SYNTHESIS AND CHARACTERIZATION OF OIL PALM FROND BASED CRYOGEL FOR HEAVY METALS REMOVAL

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

APRIL 2016

In the Name of ALLAH, The Most Gracious and The Most Merciful

Specially dedicated to
my beloved Mak & Abah and my lovely husband..

Thanks for your endless support and prayers..
They mean the world to me…

ACKNOWLEDGEMENT

Alhamdulillah. First and foremost I thank to Allah the Almighty for his Grace, Mercy and Guidance that awarded me the strength to complete this research. A memorable journey that I will always treasures.

First and foremost, my deepest gratitude's goes to my respectful supervisor, Dr Norzita Binti Ngadi, for all her dedications, counsels, encouragements and outstanding supervisions in accomplishing these whole works. Thanks a lot for all the guidance. May your good deed be rewarded by Allah SWT.

My sincere thanks and appreciations to my beloved parents, Maznah Senawi and Rusli Ismail, for all the strength and motivation given throughout my whole life. Words are not enough to express how grateful I am to have you in this journey. Not to forget, to my supportive family, thanks for your warming support.

My special thanks also goes to my dearest husband, Mohamad Arif Mohd Sulaiman, who always there for me. Thanks a lot for your love and understanding. I will always love you and forever grateful to have you by my side.

Not to forget all my friends who forever besides me and aiding my research to be successfully completed. Finally, thousand thanks to all who involved in this research project. I hope this thesis will be valuable to Islam and ummah. May Allah grants us a continued blessing. Thank you.

ABSTRACT

Heavy metal pollution has become one of the most serious environmental problems today and treatment for this problem, which is environmentally friendly, is vigorously sought. Realising that a large portion of the biomass from the oil palm plantation is just left to rot and returned to the field as fertiliser, this research aims to investigate and explore the preparation of cryogel from the lignin of oil palm frond (OPF). The potential of ultrasound-assisted extraction to extract lignin from OPF as compared to conventional heating was studied. The extraction was carried out using sodium hydroxide solution as a solvent and factors such as solvent concentration and extraction temperature effects were also examined. The presence of lignin in the corresponding extracts was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis and thermogravimetric analysis (TGA). The extracted lignin was then reacted with furfural to synthesize resin before being freeze-dried to obtain cryogel. The cryogel was characterized for their morphology and physical properties using FTIR, field emission scanning electron microscopy, x-ray diffraction, Breuner, Emmer and Teller (BET) and TGA. The performance of cryogel towards the removal of heavy metals ions (zinc (Zn(II)), copper (Cu(II)) and chromium (Cr(VI))) via adsorption process was performed. The adsorption was also described through adsorption kinetics, isotherm and thermodynamic properties. The result obtained showed that the extraction of OPF assisted with ultrasound was more efficient in giving higher lignin yield compared to conventional heating and the optimum lignin yield was 26%. Other than that, the reaction temperature was lowered and the reaction time was also shortened when the extraction was assisted by ultrasound. From FTIR analysis, OPF lignin showed similar spectra in terms of functional groups but slightly different in intensity when compared to commercial lignin. Overall, under optimum conditions of adsorption, Zn(II) gave the highest adsorption capacity followed by Cu(II) and Cr(VI) (i.e. Zn(II)>Cu(II)>Cr(VI)). The adsorption capacity for these heavy metals were 0.995, 0.935 and 0.4895 mg/g for Zn(II), Cu(II) and Cr(VI), respectively. The experimental data were appropriately described by the Langmuir model. This was validated by the R^2 values of the Langmuir model (0.999 to 0.9689) that were higher than the Freundlich model (0.8343 to 0.9539) and the Temkin model (0.8409 to 0.9502) for all the heavy metals tested. The adsorption kinetics followed the pseudo-second order. The negative values of the Gibbs free energy change indicated the adsorption was spontaneous. The negative value of enthalpy change and entropy change confirmed the exothermic nature and showed the decrement of structural changes at solid-solution interface during adsorption process, respectively. It can be concluded that the synthesized cryogel derived from OPF lignin provides a potential performance for heavy metals removal.

ABSTRAK

Pencemaran logam berat telah menjadi salah satu masalah alam sekitar yang serius pada hari ini dan langkah penyelesaian yang mesra alam bagi masalah ini adalah dicari. Menyedari bahawa sebahagian besar biojisim dari ladang kelapa sawit hanya dibiarkan mereput dan sebagai baja, kajian ini bertujuan untuk mengkaji dan meneroka penyediaan kriogel daripada lignin pelepah kelapa sawit (OPF). Potensi pengekstrakan dengan bantuan ultrabunyi untuk mengekstrak lignin dari OPF berbanding pemanasan konvensional telah dikaji. Pengekstrakan ini telah dijalankan dengan menggunakan larutan natrium hidroksida sebagai pelarut dan faktor-faktor seperti kepekatan pelarut dan suhu pengekstrakan juga diperhatikan. Kehadiran lignin dalam ekstrak tersebut telah disahkan melalui analisis spektroskopi inframerah transformasi Fourier (FTIR) dan analisis termogravimetri (TGA). Lignin itu kemudian telah ditindak balaskan bersama furfural untuk menghasilkan resin sebelum dibeku-kering bagi menghasilkan kriogel. Ciri-ciri morfologi dan fizikal kriogel telah diperiksa menggunakan FTIR, mikroskop pengimbas elektron pancaran medan, teknik pembelauan sinar-x, Breuner, Emmer dan Teller (BET) dan TGA. Prestasi kriogel terhadap penyingkiran ion-ion logam berat (zink (Zn(II)), kuprum (Cu(II)) dan kromium (Cr(VI))) melalui proses penjerapan telah diuji. Penjerapan juga diterangkan melalui kinetik penjerapan, isoterma dan sifat-sifat termodinamik. Keputusan yang diperoleh menunjukkan bahawa pengekstrakan OPF dengan bantuan ultrabunyi adalah lebih berkesan kerana memberikan hasil lignin yang lebih tinggi berbanding pemanasan konvensional dan hasil lignin optimum yang dicatatkan adalah 26%. Selain itu, tindak balas juga boleh dilakukan pada suhu yang lebih rendah dan masa tindak balas juga adalah lebih pendek dengan bantuan ultrabunyi. Melalui analisis FTIR, lignin OPF menunjukkan spektrum kumpulan berfungsi yang sama dengan lignin komersil tetapi dalam intensiti yang berbeza. Secara keseluruhan, pada keadaan penjerapan yang optimum, Zn(II) memberikan kapasiti penjerapan yang paling tinggi diikuti dengan Cu(II) dan Cr(VI) (i.e. Zn(II)>Cu(II)>Cr(VI)). Kapasiti penjerapan logam berat ini adalah masing-masing 0.995, 0.935 dan 0.4895 mg/g bagi Zn(II), Cu(II) dan Cr(VI). Data ujikaji ini adalah sesuai digambarkan oleh model Langmuir. Ini telah disahkan oleh nilai R^2 model Langmuir (0.999-0.9689) yang lebih tinggi daripada model Freundlich (0.8343-0.9539) dan model Temkin (0.8409-0.9502) untuk semua logam berat yang diuji. Kinetik penjerapan pula mengikut tertib pseudo-kedua. Nilai negatif perubahan tenaga bebas Gibbs menunjukkan penjerapan adalah spontan. Nilai negatif perubahan entalpi dan perubahan entropi pula masing-masing mengesahkan sifat eksotermik dan menunjukkan susutan perubahan struktur di permukaan larutan pepejal semasa proses penjerapan. Kesimpulannya, kriogel yang dihasilkan daripada lignin OPF ini mempunyai potensi untuk digunakan dalam penyingkiran logam berat.

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LIST OF ABBREVIATIONS

A-CCB	-	Activated carbon cryogel bead
AC	-	Activated carbon
BET	-	Breuner, Emmer and Teller
CCB	-	Carbon cryogel bead
DTA	-	Derivative thermogravimetric
EPA	-	Environmental Protection Agency
FESEM	-	Field Emission Scanning Electron Microscopy
FRIM	-	Forest Research Institute Malaysia
FTIR	-	Fourier Transform Infrared Spectroscopy
HCl	-	Hydrochloric acid
HPLC	-	High performance liquid chromatography
IUPAC	-	International Union of Pure and Applied Chemistry
KBr	-	Potassium bromide
MPOB	-	Malaysian Palm Oil Board
NaOH	-	Sodium hydroxide
OH	-	Hydroxyl
OPF	-	Oil palm frond
PAN	-	Polyacrylonitrile
R&D	-	Research and Development
RF	-	Resorcinol-formaldehyde
RSM	-	Response Surface Methodology
S_{BET}	-	BET surface area
TG	-	Termogravimetry
TGA	-	Thermogravimetric Analysis
XRD	-	X-Ray Diffraction
[BMIM]Cl	-	1-Butyl-3-Methylimidazolium Methyl Chloride

LIST OF SYMBOLS

C_e	-	Equilibrium concentration
C_o	-	Initial concentration
Hr	-	Hours
K	-	Kelvin
K_1	-	Equilibrium rate constant
K_f	-	Freundlich coefficient factor
k_1	-	Pseudo-first order equilibrium rate constant
k_2	-	Pseudo-second order equilibrium rate constant
k_{dif}	-	Intraparticle diffusion rate constant
L	-	Liter
M	-	Meter
mg	-	Miligram
min	-	Minutes
ml	-	Mililiter
mm	-	Milimeter
nm	-	Nano-meter
P	-	Gas pressure at time
P_o	-	Initial equilibrium gas pressure at time
q_e	-	Amount of adsorbent at equilibrium
q_t	-	Equilibrium rate constant
R^2	-	Correlation Coefficient
R_L	-	Langmuir constant
V	-	Volume of solution
wt%	-	Weight percent
wt/wt	-	Weight per weight
^oC	-	Degree Celcius

%	-	Percent
Å	-	Angstrom (10^{-9})
ΔG	-	Free Energy Change
ΔH	-	Enthalpy Change
ΔS	-	Entropy Change
µm	-	Micrometer
θ	-	Angle
i.e.	-	It is
>	-	Greater than
<	-	Less than
Rpm	-	Revolutions per minute
Cu	-	Copper
Cr	-	Chromium
Zn	-	Zinc

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Disposal of effluents from industries like battery manufactures, leather tanning, painting, paper, electroplating and metal finishing has resulted in serious industrial wastewater problems, especially in terms of heavy metals contamination. Various metals such as zinc, nickel, chromium, copper, cadmium and mercury have harmful effects not only to human's health but also to the environment. Nowadays, the contamination of lakes and streams due to the presence of these heavy metals has become one of the serious problems faced by the country. Heavy metals can be easily absorbed by living organism as they have high solubility in aquatic environments. The problem of these heavy metals, especially those originating from industries, domestic sewage and landfills, has been a subject of research for a very long time. As one of the prevention steps to mitigate this problem, the United States Environmental Protection Agency, or EPA, has sanctioned for these heavy metals to be reduced to acceptable levels before the wastewater is discharged into the environment.

Nowadays, numerous methods are available to treat heavy metals. Some of the methods include adsorption, chemical precipitation, ion exchange and membrane filtration. Each of these treatment methods also has their own advantages and limitations. Adsorption is identified to be among the best and most practical method among the available techniques as it offers flexibility in their design and operation.

Other than that, adsorption also can give a high-quality treated effluent and most of the adsorbents can be regenerated for several times (Gayatri, 2010).

Recently, carbon cryogels showed a very high potential to be used as adsorbent in adsorption process. Conventionally, resorcinol-formaldehyde (RF) cryogels were synthesized by sol–gel polycondensation of resorcinol with formaldehyde and freeze-drying was carried out with t-butanol. Carbon cryogels were then obtained by pyrolyzing RF cryogels in an inert atmosphere (Babić *et al.*, 2004). According to Babić *et al.* (2004), characterization by nitrogen adsorption showed that carbon cryogels were micro and mesoporous materials with high surface areas ($500\ m^2/g < S_{BET} < 750\ m^2/g$). The porous structure of carbon cryogels is potentially advantageous as an adsorbent for treating wastewater containing heavy metals and organic pollutants (Dilaeleyana *et al.*, 2012).

However, even with of all the advantages that carbon cryogels have, there are still some drawbacks in them. Carbon cryogels are costly when synthesized from conventional combination of alcohols such as resorcinol and phenol with formaldehydes. Besides that, phenol and resorcinol are categorized as harmful substances and the use of these two substances need to be reduced or eliminated as much as possible. Therefore, alternatives for phenolic compound that is low in cost, yet still effective as an adsorbent are vigorously been sought out. Consequently, it has been reported by several researchers that lignocellulosic biomasses can be used as raw materials in the substitution of phenolic compound for production of phenol-formaldehyde resin.

Lignin is one of the predominant compounds that exist in the lignocellulosic materials. Lignin is originally a macromolecule that is presented as the second major constituent after cellulose (Collinson and Thielemans, 2010). Compared to other wood components (cellulose and hemicelluloses), lignin is a much more complex polymer and has been considered for a long time as a low-quality and low-added-value material. However, new developing technologies allow the extraction of high-purity lignin which can be converted into various high-value chemicals and products such as phenol, carbon fibre and also vanillin (Ngadi *et al.*, 2014a). Many efforts have been made to improve the reactivity of lignin as the substitute for phenol in phenol-formaldehyde resin synthesis. One of the methods is to modify the chemical structure of lignin to increase its potential reactive sites toward formaldehyde. Other methods, including reduction, oxidation and hydrolysis have also been studied to improve the reactivity of lignin as well as to produce phenolic compounds from lignin (Hu *et al.,* 2011).

The ecological, techno-economic and agro-climatic conditions in Malaysia are tending to be suitable for large scale planting of the oil palm. The industry grew rapidly and today, 4.69 million hectares of land in Malaysia is under oil palm cultivation and this contributes to about 37.3% of the world's total palm oil production. It is a known fact that Malaysia is the leading producer and exporter of palm oil in the world and oil palm has been as one of the major drivers for the country's economic growth. At this time, the amount of biomass that had been left to rot and returned to the field as fertilizer is vaunting. Malaysia has generated approximately 51 million tonnes of oil palm frond (OPF), accounting for 53% of the total palm biomass in 2008 (Goh *et al.,* 2010). From this number, it is expected that the ideas of extracting the lignin from OPF is very feasible to be explored.

1.2 Problem Statement

The application of carbon cryogel beads (CCBs) as an adsorbent in adsorption of heavy metals from wastewater had earned serious attention from time to time. Conventional preparations of CCBs usually involve the use of formaldehyde and phenol. However, massive usages of these two chemicals are unsafe to human health and can cause environmental pollution problems. The use of less harmful substances and raw materials that are cheaper in price is very important and vigorously been sought nowadays. One of the possibilities to significantly decrease the harmfulness and production cost is by using natural resources derived from biomass as the precursor. Many researchers have developed various studies involving lignin derived from biomass as phenol substitute in the synthesis of lignin modified resin.

Therefore, this study was aimed to investigate and explore an easier preparation method of cryogel from lignin of a renewable source, which is oil palm frond (OPF), without any addition of phenol during the synthesis process. In addition, the effect of ultrasound application during the process of lignin liquefaction was also studied. The use of ultrasound is believed to enhance and increase the production of lignin and shorten the process reaction time by inhibiting the formation of large molecular structures during liquefaction process (Kunaver *et al.*, 2012). Other than that, the performance of synthesized cryogel as a potential adsorbent to remove heavy metals from synthetic wastewater through adsorption, kinetic and thermodynamic study was employed. Successive utilization of OPF as a renewable resource will lead to a sustainable development that can help our palm oil industry to comply with zero-waste strategy and generate additional profits for the palm oil industry and promote the benefits of waste to wealth programme.

1.3 Research Objectives

The objectives of this study are:

1) To extract lignin from oil palm frond (OPF) via ultrasound-assisted method.

2) To synthesize and characterize cryogel produced from OPF.

3) To study the performance of synthesized cryogel as potential adsorbent for removal of heavy metal ions.

1.4 Scope of Study

In order to achieve the objectives, this research was extended into more specialized scope. Two types of OPF, which were fresh OPF and old OPF, were used as the raw materials of lignin extraction. For lignin extraction, two types of heating approaches; ultrasound assisted method and conventional heating, were used during the liquefaction process. Subsequently, two other variables, which were the cooking liquor concentration (0-6.25M) and temperature (30-80°C) were manipulated in order to obtain the optimum conversion of the OPF and lignin yield.

In this study, the formation of cryogels was employed by sol-gel polycondensation of lignin-OPF with furfural, followed by freeze drying. Synthesis condition of these cryogels was manipulated by using different amounts of lignin to furfural ratio (1:1 – 1:4) and lignin to phenol ratio (1:0 – 1:0.075) during the sol-gel polycondensation process. Then, the physical properties of the best cryogels were characterized using BET, XRD, FTIR, FESEM and TGA.

The performance of the cryogels for the removal of simulated heavy metals through adsorption study was also investigated. Three types of heavy metal were used in these experiments, which were zinc, copper and chromium. The adsorption capacity was determined by using adsorption and kinetic study. The experimental conditions for adsorption test included time (1-360 minutes), initial concentration of adsorbate (0.2-5.0 mg/L), pH (2-12), weight of adsorbent (100-500 mg), and temperature (30-80^{o}C).

For determination of heavy metals adsorption rate mechanism, kinetic studies of pseudo first-order, pseudo second-order and intraparticle diffusion were applied. Meanwhile, adsorption isotherm was determined through Langmuir, Freundlich and Temkin equations and the effect of temperature on the adsorption of heavy metals were determined based on the adsorption thermodynamic.

1.5 Significance of Study

This research is an industrial-driven research approach since it is based on the future need of the local waste water treatment. Normally, the production of cryogels involves the addition of phenol or resorcinol substance. The synthesis of cryogel from OPF is seems to be very promising as lignin extracted from OPF has the potential to substitute phenol in cryogel. The synthesis of cryogels was further

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