, special note of appreciation to Ministry of Higher Education and Universiti Putra Malaysia for the opportunity and scholarship granted to me in making this research possible. I certify that an Examination Committee has met on 1<sup>st</sup> November 2012 to conduct the final examination of Ili Syazana bt Johari on her Master thesis entitled "Preparation and characterization of Poly(ethyl hydrazide) grafted oil palm empty fruit bunch for removal of copper and nickel ions from aqueous solutions" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee were as follows:

### Abdul Halim bin Abdullah, PhD

Associate Professor Faculty of Science Universiti Putra Malaysia (Chairman)

### Nor Azowa bt Ibrahim, PhD

Faculty of Science Universiti Putra Malaysia (Internal Examiner)

## Tan Yen Ping, PhD

Faculty of Science Universiti Putra Malaysia (Internal Examiner)

### Rusli bin Daik, PhD

Associate Profesor Faculty of Science and Technology Universiti Kebangsaan Malaysia (External Examiner)

## **BUJANG KIM HUAT, PhD**

Professor and Dean School of Graduate Studies Universiti Putra Malaysia Date: This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Nor Azah bt Yusof, PhD Associate Professor Faculty of Science Universiti Putra Malaysia (Chairman)

Siti Mariam bt Mohd Nor, PhD Senior Lecturer Faculty of Science Universiti Putra Malaysia (Member)

> **BUJANG BIN KIM HUAT, PHD** Profesor and Dean School of Graduate Studies Universiti Putra Malaysia

Date:

## DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

## ILI SYAZANA BINTI JOHARI

Date: 1 November 2012

## **TABLE OF CONTENTS**

A	BSTRACT	ii
A	BSTRAK	iv
A	CKNOWLEDGMENTS	vi
A	PPROVAL STOLEN	vii
L	ECLARATION IST OF TABLES	1X
L	IST OF FIGURES	xiv
L	IST OF ABBREVIATIONS	xvii
C	HAPTER D D	
1	INTRODUCTION	1
	1.1 Background of study	1
	1.2 Objectives of study	4
2	LITERATURE REVIEW	6
	2.1 Heavy metals	6
	2.1.1 Heavy metals in the environment	6
	2.1.2 Copper	10
	2.1.3 Nickel	12
	2.2 Heavy Metal Removal	14
	2.2.1 Solvent Extraction	14
	2.2.2 Chemical precipitation	17
	2.2.3 Ion exchange	19
	2.2.4 Adsorption	21
	2.3 Bioadsorbent as Chelating fiber	23
	2.4 Oil Palm Empty Fruit Bunch (opefb)	27
	2.5 Graft copolymerization onto opefb	29
	2.6 Hydrazide	31
3	METHODOLOGY	37
	3.1 Chemicals and equipments	37
	3.2 Graft Copolymerization of methyl acrylate onto opefb	38
	3.3 General procedure for preparation of poly(ethyl hydrazide)-g- opefb	40

	3.4 Optimization study for preparation of poly(ethyl hydrazide)-g-opefb	40
	3.4.1 Effect of Hydrazine hydrate concentration	40
	3.4.2 Effect of temperature	41
	3.4.3 Effect of reaction time	41
	3.5 Characterization technique	42
	3.5.1 FTIR Spectroscopy	42
	3.5.2 Elemental Analysis	42
	3.6 Thermogravimetry Analysis	42
	3.7 Scanning Electron Microscopy	43
	3.8 Screening adsorption of metal ions using poly(ethyl hydrazide)-g-opefb	43
	3.9 Metal ion uptake experiments using adsorption method	44
	3.9.1 Inductively Coupled Plasma Optical Emission Spectrrometry (ICPOES)	44
	3.9.2 Effect of pH on adsorption of copper and nickel ions	44
	3.9.3 Effect of initial concentration and temperature on copper and nickel ions	
	adsorption	45
	3.9.4 Effect of contact time on copper and nickel ions adsorption	45
	3.9.5 Effect of adsorbent dosage on copper and nickel ions adsorption	45
	3.9.6 Desorption study	46
1	DESULTS AND DISCUSSIONS	18
-	4.1 Graft copolymerization of methyl acrylate onto opefb	48
	4.2 Proposed reaction in the preparation of poly(ethyl hydrazide)-g-opefb	49
	4.3 Optimization study of preparation of poly(ethyl hydrazide)-g-opefb	51
	4.3.1 Effect of hydrazine hydrate concentration	51
	4.3.2 Effect of temperature	52
	4.3.3 Effect of reaction period	53
	4.3.4 Optimum condition of preperation of poly(ethyl hydrazide)-g-opefb	54
	4.4 Characterization of opefb, pma-g-opefb and poly(ethyl hydrazide)-g-opefb	55
	4.4.1 FTIR of opefb, pma-g-opefb and poly(ethyl hydrazide)-g-opefb	55
	4.4.2 Elemental analysis of opefb, pma-g-opefb and poly(ethyl hydrazide)-g-	
	opefb	57
	4.5 Thermogravimetric Analysis	58

Q

4.6 Surface morphology	62
4.7 Screening adsorption of metal ions using opefb, pma-g-opefb and poly (ethylhydrazide)-g-opefb	63
4.8 Adsorption study of copper and nickel ions	65
4.8.1 Effect of pH	65
4.8.2 Effect of initial concentration and temperature	67
4.8.3 Adsorption isotherm	73
4.8.4 Adsorption Thermodynamic	85
4.8.5 Adsorption kinetic	88
4.8.6 Dosage study	94
4.8.7 Desorption study	96
4.8.8 Selectivity study	98
	102
5 CONCLUSIONS	103
5.1 Recommendation for further study	105
REFERENCES	
BIODATA OF STUDENT	
APPENDICES	120

C