

# **UNIVERSITI PUTRA MALAYSIA**

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

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# 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

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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

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Assoc. Prof. Mohd. Halim Shah Ismail, PhD 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 alginatebakau 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.

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

I certify that a Thesis Examination Committee has met on 19<sup>th</sup> 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.

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# 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			
DOF	Department of Environment			
EDV	Energy Dispersive X ray Spectroscopy			
	Energy Dispersive X-ray Spectroscopy			
ГА <b>З</b> ГТІР	Ferrous Annihomum Sumate			
	Fourier Transform Infrared Spectroscopy			
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer			
HKI	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			
а	Volume of FAS used for blank (ml)			
b	Volume of FAS used for sample (ml)			
Cd	Desorbed metal ions concentration (mg/L)			
C:	Initial (Inlet) adsorbate concentration (mg/L)			
C.	Concentration of adsorbate at equilibrium $(mg/L)$			
C.	Outlet adsorbate concentration (mg/L)			
$C_t$	Adsorbed concentration of adsorbate $(mg/L)$			
$\mathbf{K}_{ad}$	Langmuir constant (L/mg)			
KL V	Eroundlich constant (mg/g)			
K <sub>f</sub> V	Pseudo first order constant (1/min)			
$\mathbf{K}_1$	Pseudo mist order constant (7/min)			
$\mathbf{K}_2$	The mass binetic as officient (m1(min mas))			
K <sub>TH</sub>	V N N L L Control (1/min.mg)			
K <sub>YN</sub>	Yoon-Neison rate of constant (1/min)			
n	Freundlich adsorption isotherm constant			
M	Molarity of FAS			
M <sub>total</sub>	Total amount of adsorbate send to the column (mg)			
m	Mass of the adsorbent (g)			
$pH_{zpc}$	Point of zero charge			
pH <sub>i</sub>	Initial pH of the solution			
pH <sub>f</sub>	Final pH of the solution			
$\mathbf{R}^2$	Correlation coefficient			
t	Time (min)			
v	Volume of sample (ml)			
V <sub>eff</sub>	Volume of effluent (ml)			
0	Volumetric flow rate (ml/min)			
Q <sub>e</sub>	Amount of adsorbate adsorbed at equilibrium $(mg/g)$			
no Omer	Maximum capacity of monolayer adsorption $(mg/g)$			
	Amount of adsorbate adsorbed at contact time $(mg/g)$			
าเ ก	Maximum adsorption canacity $(mg/g)$			
Чх	maximum ausorption capacity (mg/g)			

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q <sub>total</sub>	Total Iron ions or residue oil adsorbed quantity (mg)
q <sub>e.exp</sub>	Equilibrium adsorbate uptake (mg/g)
Ws	Weight of swallow Beads (g)
$\mathbf{W}_{i}$	Weight of initial Beads (g)
$\mathbf{W}_1$	Initial weight of the conical flask (g)
$\mathbf{W}_2$	Final weight of the conical flask (g)
Х	Total dry weight of absorbent (CCAMCB) in column (g)
Y	Total removal percentage of adsorbate
Ծ	Time required for 50% of adsorbate breakthrough (min)



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### **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.

#### 1



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  $80^{\circ}$ C and  $90^{\circ}$ 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<sup>3</sup>. They are nonbiodegradable 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 alginatemangrove 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.

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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.

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#### 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.



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