UNIVERSITI PUTRA MALAYSIA

REMOVAL OF IRON AND OIL FROM PALM OIL MILL EFFLUENT USING CHITOSAN COATED ALGINATE–MANGROVE COMPOSITE BEADS

RANA JAAFAR JAWAD

REMOVAL OF IRON AND OIL FROM PALM OIL MILL EFFLUENT USING CHITOSAN COATED ALGINATE–MANGROVE COMPOSITE BEADS

By

RANA JAAFAR JAWAD

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

September 2016

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

REMOVAL OF IRON AND OIL FROM PALM OIL MILL EFFLUENT USING CHITOSAN-COATED ALGINATE–MANGROVE COMPOSITE BEADS

By

RANA JAAFAR JAWAD

September 2016

Chairman : Assoc. Prof. Mohd. Halim Shah Ismail, PhD
Faculty : Engineering

This research focuses on the removal of iron ions and residue oil from palm oil mill effluent using chitosan-coated alginate–mangrove composite beads (CCAMCB). The Fourier transforms infrared spectroscopy (FTIR) was used to reveal the main functional groups and to prove the successful coating of beads by chitosan, and scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) and swelling studies were employed to discover the surface morphology, chemical composition and identify the crystalline nature of the beads, respectively. The adsorption process was conducted through batch studies and continuous studies. In batch studies, the influence of different experimental parameters such as pH, adsorbent dosage, contact time, and initial concentration on iron ions and residue oil removal was investigated to determine the optimum operating conditions. The results of the batch studies reveal that the maximum removal of iron ions was 92.7% at pH 3, 300 g/L of adsorbent concentration, and contact time of 72 hours, and the maximum removal of residue oil was 98.47% at pH 3, 50 g/L of adsorbent concentration, and contact time of 2.5 hours. The adsorption isotherm studies reveal that both iron ions and residue oil followed the Freundlich isotherm model, and in terms of kinetic studies, both iron ions and residue oil followed the pseudo second order. Continuous studies were performed in a fixed bed column with different bed heights, and it was found that the time of breakthrough increased with a higher bed depth. The Thomas model and Yoon-Nelson model were used to estimate the experimental data.

As a conclusion, the CCAMCB demonstrated a potential application to remove iron ions and residue oil from POME.

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

PENYINGKIRAN BESI DAN MINYAK DARIPADA EFLUEN MINYAK KELAPA SAWIT KILANG DENGAN MENGGUNAKAN MANIK KOMPOSIT ALGINATE-BAKAU BERSALUT KITOSAN

Oleh

RANA JAAFAR JAWAD

September 2016

Pengerusi : Profesor Madya Mohd. Halim Shah Ismail, PhD
Fakulti : Kejuruteraan

Kajian ini memberi tumpuan kepada penyingkiran ion besi dan minyak sisa daripada efluen minyak kelapa sawit kilang dengan menggunakan manik komposit alginate-bakau bersalut kitosan (CCAMCB). Spektroskopi inframerah transformasi Fourier (FTIR) telah digunakan untuk mendedahkan kumpulan fungsian utama dan untuk membuktikan bahawa manik berjaya disaluti dengan kitosan, dan mikroskop elektron pengimbas (SEM) dengan spektroskopi serakan tenaga (EDX) dan kajian pembengkakan telah digunakan untuk menyiasat morfologi permukaan, komposisi kimia dan mengenal pasti sifat hablur manik tersebut, masing-masing. Proses penjerapan telah dijalankan melalui kajian kelompok dan kajian berterusan. Dalam kajian kelompok, pengaruh parameter eksperimen yang berbeza seperti pH, dos penjerap, masa sentuhan, dan kepekatan awal pada penyingkiran ion besi dan minyak sisa disiasat untuk menentukan keadaan operasi yang optimum. Keputusan kajian kelompok menunjukkan bahawa penyingkiran maksimum ion besi adalah 92.7% pada pH 3, kepekatan penjerap 300 g/L, dan masa sentuhan 72 jam, dan penyingkiran maksimum minyak sisa adalah 98.47% pada pH 3, kepekatan penjerap 50 g/L, dan masa sentuhan 2.5 jam. Kajian penjerapan isoterma menunjukkan bahawa kedua-dua ion besi dan minyak sisa mengikuti model isoterma Freundlich, dan dari segi kajian kinetik, kedua-dua ion besi dan minyak sisa mengikuti perintah kedua pseudo. Kajian berterusan telah dilakukan dalam ruang lapisan tetap dengan ketinggian lapisan yang berbeza, dan didapati bahawa masa penembusan meningkat dengan kedalaman lapisan yang lebih tinggi. Model Thomas dan model Yoon-Nelson telah digunakan untuk menganggarkan data eksperimen.

Kesimpulannya, aplikasi CCAMCB itu berpotensi menyingkirkan ion besi dan minyak sisa daripada efluen minyak kelapa sawit kilang.

ACNOWLEDGEMENTS

I would like to express my deepest appreciation to my supervisor, Assoc. Prof. Dr. Mohd Halim Shah Ismail for his guidance and persistent help during the work of this thesis.

I would also like to thank my co-supervisor, Prof. Fakhrul-Razi B Ahmadun and Dr. Shamsul Izhar Siajam for their precious comments and support in this research.

Moreover, I would like to express my eternal gratitude to my husband and my beautiful children for their patience, encouragement and support.

Finally, special thanks to all my friends who helped me and supported me.

I certify that a Thesis Examination Committee has met on 19th of September 2016 to conduct the final examination of RANA JAAFAR JAWAD on her thesis entitled″Removal of Iron and Oil from Palm Oil Mill Effluent using Chitosan Coated Alginate-Mangrove Composite Beads″ in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106 15 March 1998. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Thesis Examination Committee were as follows:

Tinia Idaty Mohd. Ghazi, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairperson)

Zurina Zainal Abidin, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Abdul Aziz Abdul Raman, PhD Ir
Professor
Faculty of Engineering
University of Malaya
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy 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 fulfilment of the requirement for the degree of Master of Science.

The member of the Supervisory Committee were as follows:

Mohd Halim Shah Ismail, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Fakhrul-Razi B Ahmadun
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Shamsul Izhar Siajam, PhD
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice- Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ______________________________Date: ____________________

Name and Matric No.: Rana Jaafar Jawad, GS39775

Declaration by Members of Supervisory Committee

This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
- Supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ________________________

Name of Chairman of Supervisory Committee: Associate Professor Dr. Mohd Halim Shah Ismail

Signature: ________________________

Name of Member of Supervisory Committee: Professor Dr. Fakhrul-Razi B Ahmadun

Signature: ________________________

Name of Member of Supervisory Committee: Dr. Shamsul Izhar Siajam

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/GLOSSARY OF TERMS

Abbreviation	**Definition**
AMCB	Alginate Mangrove Composite Beads
CCAMCB	Chitosan Coated Alginate Mangrove Composite Beads
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOE	Department of Environment
EDX	Energy Dispersive X-ray Spectroscopy
FAS	Ferrous Ammonium Sulfate
FTIR	Fourier Transform Infrared Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
HRT	Hydraulic Retention Time
POME	Palm Oil Mill Effluent
SEM	Scanning Electron Microscope
TS	Total Solids
TSS	Total Suspended Solids
USDA	United States Department of Agriculture

Glossary	**Definition**
A	Area under the breakthrough curve
a	Volume of FAS used for blank (ml)
b	Volume of FAS used for sample (ml)
C_d	Desorbed metal ions concentration (mg/L)
C_i	Initial (Inlet) adsorbate concentration (mg/L)
C_e	Concentration of adsorbate at equilibrium (mg/L)
C_t	Outlet adsorbate concentration (mg/L)
C_{ad}	Adsorbed concentration of adsorbate (mg/L)
K_L	Langmuir constant (L/mg)
K_f	Freundlich constant (mg/g)
K_1	Pseudo first order constant (1/min)
K_2	Pseudo second order constant (g/mg. min)
K_{TH}	Thomas kinetic coefficient (ml/min.mg)
K_{YN}	Yoon-Nelson rate of constant (1/min)
n	Freundlich adsorption isotherm constant
M	Molarity of FAS
M_{total}	Total amount of adsorbate send to the column (mg)
m	Mass of the adsorbent (g)
pH_{zpc}	Point of zero charge
pH_i	Initial pH of the solution
pH_f	Final pH of the solution
R^2	Correlation coefficient
t	Time (min)
v	Volume of sample (ml)
v_{eff}	Volume of effluent (ml)
Q	Volumetric flow rate (ml/min)
q_e	Amount of adsorbate adsorbed at equilibrium (mg/g)
q_{max}	Maximum capacity of monolayer adsorption (mg/g)
q_t	Amount of adsorbate adsorbed at contact time (mg/g)
q_x	Maximum adsorption capacity (mg/g)

q_{total}	Total Iron ions or residue oil adsorbed quantity (mg)
$q_{e.exp}$	Equilibrium adsorbate uptake (mg/g)
W_s	Weight of swallow Beads (g)
W_i	Weight of initial Beads (g)
W_1	Initial weight of the conical flask (g)
W_2	Final weight of the conical flask (g)
X	Total dry weight of absorbent (CCAMCB) in column (g)
Y	Total removal percentage of adsorbate
Ƭ	Time required for 50% of adsorbate breakthrough (min)

CHAPTER 1

INTRODUCTION

1.1 Industrial wastewater

In the last century, since the industrial revolution, industrial wastewater has been considered as one of the major sources of water pollution. An enormous amount of industrial wastewater is being released into natural water resources, which has resulted in water pollution and severe damage to the environment (Cockab, 2011). The industrial wastewater can be classified into two types: organic and inorganic industrial wastewater. The pollutants of the industrial wastewater constitute a wide range of materials such as soluble organics that render an odour and taste to effluents, organic suspended solids, inert suspended solids that impart turbidity, heavy metals and toxic materials, oil and floating substances, and dissolved salts (chlorides, nitrates, and phosphates) (Igwe et al., 2007).

There are different types of industries in the world such as pharmaceuticals, oil and refinery, soap and detergent, textile, pulp and papers, and palm oil industries (Wang et al., 2004), and each one of these industries produce its own pollutants. Though the food industry is considered to produce fewer pollutants than the other types of industries such as the metal industry, wastewater from the food industry consists of organic pollutants with an enormous amount of sludge and solid wastes. The food industry effluent contains chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), phosphorus, and nitrogen and may have toxic heavy metals (Alam et al., 2009). Globally, wastewater pollution from the food industry poses risks to all organisms and causes many dangerous diseases to humans, especially when the water is contaminated with toxic heavy metals (Olaniyi et al., 2012).

1.2 Palm oil industry

Palm oil is a vegetable oil rich in vitamins (A and E) and three main fatty acids which are palmitic, oleic, and linoleic acids (Wang et al., 2004). Globally, palm oil is considered the most effective oil among the other kinds of oilseeds. It is used in food production as cooking oil and for the production of margarine and shortenings (Ansori Nasution et al., 2014).

Palm oil is extracted from fruitlets of the oil palm tree. These fruitlets consist of a fleshy pulp (mesocarp) that surrounds the hard seed (kernel) and the shell (endocarp) as illustrated in Figure 1.1. The palm oil is extracted from the mesocarp.

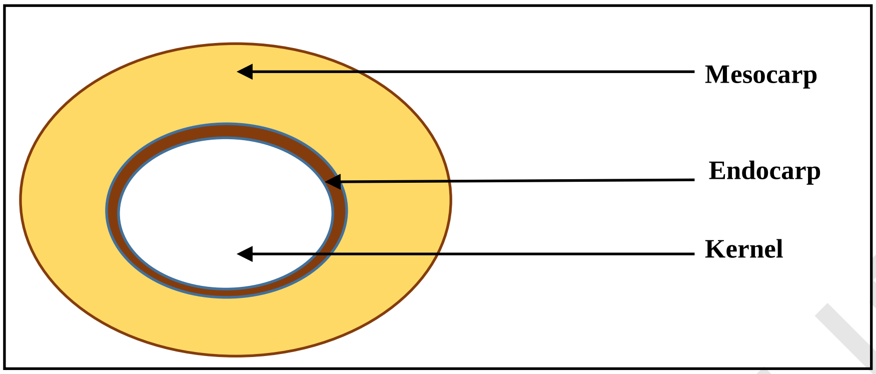

Figure 1.1: Cross-section cutting of oil palm fruitlet (adopted from (Wang et al., 2004)

Palm oil (*Elaeis guineensis*) originated in West Africa, and it was planted in South East Asia in the early 20th century. During that time, the production of palm oil increased rapidly in Malaysia. Currently, Malaysia is the second biggest producer and exporter of palm oil in the world after Indonesia (Idris et al., 2012; Kutty et al., 2011). The production of palm oil in Malaysia (as shown in Figure 1.2) has increased from 10.8 million tons in 1999/2000 to 21 million tons in 2015/2016, according to the United States Department of Agriculture (USDA).

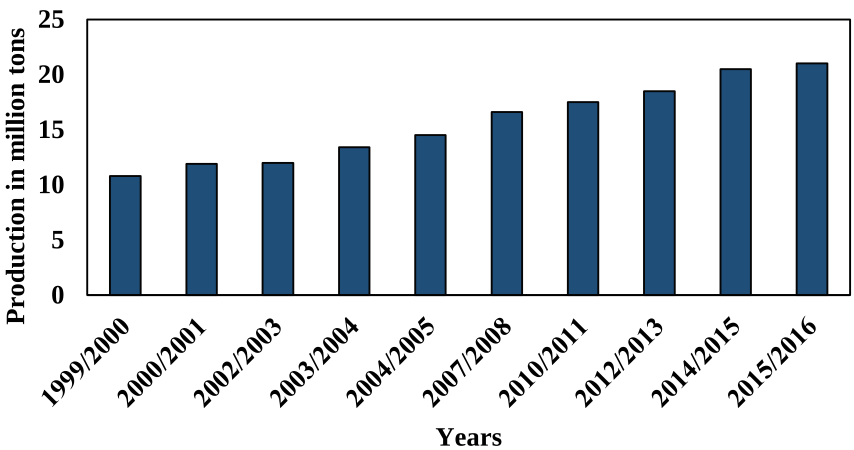

Figure 1.2: Production of palm oil in Malaysia from 1999/2000 to 2015/2016 (source: USDA)

The number of palm oil mills in Malaysia increased rapidly from about 150 mills in 1980 to 429 mills in 2010 (Figure 1.3; (Taha et al., 2014).

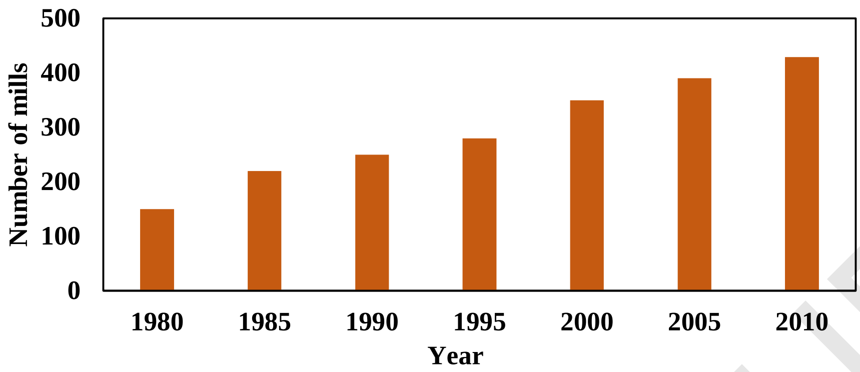

Figure 1.3: Number of mills in Malaysia from 1980 to 2010 (adopted from (Taha et al., 2014)

1.3 Palm oil mill effluent

Palm oil mill effluent (POME) is generated during the three stages of palm oil production: sterilisation, clarification and purification, and hydrocyclone operation (Nwaogu et al., 2012). POME is a dark brown liquid owing to the presence of lignin, humic acid, lipids, fatty acids, and tannin (Saeed et al., 2015). It is hot with a temperature between 80^{o}C and 90^{o}C and acidic with the pH of 4.5–5 (Chan et al., 2015).

POME mainly consists of the following: water 95%–96%, total solid 4%–5%, and oil and grease 0.6%–0.7%. In addition, POME contains pectin, amino acids, and phenolics (Ng et al., 2016). It also contains phosphorus, magnesium, calcium, potassium, and nitrogen (Mohammed et al., 2014).

Approximately, the production of 1 ton palm oil results in the generation of 2.5 tons POME. In 2010, in Malaysia, more than 60 million tons of POME was produced from 421 mills (Ng et al., 2016; Taha et al., 2014). A huge amount of POME is generated every year, which contains high COD, BOD, oil and grease, and heavy metals. This untreated POME causes severe damages to the environment.

1.4 Environmental impacts of residue oil and heavy metals in POME

1.4.1 Residue oil

POME constitutes an oily wastewater containing oil and grease, which pollutes the water resources and causes harmful effects on all aquatic creatures. POME has the ability to form an oily layer on the water surface. This reduces light penetration into the water and subsequently has an adverse effect on photosynthesis. Moreover, this oily layer decreases the transfer of oxygen from air to water, leading to a low level of dissolved oxygen in water. This creates a direct threat to marine living organisms, which in turn leads to adverse effects on humans through the food chain (Jameel et al., 2011).

1.4.2 Heavy metals

Heavy metals are elements with a specific gravity higher than 5 kg/dm^3. They are non-biodegradable and toxic and bio-accumulate in aquatic living organisms. These heavy metals get into humans through the food chain and cause many diseases such as cancer (Bernard et al., 2013). Heavy metals precipitate as hydroxide, and this formation consumes oxygen, affecting the life of aquatic organisms. The sources of heavy metals in POME may include soil and fertilisers or may result from corrosion (Osei, 2013).

1.5 Problem statement

The palm oil industry is considered as one of the major industries and the key contributor to the economic prosperity of Malaysia. A huge amount of POME is discharged during the palm oil production process, and this effluent has many negative aspects:

1. The residual oil content in untreated POME is very high, at an average of 9,065 mg/L (Bello et al., 2013), which exceeds the permissible limits issued by the Department of Environmental (DOE) Malaysia (50 mg/L). The treatment of oil in POME is a big issue because of the emulsified shape of the oil and its high stability. Moreover, the presence of glycolipids and phospholipids makes the oil recovery much harder (M. Shavandi et al., 2012b).
2. The POME contains many heavy metals such as lead (Pb^{2+}), zinc (Zn^{2+}), cadmium (Cd^{2+}), manganese (Mn^{2+}), iron (Fe^{3+}), copper (Cu^{2+}), and chromium (Cr^{2+}) (Idris et al., 2012; Ohimain et al., 2012; M. Shavandi et al., 2012a). Among all these heavy metals, iron ions have the highest concentration and are found at a dangerous level in POME with an average of 119.5 mg/L (Wu et al., 2010), which exceeds the permissible limits (5 mg/L) issued by DOE Malaysia.

The current methods used to treat POME are mainly focused on the reduction of parameters like BOD, COD, and total solid (TS). Consequently, the environmental risk of residue oil and iron ions remains underestimated. Though various methods are used to treat effluents containing residue oil and heavy metals, the adsorption process is considered as one of the best methods compared to other traditional treatments. This can be attributed to many reasons like economic viability of the method, especially when using low-cost material as adsorbents; ability to adequately remove pollutants even at low concentrations; simplicity of operation and handling; and safety (Abas et al., 2013).

1.6 Objectives

The objectives of this research comprise the following aspects:

1. To develop alginate–mangrove coated with chitosan composite beads as adsorbent.
2. To synthesise and characterise the absorbent.
3. To investigate the feasibility of the chitosan-coated alginate–mangrove composite beads for the removal of iron and oil from palm oil mill effluents in batch and continuous studies.

1.7 Scope of study

Developing a composite adsorbent of mangrove bark with alginate in bead shape, coated by chitosan, is the main focus of the present study. The potential of the adsorbent for the removal of iron ions and residue oil from POME in terms of batch, continuous, and characterisation studies has been tested. Under the batch condition, different operation parameters were set such as pH of 2–9, adsorbent dosage of 2.5–40 g, and contact time of 0.5–120 hrs. The kinetic study was evaluated by pseudo first order and pseudo second order, and the isotherm study was performed using Langmuir and Freundlich isotherms. In continuous studies, the effect of depth of adsorbent (9, 18, and 27 cm) was investigated by using a glass column, and the obtained data was evaluated using the Thomas and Yoon-Nelson model.

1.8 Significance of study

Though various studies were conducted to treat POME, the adsorption process was chosen to remove iron and oil from POME. This can be attributed to the fact that adsorption is efficient in removing different types of pollutants (organic and inorganic). Commonly and abundantly available natural materials were explored to be used as adsorbent.

In this study, a novel type of adsorbent was prepared: chitosan-coated alginate–mangrove composite beads (CCAMCB). Beads are the best form of biopolymer adsorbent to remove pollutants from wastewater and they also prevent the column clogging problems (M. Zhang et al., 2015). Moreover, beads are easy to separate from wastewater after treatment and easy to be regenerated.

Mangrove bark is chosen as the best material for removing heavy metals and residue oil due to its large availability in Malaysia as the solid waste of charcoal factories. It contains effective functional groups such as carboxylic, phenolic, and hydroxyl groups, which can aid in heavy metals removal (Rozaini et al., 2010). Moreover, mangrove bark is abundantly found outside charcoal factories, and using it will be helpful in solving the disposal problems. Alginate is a biopolymer obtained from the cell walls of brown algae. It contains effective functional groups such as carboxylate and hydroxyl groups, which are well known for their ability to adsorb heavy metals (Bée et al., 2011). Alginate is considered as one of the most eco-friendly, cost-effective, and biodegradable materials. Chitosan is a copolymer obtained from chitin that is produced from arthropods' exoskeleton, yeast and fungi cell walls, clams, krill, shellfish, squid, and shrimps (Rinaudo, 2006). It contains effective functional groups such as amino and hydroxyl groups. Amine has a great potential for adsorbing oil due to its ability to attract negative ions and bind oil (Ahmad et al., 2004). Chitosan is biodegradable and non-toxic and can flocculate and regenerate.

1.9 Outline of thesis

This thesis consists of five chapters:

Chapter 1: constitutes the introduction and describes the palm oil industry, palm oil mill effluents, research problems, objectives, significance, and the scope of the research.

Chapter 2: covers the literature review of characterisations of POME, technologies used to treat POME, adsorption process, and properties and applications of the natural adsorbent.

Chapter 3: covers the methodology that has been used in this study in detail.

Chapter 4: explains the results and discussion. In this part, the results are shown as figures, graphs, and tables.

Chapter 5: constitutes the conclusion of the work and the recommendations suggested for future works.

REFERENCES

Abas, S. N. A., Ismail, M. H. S., Kamal, M. L., & Izhar, S. (2013). Adsorption process of heavy metals by low-cost adsorbent: a review. *World Applied Sciences Journal, 28*(11), 1518-1530.

Abdulrasaq, O. O., & Basiru, O. G. (2010). Removal of copper (II), iron (III) and lead (II) ions from mono-component simulated waste effluent by adsorption on coconut husk. *African Journal of Environmental Science and Technology, 4*(6).

Agbozu, I., & Emoruwa, F. (2014). Batch adsorption of heavy metals (Cu, Pb, Fe, Cr and Cd) from aqueous solutions using coconut husk. *African Journal of Environmental Science and Technology, 8*(4), 239-246.

Ahmad, Sumathi, & Hameed. (2004). Chitosan: a natural biopolymer for the adsorption of residue oil from oily wastewater. *Adsorption science & technology, 22*(1), 75-88.

Ahmad, A., Bhatia, S., Ibrahim, N., & Sumathi, S. (2005). Adsorption of residual oil from palm oil mill effluent using rubber powder. *Brazilian Journal of Chemical Engineering, 22*(3), 371-379.

Ahmad, A., Sumathi, S., & Hameed, B. (2005). Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: equilibrium and kinetic studies. *Water research, 39*(12), 2483-2494.

Ahmad, A., Sumathi, S., & Hameed, B. (2006). Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. *Chemical Engineering Journal, 118*(1), 99-105.

Aksu, Z., & Gönen, F. (2004). Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process biochemistry, 39*(5), 599-613.

Alam, A., Hossain, K., Hossain, B., Ahmed, A., & Hoque, M. (2009). A Study on Industrial Waste Effluents and Their Management at Selected Food and Beverage Industries of Bangladesh.

Ansori Nasution, B. L. N., Ali, E., Yaakob, Z., & Kamarudin, S. K. (2014). Electrocoagulation of palm oil mill effluent for treatment and hydrogen production using response surface methodology.

Argun, M. E., & Dursun, S. (2006). Removal of heavy metal ions using chemically modified adsorbents. *J. Int. Environ. Appl. Sci, 1*(1-2), 27-40.

Argun, M. E., & Dursun, S. (2007). Activation of pine bark surface with NaOH for lead removal. *J Int Env App Sci, 2*(1), 2.

Argun, M. E., Dursun, S., Ozdemir, C., & Karatas, M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of hazardous materials, 141*(1), 77-85.

Arief, V. O., Trilestari, K., Sunarso, J., Indraswati, N., & Ismadji, S. (2008). Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies. *CLEAN–Soil, Air, Water, 36*(12), 937-962.

Asadpour, R., Sapari, N. B., Isa, M. H., & Orji, K. U. (2014a). Enhancing the hydrophobicity of mangrove bark by esterification for oil adsorption. *Water Science & Technology, 70*(7).

Asadpour, R., Sapari, N. B., Isa, M. H., & Orji, K. U. (2014b). Investigation of Modified Mangrove Bark on the sorption of oil in water. *Applied Mechanics & Materials*(567).

Bala, J. D., Lalung, J., & Ismail, N. (2014). Palm Oil Mill Effluent (POME) Treatment ''Microbial Communities in an Anaerobic Digester'': A Review. *International Journal Of Scientific And Research Publications, 4*(6).

Banerjee, K., Ramesh, S., Gandhimathi, R., Nidheesh, P., & Bharathi, K. (2012a). A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions. *Iran. J. Energy Environ, 3*, 143-156.

Banerjee, K., Ramesh, S., Gandhimathi, R., Nidheesh, P., & Bharathi, K. (2012b). A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions. *Iranica Journal of Energy and Environment, 3*, 143-156.

Bée, A., Talbot, D., Abramson, S., & Dupuis, V. (2011). Magnetic alginate beads for Pb (II) ions removal from wastewater. *Journal of colloid and interface science, 362*(2), 486-492.

Bello, M., Nourouzi, M., Abdullah, L. C., Choong, T. S., Koay, Y., & Keshani, S. (2013). POME is treated for removal of color from biologically treated POME in fixed bed column: applying wavelet neural network (WNN). *Journal of hazardous materials, 262*, 106-113.

Bernard, E., & Jimoh, A. (2013). Adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. *International Journal of Engineering and Applied Sciences, 4*(2), 95-103.

Biswas, S., & Mishra, U. (2015). Continuous Fixed-Bed Column Study and Adsorption Modeling: Removal of Lead Ion from Aqueous Solution by Charcoal Originated from Chemical Carbonization of Rubber Wood Sawdust. *Journal of Chemistry, 2015*.

Chan, Y. J., Tan, W. J. R., How, B. S., Lee, J. J., & Lau, V. Y. (2015). Fuzzy optimisation approach on the treatment of palm oil mill effluent (POME) via up-flow anaerobic sludge blanket–hollow centered packed bed (UASB–HCPB) reactor. *Journal of Water Process Engineering, 5*, 112-117.

Cockab, I. (2011). Encyclopedia of Life Support Systems (EOLSS). *World Wide Web, 1*(2).

Dawodu, F. A., & Akpomie, K. G. (2014). Simultaneous adsorption of Ni (II) and Mn (II) ions from aqueous solution unto a Nigerian kaolinite clay. *Journal of Materials Research and Technology, 3*(2), 129-141.

Deepa, C., & Suresha, S. (2013). Removal of Zn (II) Ions from Aqueous Solution and Industrial Waste Water Using Leaves of Araucaria cookii. *Archives of Applied Science Research*, *5*(4), 117-126.

Deze, E. G., Papageorgiou, S. K., Favvas, E. P., & Katsaros, F. K. (2012). Porous alginate aerogel beads for effective and rapid heavy metal sorption from aqueous solutions: effect of porosity in Cu 2+ and Cd 2+ ion sorption. *Chemical Engineering Journal*, *209*, 537-546.

Dutta, P. K., Dutta, J., & Tripathi, V. (2004). Chitin and chitosan: Chemistry, properties and applications. *Journal of scientific and industrial research, 63*(1), 20-31.

Federation, W. E., & Association, A. P. H. (2005). Standard methods for the examination of water and wastewater. *American Public Health Association (APHA): Washington, DC, USA*.

Gupta, V., Carrott, P., Ribeiro Carrott, M., & Suhas. (2009). Low-cost adsorbents: growing approach to wastewater treatment—a review. *Critical Reviews in Environmental Science and Technology, 39*(10), 783-842.

Han, R., Wang, Y., Zhao, X., Wang, Y., Xie, F., Cheng, J., & Tang, M. (2009). Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves. *Desalination, 245*(1), 284-297.

Holme, H. K., Davidsen, L., Kristiansen, A., & Smidsrød, O. (2008). Kinetics and mechanisms of depolymerization of alginate and chitosan in aqueous solution. *Carbohydrate Polymers, 73*(4), 656-664.

Hossain, M., Ngo, H., Guo, W., & Nguyen, T. (2012). Biosorption of Cu (II) from water by banana peel based biosorbent: Experiments and models of adsorption and desorption. *Journal of Water sustainability, 2*(1), 87-104.

Hosseini, S., Malekbala, M. R., Hosseini, S., Babadi, F. E., Balavandy, S. K., & Shavandi, M. A. (2013). Biosorption of azoimide on almond integument: Kinetics, isotherm and thermodynamics studies. *Journal of Environmental Chemical Engineering, 1*(4), 696-702.

Husin, N. I., Wahab, N. A. A., Isa, N., & Boudville, R. (2011). *Sorption equilibrium and kinetics of oil from aqueous solution using banana pseudostem fibers.* Paper presented at the International Conference on Environment and Industrial Innovation.

Idris, Z. M., Jamal, P., & Alam, M. (2012). Evaluation of palm oil mill effluent treatment with concomitant phenolics production by aspergillus niger IBS-103ZA. *Australian Journal of Basic and Applied Sciences, 6*(1), 55-61.

Igberase, E., Osifo, P., & Ofomaja, A. (2014). The adsorption of copper (II) ions by polyaniline graft chitosan beads from aqueous solution: Equilibrium, kinetic and desorption studies. *Journal of Environmental Chemical Engineering, 2*(1), 362-369.

Igwe, J., & Onyegbado, C. (2007). A review of palm oil mill effluent (POME) water treatment. *Global Journal of Environmental Research, 1*(2), 54-62.

Jagung, P. T. (2011). Removal of Zn (II), Cd (II) and Mn (II) from aqueous solutions by adsorption on maize stalks. *Malaysian Journal of Analytical Sciences, 15*(1), 8-21.

Jameel, A. T., Muyubi, S. A., Karim, M. I. A., & Alam, M. Z. (2011). Removal of oil and grease as emerging pollutants of concern (EPC) in wastewater stream. *IIUM Engineering Journal, 12*(4).

Jusoff, K. (2013). Malaysian mangrove forests and their significance to the coastal marine environment. *Polish Journal of Environmental Studies, 22*(4).

Kleinübing, S. J., Da Silva, F. G. C., Bertagnolli, C., & Da Silva, M. G. C. (2011). Heavy metal sorption by calcium alginate beads from Sargassum filipendula. *Chemical Engineering Transactions, 24*, 1201-1206.

Kumar, P. S., & Kirthika, K. (2009). Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. *Journal of Engineering Science and Technology, 4*(4), 351-363.

Kutty, S., Ngatenah, S., Johan, N., & Amat, K. (2011). *Removal of Zn (II), Cu (II), chemical oxygen demand (COD) and colour from anaerobically treated palm oil mill effluent (POME) using microwave incinerated rice husk ash (MIRHA).* Paper presented at the Int Conf Environ Ind Innov IPCBEE.

Lai, Y.-L., Annadurai, G., Huang, F.-C., & Lee, J.-F. (2008). Biosorption of Zn (II) on the different Ca-alginate beads from aqueous solution. *Bioresource technology, 99*(14), 6480-6487.

Lee, K. Y., & Mooney, D. J. (2012). Alginate: properties and biomedical applications. *Progress in polymer science, 37*(1), 106-126.

Li, X., Kong, X., Shi, S., Zheng, X., Guo, G., Wei, Y., & Qian, Z. (2008). Preparation of alginate coated chitosan microparticles for vaccine delivery. *BMC biotechnology, 8*(1), 89.

Lim, A. P., & Aris, A. Z. (2014). Continuous fixed-bed column study and adsorption modeling: Removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons. *Biochemical Engineering Journal, 87*, 50-61.

Lin-Vien, D., Colthup, N. B., Fateley, W. G., & Grasselli, J. G. (1991). *The handbook of infrared and Raman characteristic frequencies of organic molecules*: Elsevier.

Liu, X., & Zhang, L. (2015). Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies. *Powder Technology, 277*, 112-119.

Malekbala, M. R., Soltani, S. M., Yazdi, S. K., & Hosseini, S. (2012). Equilibrium and Kinetic Studies of Safranine Adsorptionon Alkali-Treated Mango Seed

Integuments. *International Journal of Chemical Engineering and Applications, 3*(3), 160.

Marques Neto, J. d. O., Bellato, C. R., Milagres, J. L., Pessoa, K. D., & Alvarenga, E. S. d. (2013). Preparation and evaluation of chitosan beads immobilized with Iron (III) for the removal of As (III) and As (V) from water. *Journal of the Brazilian Chemical Society, 24*(1), 121-132.

Mohammed, R. R., Ketabchi, M. R., & McKay, G. (2014). Combined magnetic field and adsorption process for treatment of biologically treated palm oil mill effluent (POME). *Chemical Engineering Journal, 243*, 31-42.

Narayanan, A., & Dhamodharan, R. (2015). Super water-absorbing new material from chitosan, EDTA and urea. *Carbohydrate Polymers, 134*, 337-343.

Ng, K. H., Lee, C. H., Khan, M. R., & Cheng, C. K. (2016). Photocatalytic degradation of recalcitrant POME waste by using silver doped titania: Photokinetics and scavenging studies. *Chemical Engineering Journal, 286*, 282-290.

Ngah, W. W., & Fatinathan, S. (2008). Adsorption of Cu (II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads. *Chemical Engineering Journal, 143*(1), 62-72.

NiŃa, I., Iorgulescu, M., Spiroiu, M. F., Ghiurea, M., Petcu, C., & Cinteza, O. (2007). The adsorption of heavy metal ions on porous calcium alginate microparticles. *Analele UniversităŃii din Bucuresti–Chimie, Anul, 16*, 1.

Nwaogu, L., Agha, N., & Ihejirika, C. (2012). Investigation on the long term effects of palm oil mill effluent-pollution on soil catalase and dehydrogenase activities of soil micro organism. *J. Biodiv. Environ. Sci, 2*(4), 10-14.

Ohimain, E., Seiyaboh, E., Izah, S., Oghenegueke, V., & Perewarebo, T. (2012). Some selected physico-chemical and heavy metal properties of palm oil mill effluents. *Greener Journal of Physical Sciences, 2*(4), 131-137.

Olaniyi, I., Raphael, O., & Nwadiogbu, J. O. (2012). Effect of industrial effluent on the surrrounding environment. *Archives of Applied Science Research, 4*(1), 406-413.

Olu-owolabi, B., Pputu, O., Adebowale, K., Ogunsolu, O., & Olujimi, O. (2012). Biosorption of Cd 2+ and Pb 2+ ions onto mango stone and cocoa pod waste: kinetic and equilibrium studies. *Sci Res Essays, 7*(15), 1614-1629.

Osei, E. Y. (2013). *COLLEGE OF SCIENCE DEPARTMENT OF BIOCHEMISTRY AND BIOTECHNOLOGY.* COLLEGE OF SCIENCE DEPARTMENT OF BIOCHEMISTRY AND BIOTECHNOLOGY TREATMENT OF LEAD-POISONED RATS THROUGH ORAL ADMINISTRATION OF PALM OIL EXTRACTS A THESIS SUBMITTED TO THE DEPARTMENT OF BIOCHEMISTRY AND BIOTECHNOLOGY, KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY.

Pandhram, P., & Nimbalkar, S. (2013). Adsorption of chromium from industrial waste water by using neem leaves as a low cost adsorbent. *International Journal of Chemical and Physical Sciences, IJCPS, 2*.

Pasparakis, G., & Bouropoulos, N. (2006). Swelling studies and in vitro release of verapamil from calcium alginate and calcium alginate–chitosan beads. *International journal of pharmaceutics, 323*(1), 34-42.

Popuri, S. R., Vijaya, Y., Boddu, V. M., & Abburi, K. (2009). Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. *Bioresource technology, 100*(1), 194-199.

Quek, S., & Al-Duri, B. (2007). Application of film-pore diffusion model for the adsorption of metal ions on coir in a fixed-bed column. *Chemical Engineering and Processing: Process Intensification, 46*(5), 477-485.

Rahim, A. A., Rocca, E., Steinmetz, J., Kassim, M., Adnan, R., & Ibrahim, M. S. (2007). Mangrove tannins and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium. *Corrosion Science, 49*(2), 402-417.

Rinaudo, M. (2006). Chitin and chitosan: properties and applications. *Progress in polymer science, 31*(7), 603-632.

Rozaini, C., Jain, K., Oo, C., Tan, K., Tan, L., Azraa, A., & Tong, K. (2010). Optimization of nickel and copper ions removal by modified mangrove barks. *Int J Chem Eng Appl, 1*(1), 84-89.

Saeed, M. O., Azizli, K., Isa, M. H., & Bashir, M. J. (2015). Application of CCD in RSM to obtain optimize treatment of POME using Fenton oxidation process. *Journal of Water Process Engineering, 8*, e7-e16.

Saifuddin, N., & Dinara, S. (2011). Pretreatment of palm oil mill effluent (POME) using magnetic chitosan. *Journal of Chemistry, 8*(S1), S67-S78.

Seey, T. L., & Kassim, M. (2012a). Acidic and basic dyes removal by adsorption on chemically treated mangrove barks. *International Journal of Applied, 2*(3).

Seey, T. L., & Kassim, M. J. N. M. (2012b). CHARACTERIZATION OF MANGROVE BARK ADSORBENT AND ITS APPLICATION IN THE REMOVAL OF TEXTILE DYES FROM AQUEOUS SOLUTIONS. *Journal of applied phytotechnology in environmental sanitation, 1*(3).

Sethupathi, S. (2004). *Removal Of Residue Oil From Palm Oil Mill Effluent (Pome) Using Chitosan [TD899. I27 S955 2004 f rb][Microfiche 7577]*. Universiti Sains Malaysia.

Shaker, M. A. (2015). Adsorption of Co (II), Ni (II) and Cu (II) ions onto chitosan-modified poly (methacrylate) nanoparticles: Dynamics, equilibrium and thermodynamics studies. *Journal of the Taiwan Institute of Chemical Engineers, 57*, 111-122.

Shavandi, M., Haddadian, Z., Ismail, M., Abdullah, N., & Abidin, Z. (2012a). Removal of Fe (III), Mn (II) and Zn (II) from palm oil mill effluent (POME) by natural zeolite. *Journal of the Taiwan Institute of Chemical Engineers, 43*(5), 750-759.

Shavandi, M., Haddadian, Z., Ismail, M., Abdullah, N., & Abidin, Z. (2012b). Removal of residual oils from palm oil mill effluent by adsorption on natural zeolite. *Water, Air, & Soil Pollution, 223*(7), 4017-4027.

Shavandi, M. A., Haddadian, Z., Ismail, M. H. S., & Abdullah, N. (2012). Continuous metal and residual oil removal from palm oil mill effluent using natural zeolite-packed column. *Journal of the Taiwan Institute of Chemical Engineers, 43*(6), 934-941.

Socrates, G. (2004). *Infrared and Raman characteristic group frequencies: tables and charts*: John Wiley & Sons.

Soleimani, F., Sadeghi, M., & Shahsavari, H. (2012). Preparation and swelling behavior of carrageenan-graft-polymethacrylamide superabsorbent hydrogel as a releasing drug system. *Indian Journal of Science and Technology, 5*(2), 2143-2147.

Su, H., Bajpai, R., & Preckshot, G. W. (1989). Characterization of alginate beads formed by a two fluid annular atomizer. *Applied Biochemistry and Biotechnology, 20*(1), 561-569.

Sugashini, S., Begum, S., & Meera, K. (2012). Column adsorption studies for the removal of Cr (VI) ions by ethylamine modified chitosan carbonized rice husk composite beads with modelling and optimization. *Journal of Chemistry, 2013*.

Taha, M. R., & Ibrahim, A. (2014). COD removal from anaerobically treated palm oil mill effluent (AT-POME) via aerated heterogeneous Fenton process: Optimization study. *Journal of Water Process Engineering, 1*, 8-16.

Tanhaei, B., Ayati, A., Lahtinen, M., & Sillanpää, M. (2015). Preparation and characterization of a novel chitosan/Al 2 O 3/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of Methyl Orange adsorption. *Chemical Engineering Journal, 259*, 1-10.

Tiwari, A., Dewangan, T., & Bajpai, A. (2008). Removal of toxic As (V) ions by adsorption onto alginate and carboxymethyl cellulose beads. *Journal of the Chinese Chemical Society, 55*(5), 952-961.

Vipin, A. K., Ling, S., & Fugetsu, B. (2016). Removal of Cs+ and Sr 2+ from water using MWCNT reinforced Zeolite-A beads. *Microporous and Mesoporous Materials, 224*, 84-88.

Wang, L. K., Hung, Y.-T., Lo, H. H., & Yapijakis, C. (2004). *Handbook of industrial and hazardous wastes treatment*: CRC Press.

Welna, M., Szymczycha-Madeja, A., & Pohl, P. (2011). *Quality of the trace element analysis: sample preparation steps*: INTECH Open Access Publisher.

Wu, T. Y., Mohammad, A. W., Jahim, J. M., & Anuar, N. (2010). Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. *Journal of Environmental Management, 91*(7), 1467-1490.

Xu, Z., Cai, J.-g., & Pan, B.-c. (2013). Mathematically modeling fixed-bed adsorption in aqueous systems. *Journal of Zhejiang University SCIENCE A, 14*(3), 155-176.

Zhang, J., Xia, W., Liu, P., Cheng, Q., Tahi, T., Gu, W., & Li, B. (2010). Chitosan modification and pharmaceutical/biomedical applications. *Marine drugs, 8*(7), 1962-1987.

Zhang, J., Xu, S., Zhang, S., & Du, Z. (2008). Preparation and characterization of tamarind gum/sodium alginate composite gel beads. *Iranian Polymer Journal, 17*(12), 899-906.

Zhang, M., Zhang, Y., & Helleur, R. (2015). Selective adsorption of Ag+ by ion-imprinted O-carboxymethyl chitosan beads grafted with thiourea–glutaraldehyde. *Chemical Engineering Journal, 264*, 56-65.

Zheng, H., Han, L., Ma, H., Zheng, Y., Zhang, H., Liu, D., & Liang, S. (2008). Adsorption characteristics of ammonium ion by zeolite 13X. *Journal of hazardous materials, 158*(2), 577-584.

Zhuang, Y., Yu, F., Chen, J., & Ma, J. (2016). Batch and column adsorption of methylene blue by graphene/alginate nanocomposite: Comparison of single-network and double-network hydrogels. *Journal of Environmental Chemical Engineering, 4*(1), 147-156.

BIODATA OF STUDENT

The student is Rana Jaafar Jawad. She was born in Baghdad/Iraq on 16 May 1980. She passed her Bachelor's Degree in Chemical Engineering at University of Technology in 2002. She continued her study in the Master's Degree of Chemical Engineering at Universiti Putra Malaysia (UPM) in February 2014.

LIST OF PUBLICATIONS

Rana Jaafar Jawad, Mohd Halim Shah Ismail, and Shamsul Izhar Siajam. Removal of Residual Oil from Palm Oil Mill Effluent by Novel Adsorbent of Alginate and Mangrove Composite Beads Coated by Chitosan (2016). Published in: World Applied Sciences Journal. DOI: 10.5829/idosi.wasj.2016.34.9.200, 34(9): 1159-1166.

Rana Jaafar Jawad, Mohd Halim Shah Ismail, and Shamsul Izhar Siajam. Removal of Heavy Metals and Colour from Industrial Wastewater by novel composite adsorbent of Alginate and Mangrove beads Coated by Chitosan. Published in: Journal of Purity, Utility Reaction and Environment, 5(5): 118-129

Rana Jaafar Jawad, Mohd Halim Shah Ismail, and Shamsul Izhar Siajam. Adsorption of Iron Ions from Palm Oil Mill Effluent using a Novel Adsorbent of Alginate–Mangrove Composite Beads Coated with Chitosan. Published in: Iranica Journal of Energy & Environment. DOI: 10.5829/idosi.ijee.2016.07.04.1, 7(4): 393-400.

Rana Jaafar Jawad, Mohd Halim Shah Ismail, and Shamsul Izhar Siajam. Adsorption of Heavy Metals and Residual Oil from Palm Oil Mill Effluent using Novel Adsorbent of Alginate and Mangrove Composite Beads Coated by Chitosan in a Packed Bed Column. Submitted to: IIUM Engineering Journal.

UNIVERSITI PUTRA MALAYSIA

STATUS CONFIRMATION FOR THESIS / PROJECT REPORT AND COPYRIGHT

ACADEMIC SESSION : ___________________

TITLE OF THESIS / PROJECT REPORT :

REMOVAL OF IRON AND OIL FROM PALM OIL MILL EFFLUENT USING CHITOSAN COATED ALGINATE–MANGROVE COMPOSITE BEADS

NAME OF STUDENT : RANA JAAFAR JAWAD

I acknowledge that the copyright and other intellectual property in the thesis/project report belonged to Universiti Putra Malaysia and I agree to allow this thesis/project report to be placed at the library under the following terms:

1. This thesis/project report is the property of Universiti Putra Malaysia.

2. The library of Universiti Putra Malaysia has the right to make copies for educational purposes only.

3. The library of Universiti Putra Malaysia is allowed to make copies of this thesis for academic exchange.

I declare that this thesis is classified as :

*Please tick (√)

☐	**CONFIDENTIAL**	(Contain confidential information under Official Secret Act 1972).
☐	**RESTRICTED**	(Contains restricted information as specified by the organization/institution where research was done).
☐	**OPEN ACCESS**	I agree that my thesis/project report to be published as hard copy or online open access.

This thesis is submitted for :

☐	**PATENT**	Embargo from_____________ until ______________ (date) (date)

Approved by:

_____________________ (Signature of Student) New IC No/ Passport No.: Date :	_____________________ (Signature of Chairman of Supervisory Committee) Name: Date :

[Note : If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization/institution with period and reasons for confidentially or restricted.]