Desulphurization of Diesel by Cellulosic Fiber

by

Ariff Fikri bin Mohamed Zikri

Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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Approved by,

…………………………………………………

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TRONOH, PERAK

September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ARIFF FIKRI BIN MOHAMED ZIKRI

ABSTRACT

The new stringent global regulation to produce low sulfur petroleum products has put most refineries in alert to research and implement new technology to meet the requirement to lower emission of Sulfur Dioxide and Hydrogen Sulfide. European country has set Euro 4 rule in 2005 to limit sulfur content in gasoline and diesel to 50 ppm maximum. In Malaysia, Euro 4 M standards will be implemented in two years' time from current Euro 2M standard of 500 ppm sulfur content. Most oil and gas and petrochemical companies are developing technologies that cover enhanced hydrotreatment process. This project explored the use of abundant palm oil fibers as the mean of desulphurization. OPEFB cellulose structure was modified with carboxylic group treatment such as acetic acid, oxalic acid, and EDTA. Metal ions such as Copper, Zinc, and Lead are loaded into the pores of modified cellulose such that the positively charged metal ions will capture the slightly polar sulphur atom of Dibenzothiophene by removing the organosulphur and toxicity due to the Benzene ring.

The sorption processes of heavy metals on modified cellulose were performed in a batch mode by varying the contact time, initial metal concentration and pH of the solution. The samples were tested with Atomic Absorption Spectrum analyzer to measure the concentration of metal ions adsorbed. Lead has shown highest adsorption capacity of 8.5mg/g cellulose EDTA adsorbent with 120 minutes contact time and 8.1mg/g in cellulose oxalic. Zn adsorption came second at 6.8 and 6.4 mg/g cellulose EDTA and cellulose oxalic respectively while Copper was recorded at 6.6 and 6.2mg/g adsorbent. The metal ions adsorption fit Freundlich isotherm model and Pseudo 2nd Order kinetic trending. Sulphur removal study is performed by batch contacting 0.1 g of the metal loaded cellulose with 10 mL of diesel. Treatment by cellulose EDTA loaded with Lead provide sulphur removal of 52.2%, Copper (14.9%) and Zinc (16.4%) while cellulose oxalic dispersed in Lead solution result in reduction of 44.8%, Copper (29.9%), and Zinc (28.4%).

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INTRODUCTION

1.1 Background of Study

Desulphurization is a process of sulphur removal from bulk organosulphur compounds in the hydrocarbon feedstock. The feedstock can be narrow down to diesel and motor gasoline. These petroleum products are produced via straight run crude distillation or blended together with Light Gas Oil from Fluidized Catalytic Cracker (FCC) (Topsoe et al,1999). Organosulphur compounds such as thiophene, benzothiophene, dibenzothiophene (DBT), and alkylated dibenzothiophene that exist in the products should be treated to remove the sulphur content. Current technology of hydrotreatment is via Hydrodesulphurization (HDS) and Direct Desulphurization (DDS) pathway (Ergorova, 2003).

Instead of using conventional Hydrotreatment method which can be risky and costly due to demand of high operating conditions and modern catalyst cost, research on green technology can be explored for the removal of sulphur. Abundances of biomass resource such as Oil Palm Empty Fruit Bunch (OPEFB) can be harness to develop effective porous lignocellulosic matrix as a medium for sulphur adsorption (Siró & Plackett, 2010).

1.2 Problem Statement

Petroleum products have their own specification that must be achieved to meet market requirement and satisfy government standard. Malaysian Government has fixed 2014 as the year of implementation of Euro 4M fuels standard, in place of current Euro 2M standard. This regulation means refineries has to ensure their gasoline and diesel products to contain sulphur at maximum of 50 ppm instead of 500 ppm presently. High sulphur

fuels are hazardous to air quality. Advantage of Euro 4M implementation is the capability to use fuel emission engine vehicles that require use of ultra-low sulphur fuels.

Present hydrotreatment method possesses great challenges in terms of energy, cost, and efficiency. Those include:

(i) The cost of purchasing and maintaining modern catalyst is without tolerant expensive. Lots of time is spent on optimization before catalysts can be used in the hydrotreatment reactor.

(ii) It is an energy-intensive process requiring high temperature and hydrogen pressure. High operating temperature could also reduce activity and shelf-life of the catalyst.

(iii) Current reactor size is insufficient to remove more sulphur, thus requiring multiple reactors or large single reactor. These certainly increase the cost of hydrotreatment and maintenance.

1.3 Objectives of Study

The objectives of the study are;

I. To characterize morphologically and chemically the structure of modified cellulose fibers.
II. To study the kinetics of heavy metal sorption onto modified cellulose fibers.
III. To determine importance factors for desulphurization of diesel

1.4 Scope of Study

The scope of the project is to remove organosulphur compounds such as thiophene, benzothiophene, dibenzotiophene, and alkylated dibenzothiophene associated in diesel by minimum of 50% of sulphur. This is achieved by means of adsorption onto metal ions attached to modified cellulosic fibers. The development of green technology involves the

use of cellulose from palm oil fiber as porous medium which is available abundantly in this country as waste material. Thus, the use of metal dispersion into fiber matrices to capture sulphur ions is less energy-intensive, providing more economical solution for desulphurization process.

1.5 Relevancy of Project

Due to government regulation of Euro 4M, it is compulsory for refineries to produce gasoline and diesel with 50 ppm maximum sulphur content in 2014. Research on desulphurization of diesel is crucial especially with regards to economic and environmental impact of the process. Cellulosic fibers from palm oil is the best material to explore as Malaysia is the second world palm oil producer (Yusoff, 2006).

1.6 Feasibility of Project

The project is totally on laboratory experimental based, with equipment available in UTP. Length of the project is appropriate with the time given since the experiments conducted can be done in few months meanwhile most all of the chemicals are within the stock of Chemical Engineering Department

CHAPTER 2
LITERATURE REVIEW

2.1 Low Sulphur Regulation

Increasing mankind consideration on environment quality has changed much of the regulation in industrial sector, especially on the amount of toxic gases and particulate matter released to the atmosphere. Sulphur, which comes abundantly from fuel combustion, either from refinery or vehicle emissions id one of the major air pollutant. Worldwide effort to reduce sulphur emission in fuel begins in Europe with the implementation of uniform standard of 50ppm sulphur content in both diesel and gasoline. In 2001, the European also proposes the directive calling to introduce "near zero sulphur" fuels, defined as the maximum allowable of 10ppm sulphur content, implemented in 2009 (Blumberg, 2010). In United States, The Tier II rules capped 300ppm sulphur contents for diesel and gasoline until year 2005, before reducing further to 80ppm in January 2006 (EPA, 2000).

The Malaysian Government has instructed petroleum refineries to upgrade their products from current Euro 2 grade (500ppm max) to Euro 4 grade (50 ppm max) within two years. The Government has previously set 2012 as the deadline, but extended for another two years (Loh, 2011). There are four petroleum refineries operating to produce motor gasoline and diesel, Petronas Melaka Refinery, Petronas Kerteh Refinery, Shell Port Dickson Refinery and Esso Port Dickson Refinery, processing 660 kilo barrels crude oil per day. Producing 500ppm sulphur content is already a big challenge for refineries in Malaysia, since the current equipment is limited by treatment capability. The reactor performance is only capable of processing sweet crude with readily low sulphur (600-1500ppm). The crude comes from local oil fields such as Tapis, Belanak, Kidurong, Cakerawala, and Labuan (Hanafi, 2011). The challenges rise when sour crude is introduced, to minimize the crude cost. The refinery equipment is not able to tolerate heavy components containing large amount of sulphur, mercaptan, mercury, and heavy metals.

2.2 Organosulphur Compound

Organosulphur has varied reactivities based on their structures and local atom environment. Light crude oil fraction is divided mainly to aliphatic type: mercaptans, sulfides and disulfides. These components are highly reactive and can be removed easily in conventional hydrotreatment process. Heavier crude feedstock fraction composed of straight run naphtha, straight run diesel and light Fluid Catalytic Cracking (FCC) naphtha. The Organosulphur compounds are dominated by thiophenic rings including thipohenes, benzothiophenes, and their alkyl derivatives. The heaviest fraction coming from bottom FCC naphtha, Coker naphtha, FCC and Coker Diesel are blended together in the straight run naphtha and diesel. These fractions contain more complex organosulphur compound such as dibenzothiopenes and alkylated dibenzothiphenes which have very low reactivity towards HDS (Topsoe, et al, 1999).
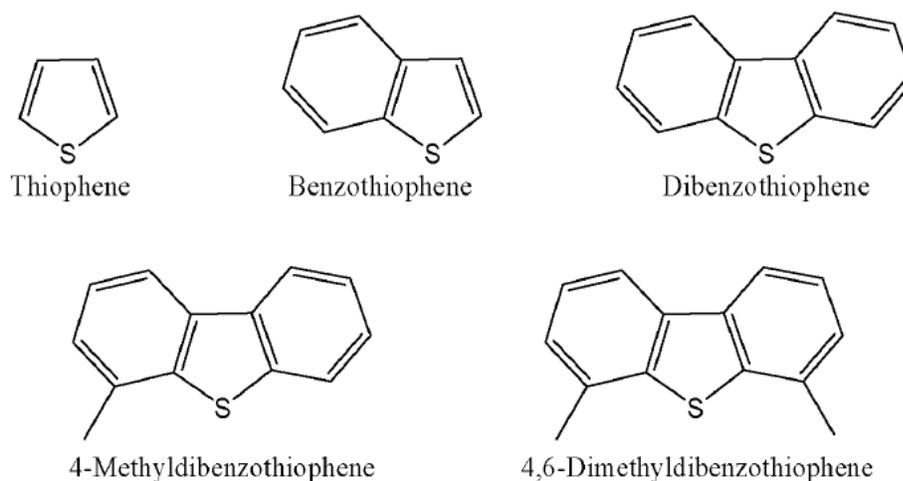

Figure 1. Sulphur Containing Molecules in Petroleum Compound (Topsoe, et al, 1999)

2.2 Conventional Sulphur Treatment

Conventional hydrotreatment is widely used in worldwide refinery. It is a commercially established process that pass the heated feedstock with hydrogen into a packed bed

reactor loaded with catalyst to remove sulphur and other impurities (Lee, 2003). Hydrotreatment or hydroprocessing refers to several processes that saturate the unsaturated hydrocarbon by removing Sulphur [by hydrodesulphurization (HDS)], Nitrogen [by hydrodehydrogenation (HDN)], Oxygen [by hydrodeoxygenation (HDO)], and metals [by hydrodemetalization (HDM)] (Egorova, 2003). This method usually proceeds over sulfided $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ catalyst (Fujikawa, 2009). Its performance in terms of desulphurization level, selectivity, and activity depends on the properties of selected catalyst used (synthesis route, active species, support properties, concentration), concentration of sulphur compounds present in feed stream, reaction conditions (temperature, sulfiding procedure, partial pressure of hydrogen and H_2S), together with reactor and process design.

2.3.2 Advanced HDS

Advanced HDS in refinery system seems possible with increasing HDS process severity. However, undesired side reaction may occur due to extended operating condition. For example, desulphurizing the FCC gasoline in higher hydrogen pressure will saturate the olefin and reducing octane number. Running at higher temperature tend to increase coke formation and faster catalyst deactivation. The severity of operating condition is limited mainly by the HDS unit design itself (Gates et al, 1979). The refinery could also use new HDS catalyst with improved activity and selectivity. Modern hydrotreating catalyst has higher capability to reduce sulphur, nitrogen and metal atoms. Another approach is through advanced reactor design such as multiple reactors. However both steps; on new modern catalyst and reconfiguration of reactor design may result in astronomical investment and operating cost and with large reactor size.

2.3.3 Catalyst Development

To achieve enhanced desulphurization via catalytic reaction, improvement has to be made on the catalyst for better selectivity and cleaner reaction. The key parameters are the choice precursor of the active species, support, synthesis and post treatment of the

catalyst. The physical aspect of active phase can be altered by modification of active component. Various additives had been studied in the early 2000, such as phosphorus, fluorine, nitrides and carbides to increase reaction performance (Nagai et al, 2000). Later a lot more supports have been used to enhance catalytic activity such as carbon, silica, zeolite, titania and zirconia, and silica-alumina (Qu et al, 2003). The combination of new catalytic species such as ASA (amorphous silica-alumina) can increase desulphurization performance significantly such as ASA-supported noble metal-based catalysts for the second stage deep desulphurization of gas oil (Reindhoudt et al, 2003).

However, noble metal catalyst application for deep HDS is hindered by sulphur resistance. The catalysts can only be used when most of the sulphur compound and H_2S have been removed from the process stream. To overcome the problem, a new method of bifunctional catalysts is introduced to improve sulphur resistance of noble metal hydrotreating catalyst through the combination of catalyst support with bimodal pore size distribution and two types of active sites; the first is placed as large pores accessible for organosulphur compounds and sensitive to sulphur inhibition, while the later active site as placed in small pores, not accessible to heavy S-containing molecules and has higher resistance to H_2S poisoning. Hydrogen accessibility in small pores can be adsorbed dissociatively and transported within the pore system to regenerate the polluted metal sites in the large pores (Egorova, 2003).

2.4 Alternative Sulphur Removal Method- Metal Adsorption

2.4.1 Metal Sorption

Non-catalytic researches are widely pursued worldwide to explore alternative to the costly conventional HDS. Sulphur removal using classical coordination compound, $Ru(NH_3)_5(H_2O)^{2+}$ reacting with thiophene, benzothiophene, and dibenzothiphene has been reported, resulting in $Ru(NH_3)_5(DBT)^{2+}$ complex (Angelici, 2001) with 50% organosulphur removed at atmospheric temperature. The bound metal ions can be re-oxidized to $Ru(NH_3)5(H2O)^{2+}$ and recycled. The major limitation of the process is the high price of Ruthenium.
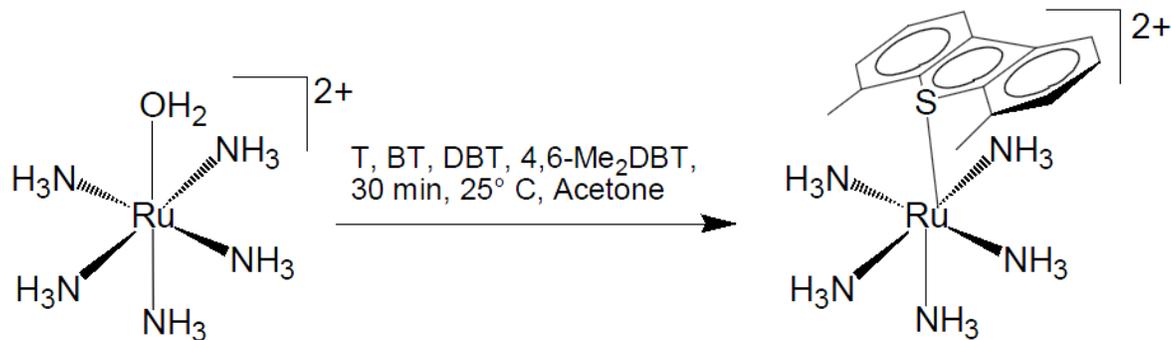
Figure 2. Reaction of 4,6- dimethyldibenzothiophene with $Ru(NH_3)5(H2O)^{2+}$ ions (Angelici, 2001).

2.4.2 Biocatalytic Desulphurization (BDS)

Sulphur removal reaction can be achieved by Biocatalytic Desulphurization (BDS) where organosulphur is removed from petroleum fraction using bacteria without degrading the carbon skeleton of the organosulphur compounds. Alkylated dibenzothiphenes are converted to non-sulphur compounds such as 2-hydroxybyphenyl (2-HBP) and sulfate. The reaction can be conducted in mild operating condition with less requirement of hydrogen. In addition, there is estimation of greenhouse gas emission reduction by means of BDS (Linguist, 1999). One of the specific study is via 4S pathway in which DB is desulphurized and converted to 2-NBP by mean of *Rhodococcus sp*. in aerobic condition. In this pathway, DBT carbon skeleton is released intact so that the calorific value of the fuel is maintained. However this pathway is energetically expensive due to unmineralized carbon skeleton to retrieve back the energy invested (Mohebali and Ball, 2008).
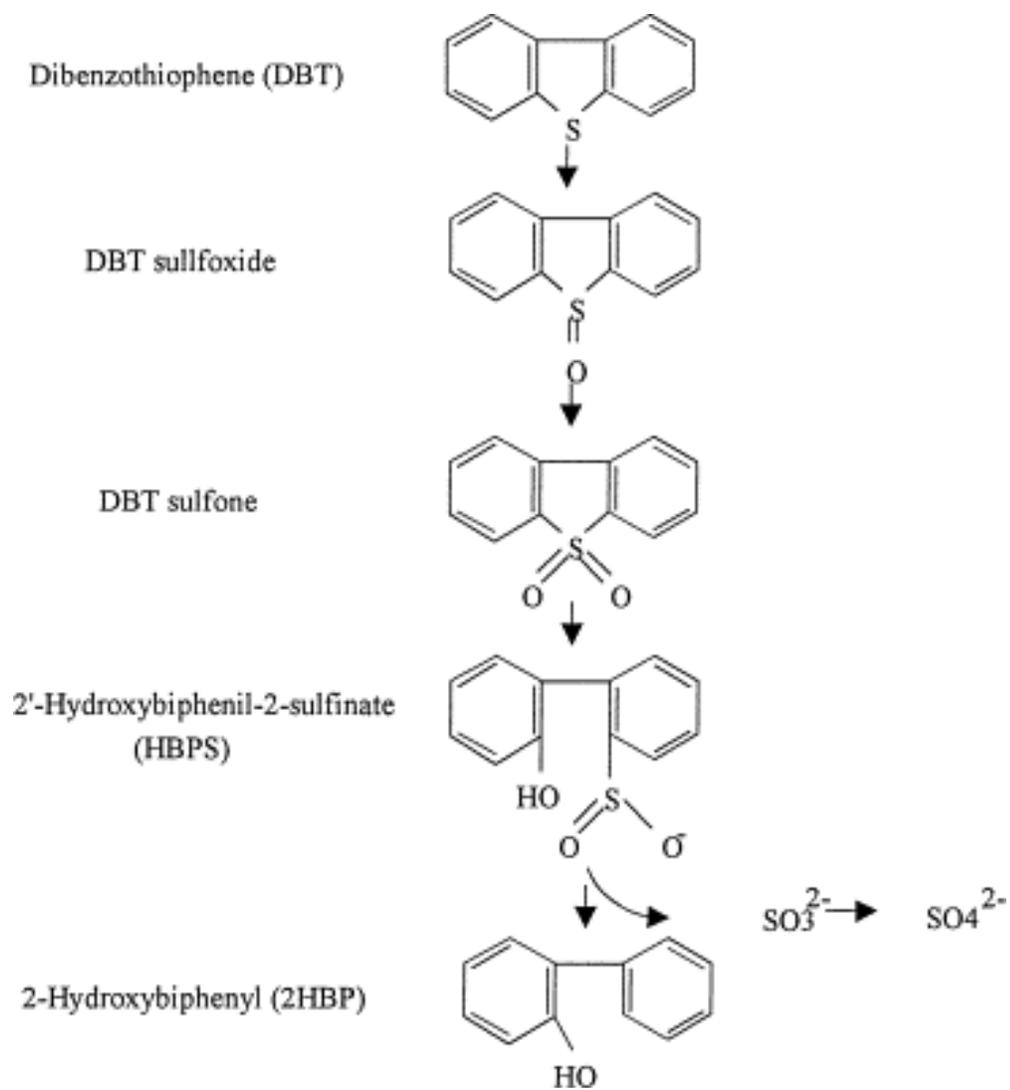
Figure 3. The 4S pathway for Biocatalytic Desulphurization of DBT and its derivatives. DBT, dibenzothiophene; HPBS, hydroxyphenyl-benzene sulfonate; 2-BHP, 2-hydroxybiphenyl; DszA, DBT sulfone monooxygenase; DszB, HBPS desulfinase; DszC, DBT monooxygenase (Mohebali and Ball, 2008).

2.4.3 Adsorption onto a matrix

There are few studies of desulphurization process via adsorption technique, using metal ions dispersed in a matrix material. A patent in 2008 has been filed on desulphurization of hydrocarbon via dispersing metal ions in a matrix structure, allowing the polar sulphur site of organosulphur to attach with the metal ions. The metal phase is being selective to reversible adsorption of sulphur using thiophene and dibenzothiophene as organosulphur compounds (Ramirez-Corredores, 2008). To enable this process, surface area of the matrix must be large enough to enable metal ions dispersion on the surface. The higher surface area of the matrix will guarantee better sorption of organosulphur compounds with acceptable surface area range estimated between 400 to 1200 m^2/g. The matrix is then extruded using a selected binder to compromise the acidic sorption medium. The shaped adsorbent matrix is preferably dried for overnight at a temperature between 80 to 250°C.

The matrix is then being made into contact with metal solution by means of adsorption, impregnation or any conventional way of metal dispersion on high surface area material. Metal selection is important to ensure strong interaction with the surface species of the matrix with size of about 10 nm. The metal should be the type that provides high electron attraction to interact with sulphur compounds present in the hydrocarbon feed for good surface adsorption. It is also compulsory to render the adsorption to be reversible so that used metal could be regenerated. Hence, the metal should be chosen into a d5 or d10 electron configuration. Some literature propose several good active metals, holding suitable oxidation states, including most of the transition metal elements from the first to third row of Periodic Table of Elements, and from column of group IB, IIB, VIIB, and VIII. Most studies preferred metals include those of Group VII from the table.

2.5 Cellulosic Fibres as Adsorbent

Plant cells are made made mostly of cellulose, hemicellulose, and lignin. Cell walls are developed by cellulose microfibrils which are units of partially crystalline cellulose, with

4-30nm wide. The fibres are embedded in amorphous matrix of hemicellulose and lignin. Cellulose accounts for 37-45% of the normal wood cell (Alen, 2000). Cellulose is of the most abundant, renewable polymer resource available today worldwide with large distribution of its application ranging from housing bricks to paper and textiles. It is one of the most important chemical compounds in the history of human culture. Cellulose is a linear homopolymer composed of (1→4)-β-glucopyranose. The basic structural form of cellulose is the anhydroglucose unit whose number determines the degree of polymerization. Cellulose chain has a direction since the terminal groups on the chain ends are different: a non-reducing end with closed ring structure and a reducing end with aliphatic structure and a carbonyl group in equilibrium with cyclic hemiacetals (Kontturi, 2005). From chemistry point of view, the free hydroxyl group on its monomer is useful in many ways to react and absorb most chemical through various ways of modifications.
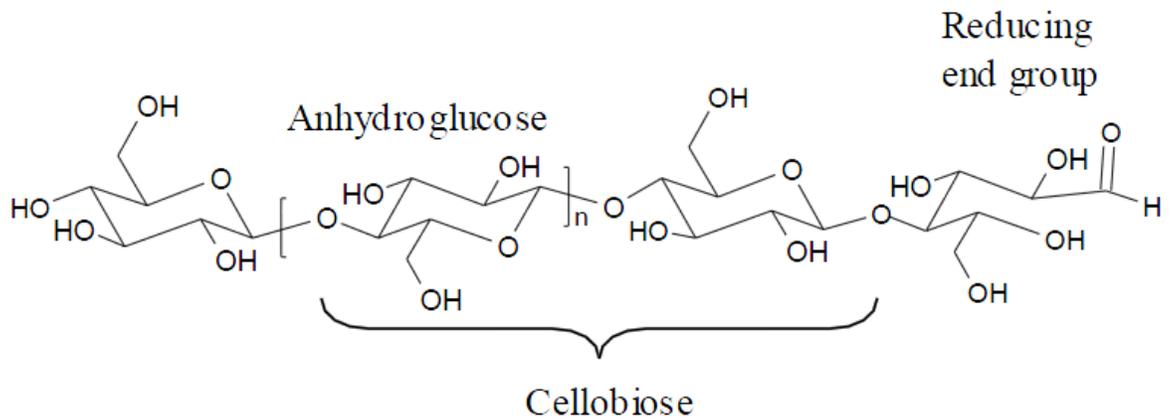

Figure 4. The structure of cellulose (Konturri, 2005).

Hemicelluloses are water soluble polysaccharides with less degree of polymerisation (100-200). The most frequent hemicellulose found in woods is galactoglucomannan with ratio of galactose:glucose:mannose at 0.1-0.2:1:3-4. Hemicelluloses are more complex compared to cellulose as far as carbohydrate components are concerned in figure 5.
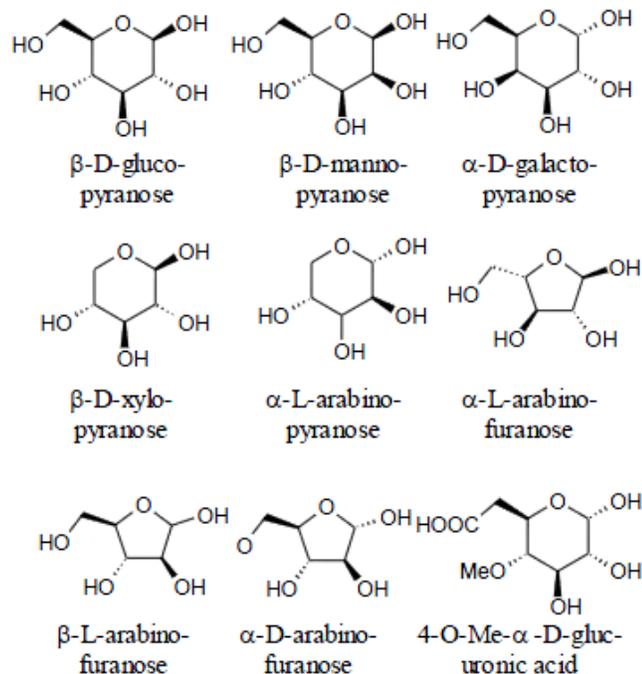
Figure 5. Among the most abundant monomers of hemicelluloses. The structures in the first row are examples of galactoglumannan (Alen, 2000).

Another main component of plant cell wall is lignin, a non-linear polymer made of phenylpropanoid units, responsible as binder of wood cells, to control water content inside the cell wall, and made up the colour of the wood. The structure of lignin is irregular in nature, yet is harder to study. Lignin made a portion of 20-25% in hardwood.
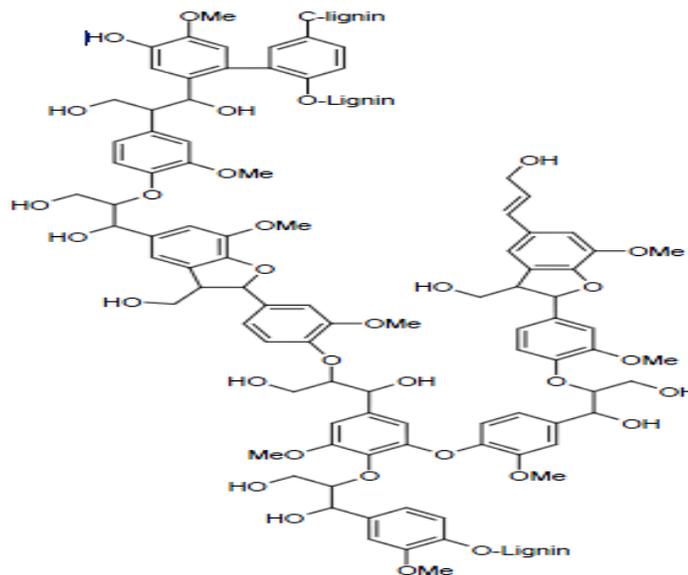
Figure 6. A representative fragment of lignin molecule in native softwood. The diversity of ether and carbon-carbon bonds is evident (Alen, 2000).

2.5.1 Cellulose Mercerization

Cellulose fibers can be chemically treated to remove lignin-containing materials such as pectin, waxy substances, and natural oils that cover the external surface of the cell wall. The contaminants may cause rough surface topography to the fiber. Sodium Hydroxide (NaOH) is the most common chemical used to bleach the cellulose surface, which change the basic structure of Cellulose I to Cellulose II via mercerization (Johnson, 1979). The reaction is as follows:

$$\text{Cell-OH} + \text{NaOH} \longrightarrow \text{Cell-ONa} + H_2^- + O^+ \text{ [surface impurities]}$$

The standard of mercerization process is proposed by ASTM D 1695, by subjecting fibre to the action of a fairly concentrated aqueous solution of a strong base so as to produce great swelling with resultant changes in the fine structure, dimension, morphology and mechanical properties (ASTM, 2012)

2.5.2 Modification of Cellulose

Novel studies on adsorption ability of cellulose free hydroxyl groups expand from 2010 onwards. Since the group can be treated in various ways to remove OH⁻, the structure can easily be attached with electron donor particles. Modified cellulose is a cheaper material and can be more effective adsorbent. Cellulose is not only renewable, inexpensive, biodegradable, but also has many primary active hydroxyls which are easy to trigger many reactions, including free radical reaction, halogenation, esterification, oxidation and etherification (Stenstad et al, 2008). Takagai et al, 2011 reported on seven types of thio- and/or amine-modified cellulose resin materials for mercury (II) adsorption. Zhou et al, 2011 modified cellulose with *β*-CD and quartenary ammonium groups to remove Cr(VI) from aqueous solutions while, Gurgel et al,2009 modified cellulose using succinic anhydride to treat heavy ions. Esterification of cellulose can be done by substituting the OH⁻ group with COOH group from acetic acid (1 COOH group), oxalic acid (2 COOH groups) and Ethylenediaminetetraacetic acid (EDTA) (4 COOH groups). COOH groups in each acid are illustrated as red color in figure below. The structure of cellulose after modification with COOH groups is also shown in the figure.
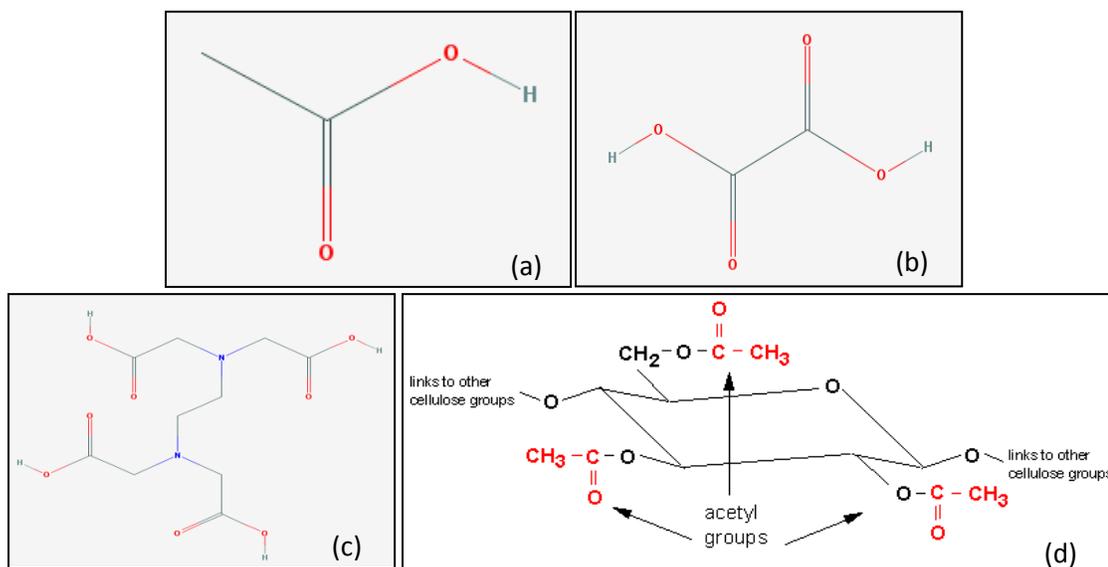

Figure 7. COOH presents in acetic acid (a), oxalic acid (b), and EDTA (c). Structure of substituted OH⁻ groups with COOH is shown in (d).
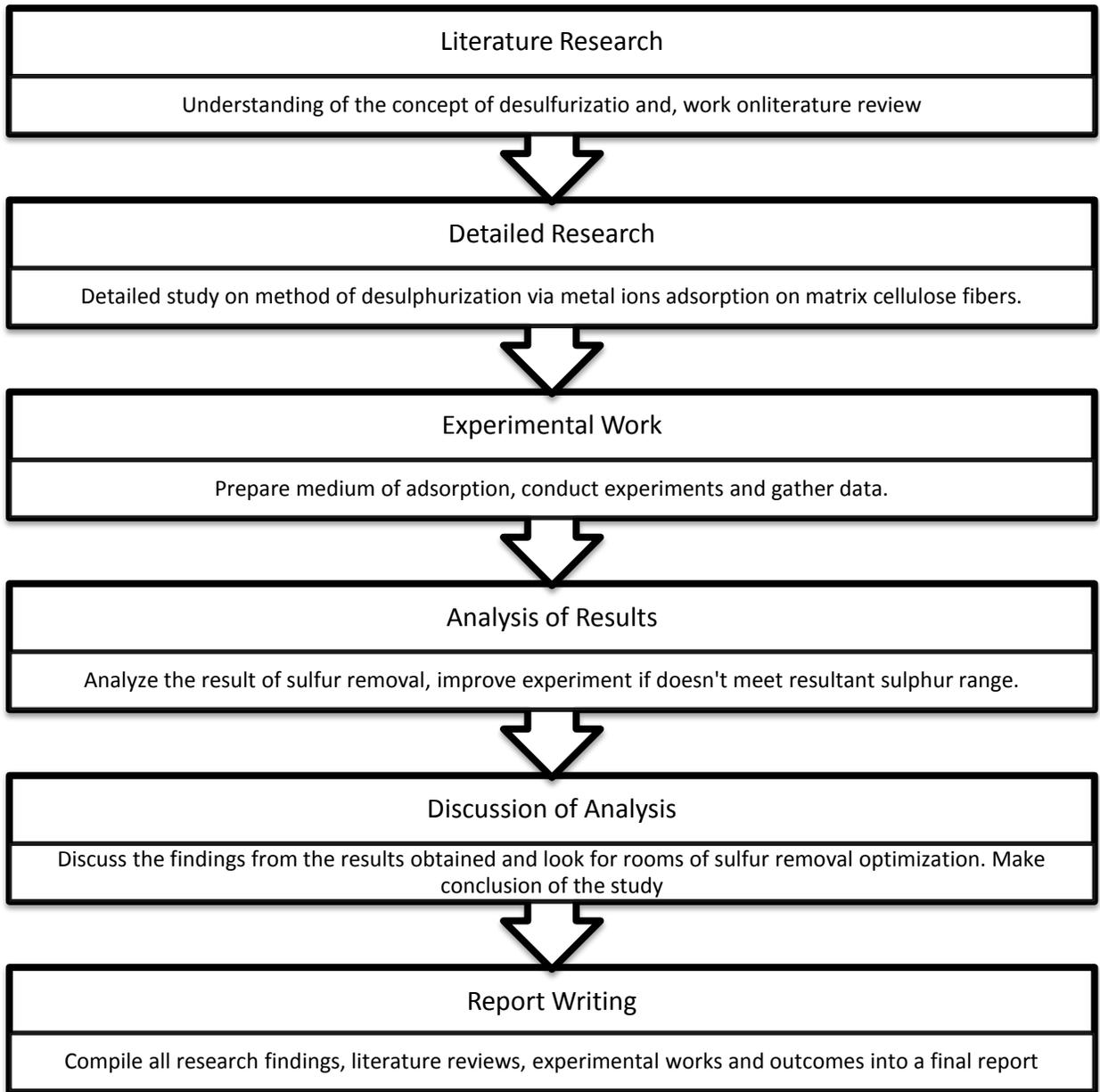
2.6 Palm Oil in Malaysia

Palm oil industries in Malaysia are at the forefront of technology and production either in plantation or oleo-chemical products for global exports. With total plantation area of 5 million hectares consisting of 4.3 million hectares mature and 0.7 million hectares of immature plantation, the total production in 2011 is estimated to be 19 million tons of palm oil (MPOB, 2012), with the export earnings of RM 70.1 billion. Malaysia produces about 41% of the world's supply of palm oil, second to Indonesia at 44.8% (19.3million tons). After processing of the crude palm oil (CPO), the leftover is considered as biomass wastes including trunks, pulps, and Empty Fruit Bunch (EFB). Amount of EFB produced increase from 5 million metric tons in 2004 to 5.3 million metric tons in 2005 and is projected to be 7.6 million metric tons in 2015 (NIRAS, 2006). EFB constitutes more than 20% of the fresh fruit bunch weight. It is a fibrous and relatively wet material with moisture level of 65-70%, are made of lignocellulose (cellulose, hemicellulose, and lignin) (Yusoff, 2006). There is now increasing initiative to reuse the fiber-rich biomass as incinerating alone only limits the value-added conversion. Most of local research on EFB is focused on biofuel generation by treating cellulose into cellulosic ethanol.

By combining the used of abundantly source of empty fruit bunch (EFB) in Malaysia which provides tremendous amount of lignocellulose fiber and surface modification with metal ions on the fiber matrix, a new invention of hydrocarbon desulphurization technique can be invented. The invention does not only develop a low cost process at low operating condition, it also helps much on taking care of the environment by means of biotechnology approach.
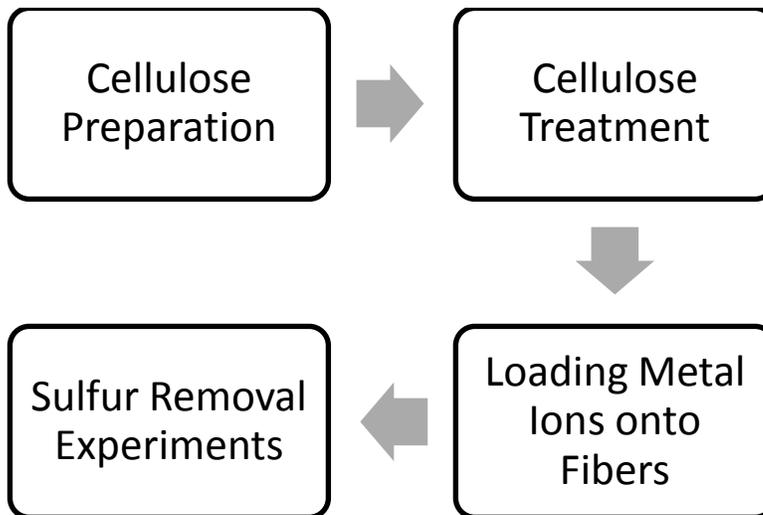
CHAPTER 3
METHODOLOGY

3.1 Research Methodology

Methodology of this project is as waterfall type, it follows step by step instruction from beginning to the end of project. However, the experimental part of the project is quite complex. It need to be done in multiple stages including sample and fibers preparation and sulphur removal experiments.

Literature Research
Understanding of the concept of desulfurizatio and, work onliterature review

↓

Detailed Research
Detailed study on method of desulphurization via metal ions adsorption on matrix cellulose fibers.

↓

Experimental Work
Prepare medium of adsorption, conduct experiments and gather data.

↓

Analysis of Results
Analyze the result of sulfur removal, improve experiment if doesn't meet resultant sulphur range.

↓

Discussion of Analysis
Discuss the findings from the results obtained and look for rooms of sulfur removal optimization. Make conclusion of the study

↓

Report Writing
Compile all research findings, literature reviews, experimental works and outcomes into a final report

3.2 Project Activity

To ensure the project activity runs smoothly, a good experimental flow is required since the project is dealing with multi stages experiments.

```
┌──────────────┐         ┌──────────────┐
│  Cellulose   │   ➡     │  Cellulose   │
│ Preparation  │         │  Treatment   │
└──────────────┘         └──────────────┘
                                │
                                ⬇
┌──────────────┐         ┌──────────────┐
│ Sulfur Removal│   ⬅    │ Loading Metal│
│ Experiments  │         │   Ions onto  │
│              │         │    Fibers    │
└──────────────┘         └──────────────┘
```

3.2.1 Cellulose Preparation

Cellulose is material used as matrix fibers to load metal ions on it. Before modifying the functional group, cellulose first need to be mercerized, this means removal of impurities in cellulose and change the structure from Cellulose 1 to Cellulose 2. Mercerization can be done by treating in NaOH solution. The OH groups of NaOH will remove all the impurities. Standard method of mercerization is used in this process, which is ASTM D1695.

Experimental Procedure:

20 grams of NaOH pellet is weighed before transferred into 1L conical flask and distilled water is added up to the mark. 100 grams of Cellulose are measured and poured into the conical flask. A magnetic bar is inserted into the conical flask and the top opening is wrapped with aluminum foil. Conical flask is placed over a magnetic stirrer at 350 rpm for 4 hours. When the stirring is complete, the solution is filtrated using filter paper and filter funnel. The filtrated cellulose is let dried in fume chamber and the mass is weighted.

3.2.2 Cellulose Treatments

Cellulose can to be treated by few ways to modify the hydroxyl group. Treatment can be done by reacting cellulose with certain chemical having different functional group. I this study, carboxylic group is chosen as modifying group. 3 reagents containing Carboxylic group have been selected for this purpose. They are;

i. Acetic Acid (1 COOH group)
ii. Oxalic Acid (2 COOH groups)
iii. EDTA (4 COOH groups)

3.2.2.1 Preparation of treatment solution:

a) 10wt% Acetic Acid Solution

1.5mL of concentrated acetic acid is measured using micropipette and transfer into 250mL conical flask. Distilled water is added up to 250mL mark. The flask is stirred for few minutes to let good mixing.

b) 10wt% Oxalic Acid Solution

3.15175 grams of oxalic acid is measured and transfer into 250mL conical flask. Distilled water is added up to 250mL mark. The flask is stirred for few minutes.

c) 10wt% EDTA Solution

9.306 grams of EDTA is measured and transfer into 250mL conical flask. Distilled water is added up to 250mL mark. The flask is stirred for few minutes.

3.2.2.2 Cellulose Modification Procedure:

20 grams of mercerized cellulose is weighted and placed in 250 mL round bottom flask while 200 mL of acetic acid solution is measured using measuring cylinder and added in. The flask is then plugged in soxhlet apparatus. Ensure the apparatus is clamped correctly. Water is let to flow via the condenser section. Heating mantle is switched on, set at 105'C and the reflux is allowed for 6 hours. The solution in round

bottom flask is filtrated using filter paper and funnel. Filtrated cellulose is than dried in oven at 105'C for 1 hour. The product is weighted and stored carefully. The steps are repeated using oxalic acid and EDTA solutions.

Samples of treated cellulosed are analyzed in Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Analysis (EDX), Thermogravimetric Analysis (TGA), Fourier transformed Infra-Red (FTIR), and X-Ray Dispersion (XRD) to study the structure of the fibers.

3.2.3 Loading Metal Ions onto Fibers

The next stage is to load metal ions of Copper, Lead, and Zinc onto the treated fibers. Before loading, the metals need to be dissolved to form aqueous solution. The metal ions are expected to load on pores of treated cellulose. In this stage, two variables are identified to paly role in adsorption process, which are contact time and concentration. Two hypothesizes can be made;

a) Metal adsorption rate is increasing as function of contact time up till its equilibrium.
b) Metal adsorption capacity is proportional to its concentration.

In this situation, contact time experiment is given priority as it is necessary to find equilibrium contact time for each metal. The resulting time then is used as fixed variables to study the effect of concentration to adsorption capacity.

Experimental Procedure

Preparation of 1000 ppm metal ions stock solutions.

1 gram of $ZnCl_2$ powder is measured placed into 1 L conical flask and distilled water is added until 1 L mark. The steps are repeated for preparing $CuSO_4$ and $PbSO_4$ stock solutions.

3.2.3.1 Contact Time Study Procedure

1 L of 100ppm metal solution is prepared by diluting 10 mL of $ZnCl_2$, $CuSO_4$ and $LdSO_4$ stock solution with distilled water in 1 L conical flask. 0.5 gram of cellulose treated with acetic acid is measured and transferred into Erlenmeyer flask before adding 50 mL of 10 ppm every solution (one type of metal solution in one flask). Covered the flasks with aluminum foil and labeled for 30, 60, 90,120, and 150 minutes. The same procedure is repeated using cellulose treated with oxalic acid and EDTA. All the samples are placed on orbital shaker with time set at 30, 60, 90,120, and 150 minutes. For each contact time, the samples are collected and filtered using filter paper and funnel. The filtrated cellulose is kept in sampling plastic while the sorbent solution is collected in plastic beaker. The sorbent solution is tested using Atomic Absorption Spectroscopy (AAS) to determine equilibrium contact time for each metal solution.

3.2.3.2 Concentration Study Procedure

Different concentration metal solutions (10ppm, 20ppm, to 100 ppm) are prepared by diluting $ZnCl_2$, $CuSO_4$ and $LdSO_4$ stock solution with distilled water in 1 L conical flask. 0.5 gram of cellulose treated with acetic acid is measured and transferred into Erlenmeyer flask before adding 50 mL of solution (one type of metal solution in one flask). The flasks are placed on orbital shaker at 150 rpm for 120 minutes. The steps are repeated with cellulose treated with oxalic acid and EDTA. All the samples are placed on orbital shaker with time set at equilibrium time from previous experiment. The samples are collected and filtered using filter paper and funnel. The filtrated cellulose is kept in sampling plastic while the sorbent solution is collected in plastic beaker. The sorbent solution is tested using Atomic Absorption Spectroscopy (AAS) to determine the degree of metal absorption.

3.2.3.3 pH Study Procedure

1 L of 100ppm metal solution is prepared by diluting 10 mL of $ZnCl_2$, $CuSO_4$ and $LdSO_4$ stock solution with distilled water in 1 L conical flask. 0.5 gram of cellulose treated with acetic acid is measured and transferred into Erlenmeyer flask before

adding 50 mL of 10 ppm every solution (one type of metal solution in one flask). pH of the solution is measured by pH meter. A few drops of 0.1 molar NaOH solution is added to increase the pH and 0.1 molar of acetic acid is added to reduce the pH. Covered the flasks with aluminum foil and labeled as pH4, pH5, pH6, pH7, and pH8. The flasks are placed on orbital shaker at 150 rpm for 120 minutes. The same procedure is repeated using cellulose treated with oxalic acid and EDTA. All the samples are placed on orbital shaker with time set at 30, 60, 90,120, and 150 minutes. For each contact time, the samples are collected and filtered using filter paper and funnel. The filtrated cellulose is kept in sampling plastic while the sorbent solution is collected in plastic beaker. The sorbent solution is tested using Atomic Absorption Spectroscopy (AAS) to determine equilibrium contact time for each metal solution.

After the loading process, the fibers are let dried in microwave oven for 1hour at 105'C. Another SEM images with EDX analysis is taken. The images of fibers before and after treatment are analyzed to ensure metal ions are dispersed throughout the cellulose pores.

3.2.4 Sulphur Removal Experiment

Normal market gasoline and normal market diesel are purchased from PETRONAS Station. Diesel is prepared in 1 L bottling sample and tested in CHNS Analyzer to test for containing components of Carbon, Hydrogen, Nitrogen, and Sulphur.

Sulphur Removal Procedure

0.1 g of different type treated celluloses are weighted and filled in Erlenmeyer flask. 10 mL of diesel is measured and added into the flask. The flasks are covered with aluminum foil and labeled for each adsorbent type. Place the flask on orbital shaker at 150 rpm and let for 24 hours. After the experiment, all the samples are tested with CHNS Analyzer to identify final components existed.

3.3 Project Gantt's Chart

Activities	Final Year Project I (FYP-1)														Final Year Project II (FYP-2)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Topic selection	�	▮																										
Study on conventional HDS and cellulose potential			▮	▮	▮	▮																						
Preparation of cellulose							▮	▮																				
Modification of cellulose structure									▮	▮	▮	▮																
Metal Ions loading onto Cellulosic Fibers													▮	▮	▮													
Sulphur removal experiments																▮	▮	▮	▮									
Chemical Structure Analysis																				▮	▮							
Optimization of sulphur removal process																						▮	▮					
Result and analysis																								▮	▮			

| Milestone	Final Year Project I (FYP-1)														Final Year Project II (FYP-2)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Completion of study in conventional HDS and Cellulose hydroxyl group						▮																						
Modify cellulose structure												▮																
Metal Ions loading onto Cellulosic Fibers															▮													
Sulphur removal in diesel																			▮									
Result analysis																									▮			
Complete report writing																											▮	

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CHAPTER 4
RESULTS & DISCUSSION

4.1 Cellulose Characterization

The study of cellulose structure consist of several branches; surface, thermal analysis, crystal lattice, particle size, and availability of absorption sites. Those criteria can be localized by certain analysis, respect to the objective required. The results of the study will be displayed in upcoming figures and graphs.
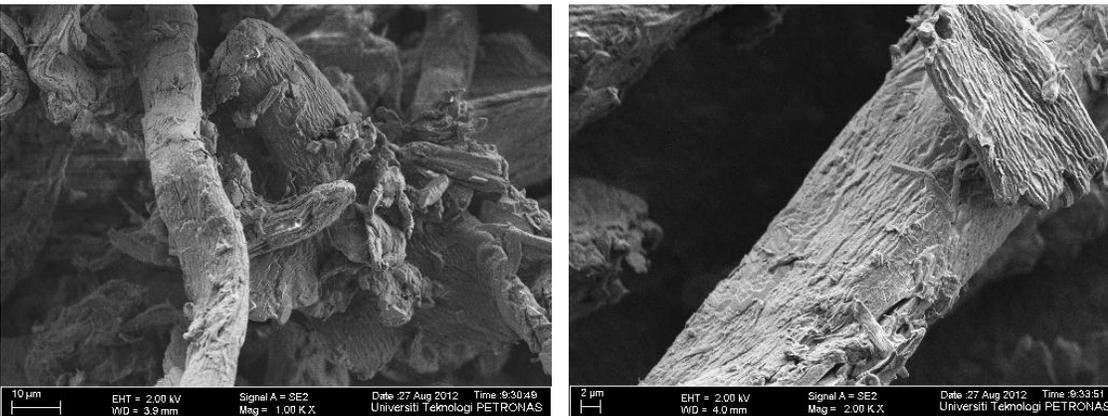
4.1.1 FESEM Imaging

The Field Emission Scanning Electron Microscope (FESEM) micrographs of treated cellulose at different magnification are shown in the figure below. By relatively comparing all the structure, the surface of the samples become more rough and irregular from cellulose acetate to cellulose EDTA due to swelling effect of cellulose after grafted with carboxylic group. The specific surface area is also increasing because of the heterogeneous grafted surface. Considerable COOH groups originated from the oxalic and EDTA produce strong electrostatic repulsion in the cross-linking network of cellulose polymer, thus the polymeric network expands to form a porous structure. Increasing in porous structure will favor the diffusion of metal ions because of the increased surface area.
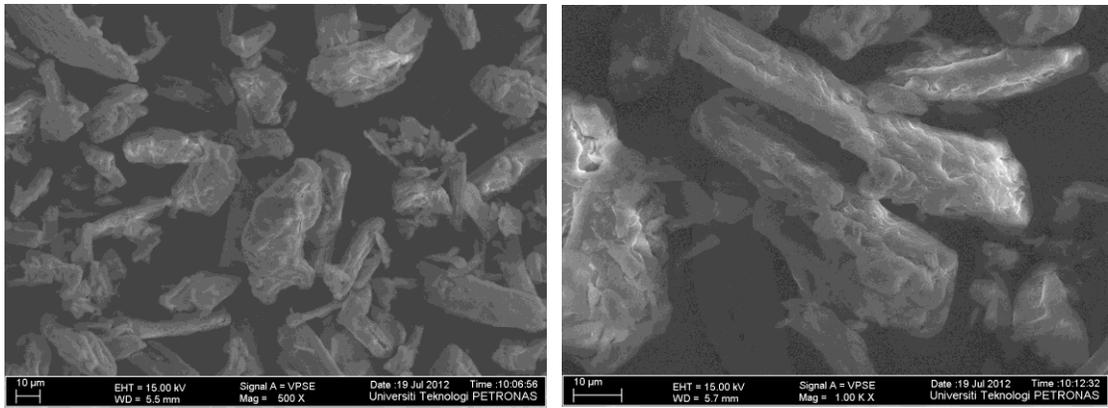
(a)
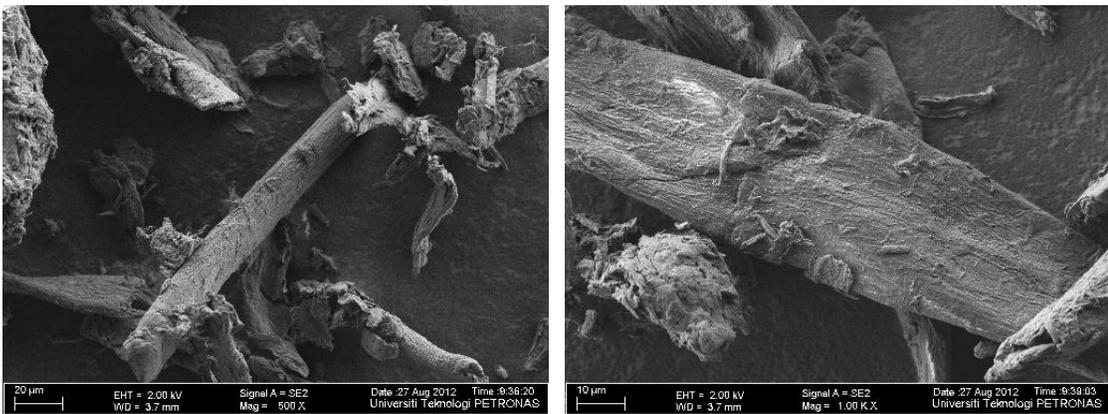
(b)

(c)

Figure 8. FESEM images of cellulose treated with acetic acid (a), oxalic acid (b), and EDTA (c).

Together with FESEM imaging, Energy Dispersive X-Ray analysis (EDX) is carried to figure out the present of elements in the cellulose samples. The graphs below showed the elemental composition of cellulose acetate, cellulose oxalic, and cellulose EDTA. The main compositions of the samples are Carbon and Oxygen, with data tabulated in Table 1. The weight percentage of Carbon is decreasing due to substitution of COOH replacing OH in the pure cellulose structure. As a result, the weight percentage of Oxygen increases, overrating the Carbon atom.

Table 1. Weight percentage of carbon and oxygen in cellulose

| Cellulose	Carbon wt%	Oxygen wt%
Acetate	56.00	44.00
Oxalic	49.68	50.32
EDTA	48.96	51.04
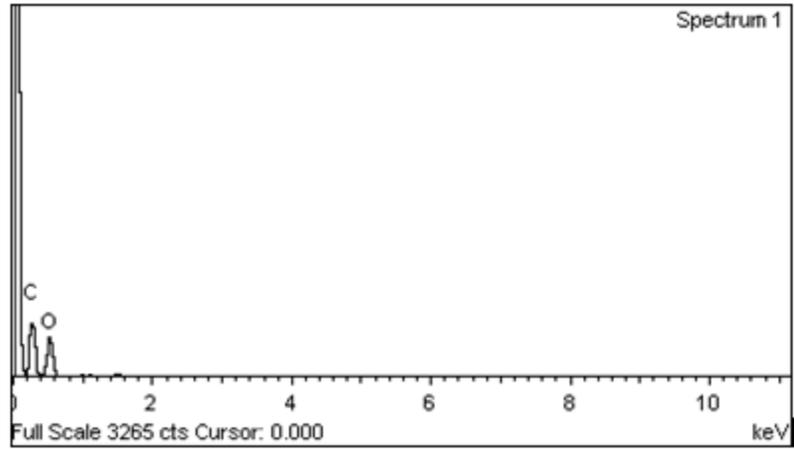
(a)
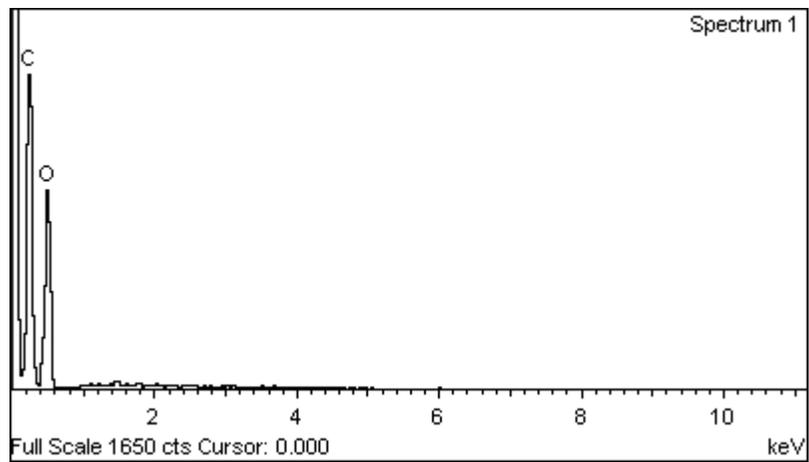
(b)
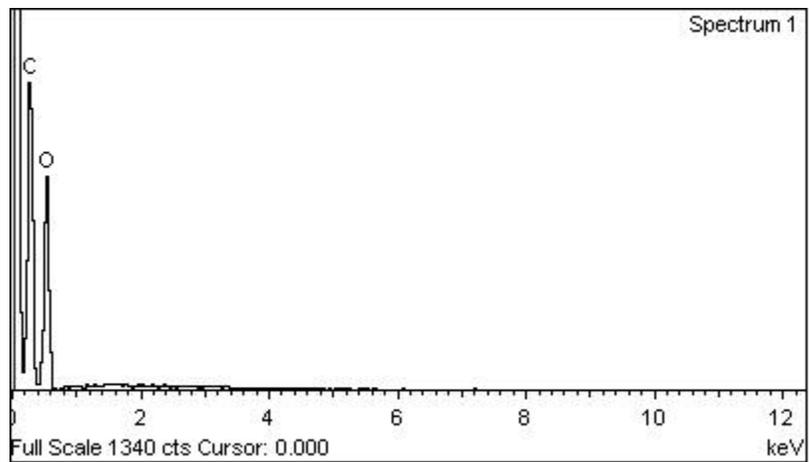
(c)

Figure 9. EDX Spectrum of cellulose treated with acetic acid (a), oxalic acid (b), and EDTA (c).

4.1.2 Fourier Transform Infra-Red Spectrum

The pictures below show FTIR spectrum of three samples; pure cellulose, cellulose oxalic and cellulose EDTA. These spectrums display absorption peaks indicating the presence of different functional groups. The most important change observed in the spectra is the appearance of bonds at 1600-1650 cm^{-1} indicate the absorption of C=O stretch in carboxylic group. The transmittance of this peak decrease from 99.31% to 97.26% to prove COOH group substitution. A wide absorption peak at 3277.50 cm^{-1} is assigned to aromatic and aliphatic OH groups while peak at 2889.71 cm^{-1} represents C-H vibration of CH_2 and CH_3. Sharp peaks at 996.59-1051.34 cm^{-1} relates with the β-glucose cross-linking of polymeric cellulose structure.
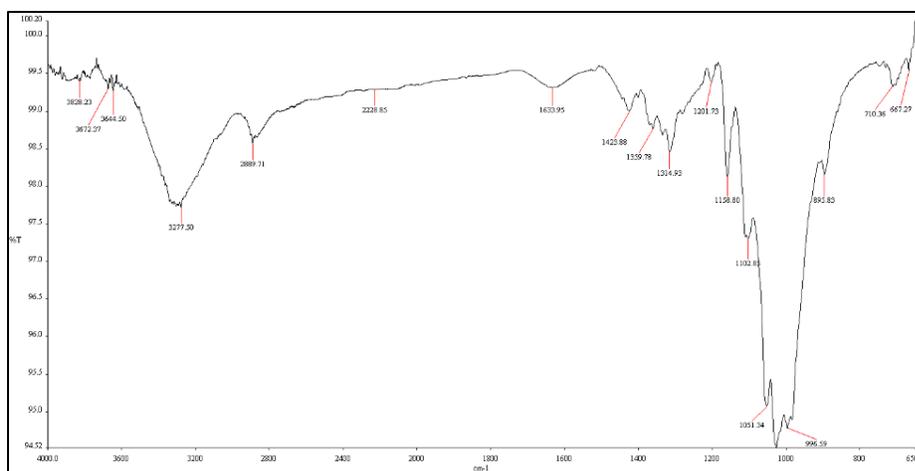
(a)
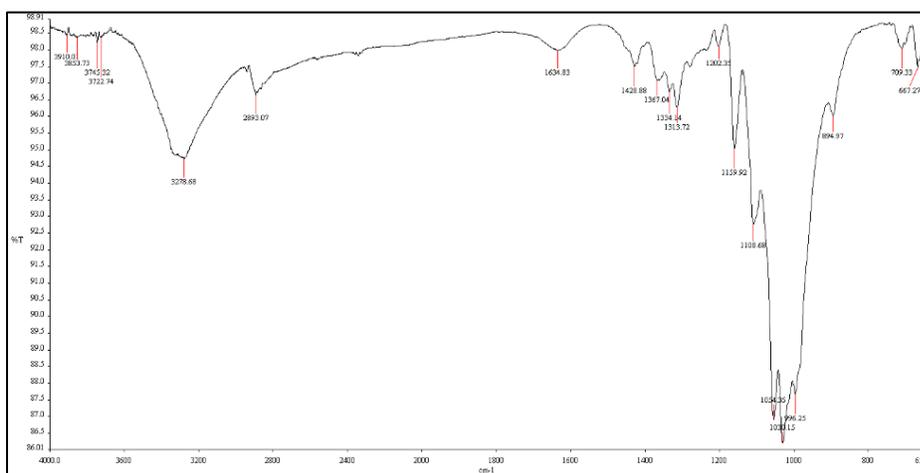
(b)
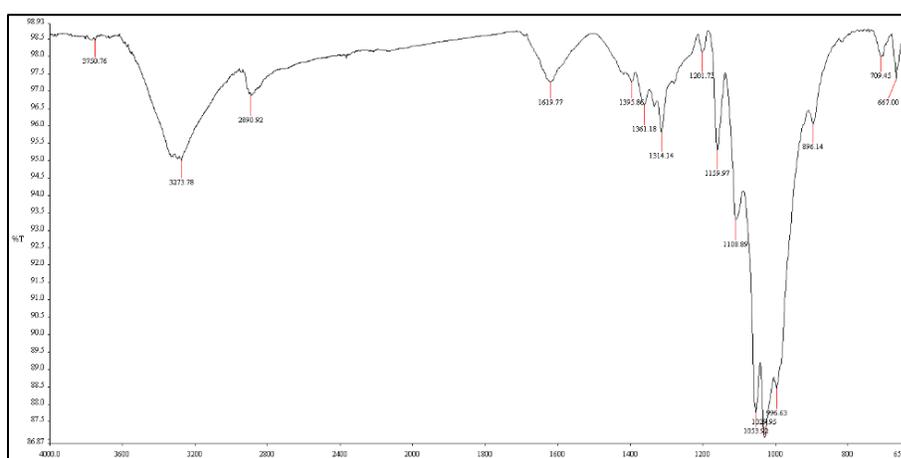
(c)

Figure 10. FTIR Spectrum of pure cellulose (a), cellulose treated with oxalic acid (b), and EDTA (c).

4.1.3 Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) is used to measure the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperature up to 1000'C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.
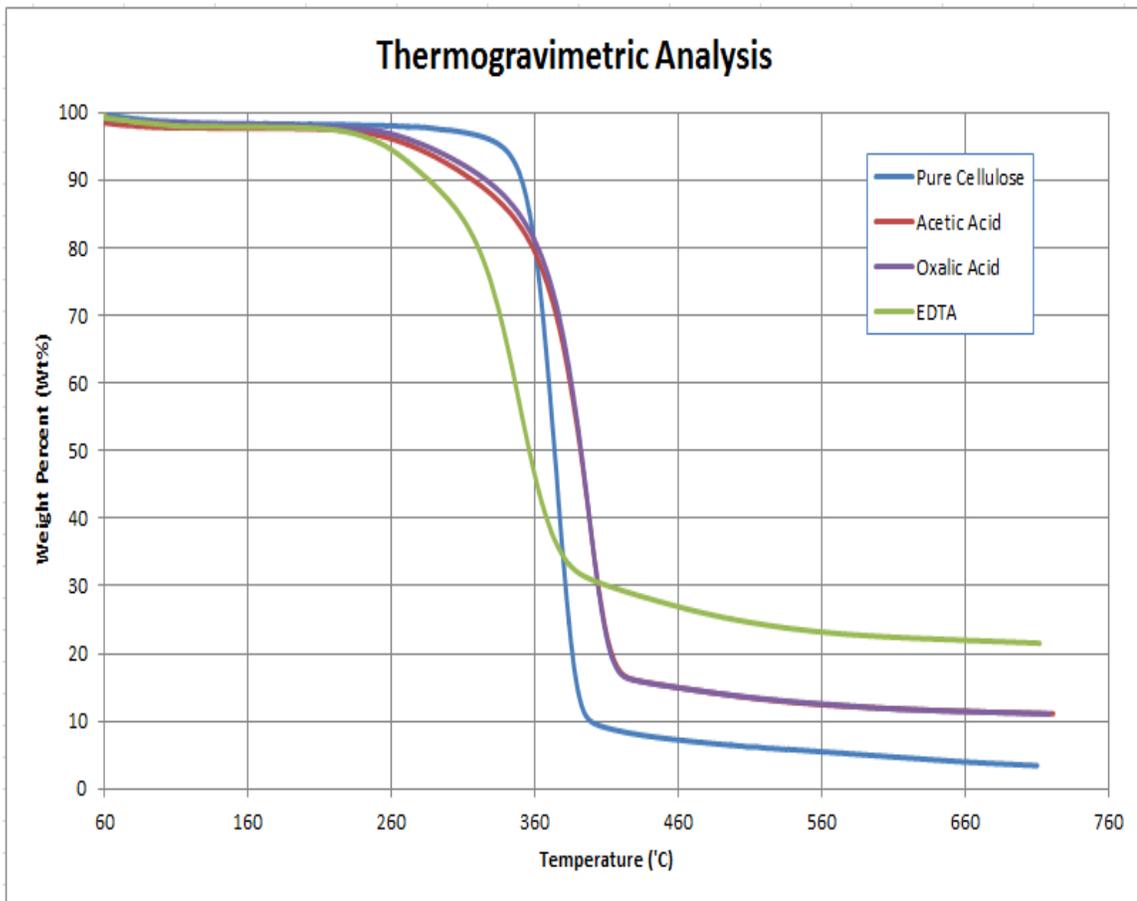
Figure 11. Graph showing TGA result of Pure Cellulose, Cellulose treated with acetic acid, oxalic acid, and EDTA.

As discussed in Chapter 2, the structure of cellulose is divided into three parts; cellulose, hemicellulose, and lignin. Hemicelluloses are less stable thermally than cellulose and emit more noncombustible gasses (LeVan S.L, 1989). The hemicelluloses degrade at temperature from 200°C to around 260°C. Between 150°C and 300°C, cleavage of α- and β-aryl-alkyl-ether linkages occurs. Around 300°C, aliphatic side chains start splitting off from the aromatic ring. Finally, the carbon-carbon linkages between lignin structural units are cleaved at 370°C-400°C. The degradation of lignin is an exothermic reaction, with peaks occurring between 225°C and 450°C. Beyond this temperature, the cellulose structure mostly decomposed, depending on the atmospheric pyrolysis agent. The degradation curve become less steeper from Pure Cellulose to Cellulose EDTA due to weaker bond stretch of COOH compared to OH group, causing Cellulose with higher degree of COOH substitution to decompose faster.

4.1.4 Particle Size Analyzer

The analysis of cellulose particle is carried out to justify modification of –OH group with –COOH groups. Figure 12(a) shows the particle size of pure cellulose without treatment. The pure cellulose size consist of fibers with diameter ranging from 1-100 um, with most of them distributed around 50 um. The secondary peak might be cellulose with higher Degree of Polymerization.
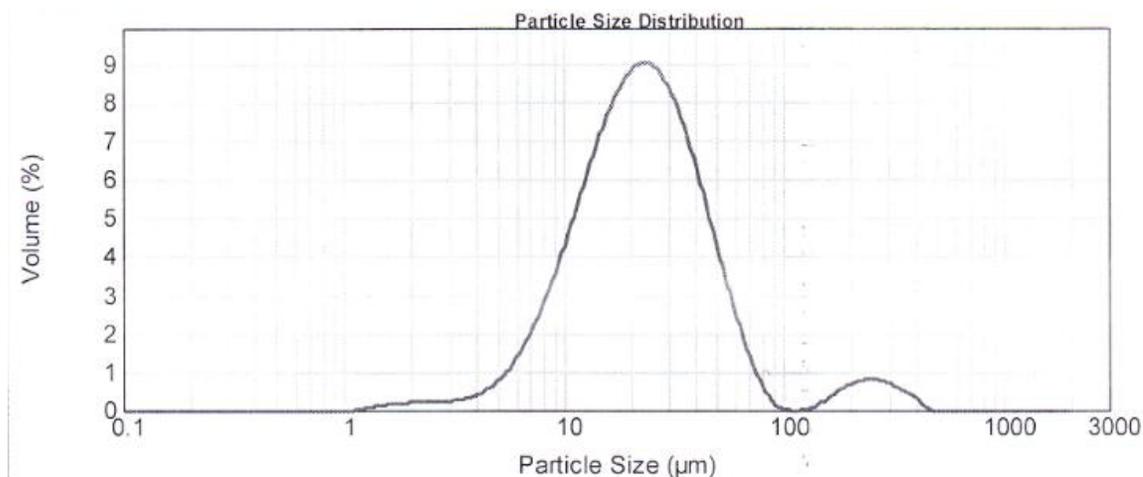

Figure 12(a)

In Figure 12(b), cellulose treated with oxalic acid shows reduced volume of normal cellulose, with broader peak shifting to 300 um. New critical peak emerges at 1000-2000 um, proving the modification of low diameter cellulose with –OH groups to larger diameter cellulose with –COOH groups.

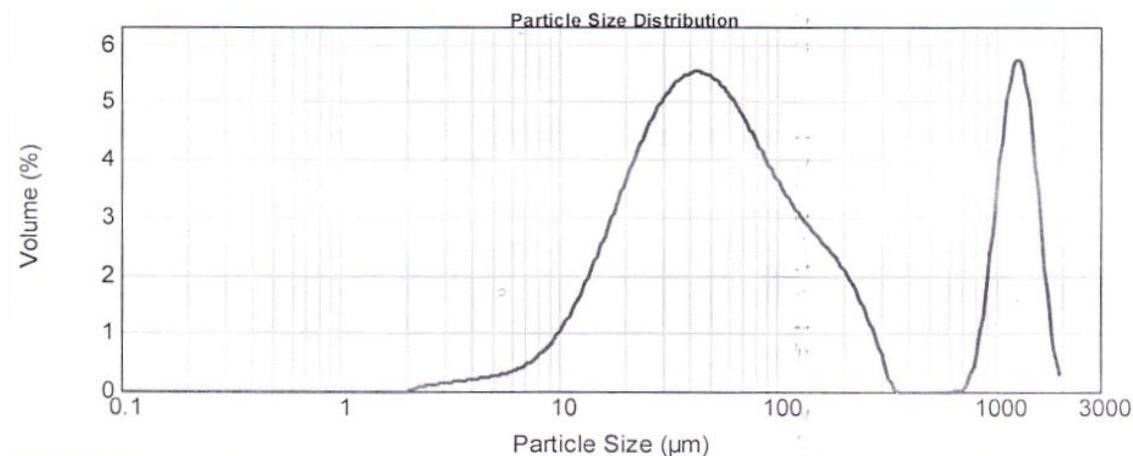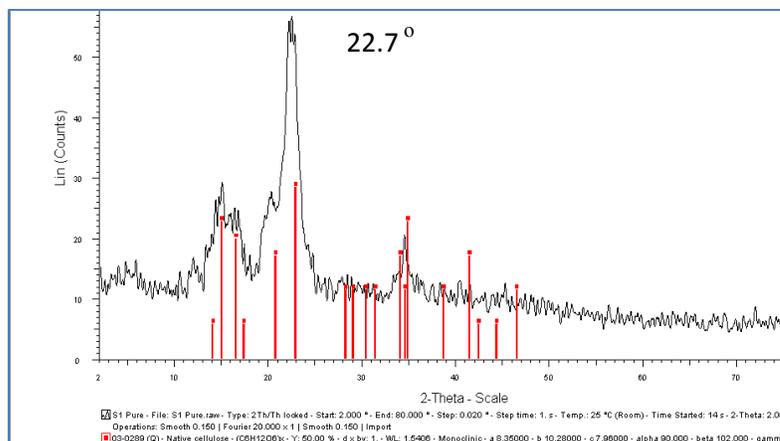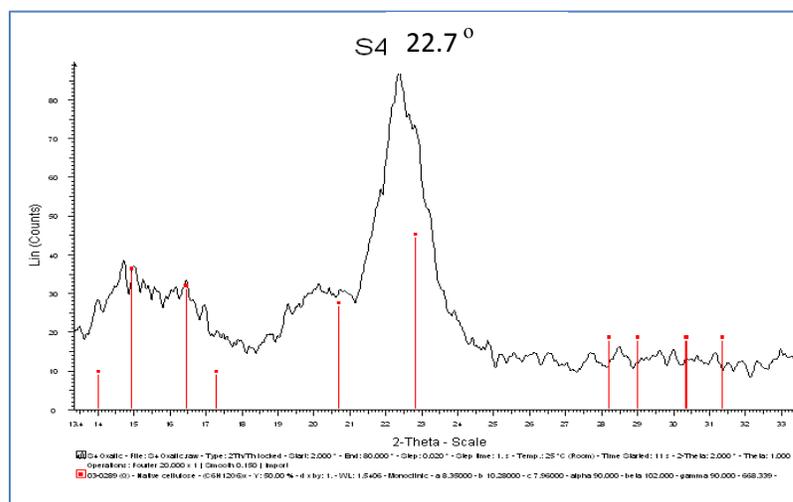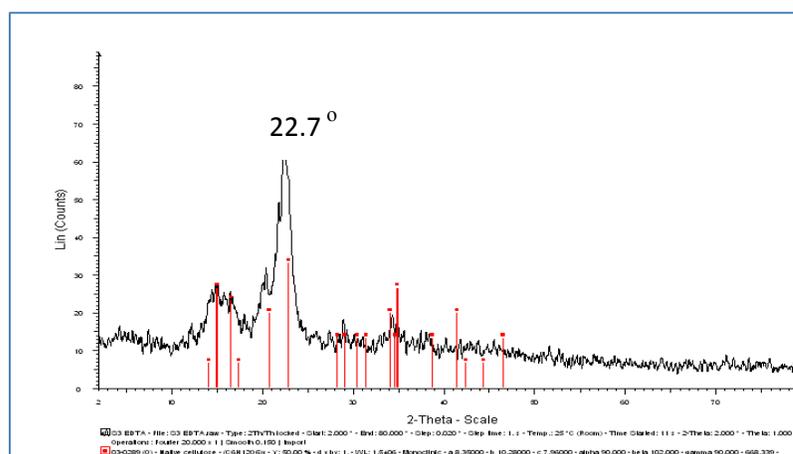

Figure 12(b)

4.1.5 Crystal Lattice

The crystal lattices of cellulose samples are identified using X-Ray Diffraction analysis, with results are collected in the 2θ range of 2° to 70°. The native cellulose had typical diffraction peaks at $2\theta = 14.9^{o}$, 16.5^{o} and 22.7^{o}. In figure 13 below, the peak at 22.7^{o} is reduced when cellulose is treated with oxalic acid and EDTA. This proves that the structure of cellulose has been modified COOH groups.

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(a)

(b)

(c)

Figure 13. Graph showing XRD result of Pure Cellulose, Cellulose treated with oxalic acid, and EDTA.

4.2 Metal Adsorption

4.2.1 Contact Time Study

The effect of contact time is studied by regulating shaking time of cellulose samples in metal solution at constant shaking speed of 140 rpm. From the figures below, the adsorption of metal ions show rapid diffusion into cellulose active site, but gradually decreases by time. The reason of the rate reduction is due to large number of vacant active sites are available in the initial stage, and the availability of this sites are reduces as function of time. The adsorption is difficult because of lower concentration gradient of metal ions and repulsive forces between solute molecules on the solid and bulk phases. According to the graphs, the equilibrium adsorption times are recorded at 90 minutes for Copper and Zinc, while 120 minutes are required for Lead to fulfill all the active sites. The reason is due to smaller radius of Copper and Zinc compared to Lead, that allow them to flux faster into the active sites of cellulose. The equilibrium time is almost the same for both adsorbent, Cellulose Oxalic and Cellulose EDTA.
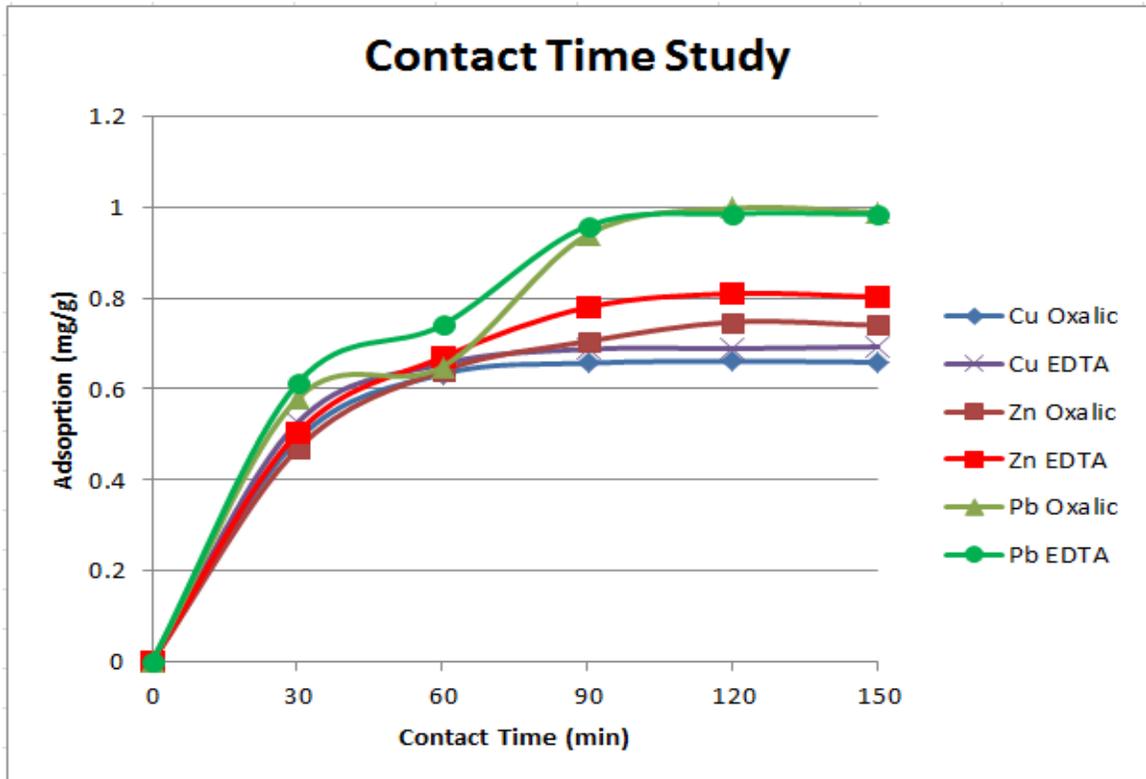

Figure 14. Adsorption of heavy metals at different contact time.

4.2.2 Concentration Study

Studying the effect of initial concentration is conducted using different concentration of metal ion solutions from 10ppm to 100 ppm. The adsorption of metal ions in cellulose active sites increase almost linearly up to 60 ppm concentration before the rate is gradually decreased at 80 and 100 ppm. The initial concentration of metal ions provide important driving force to overcome the mass transfer resistance between aqueous and solid phases, proving that higher initial concentration enhance the rate of adsorption. The rate starts to decrease at certain concentration due to limitation of active sites available for adsorption.
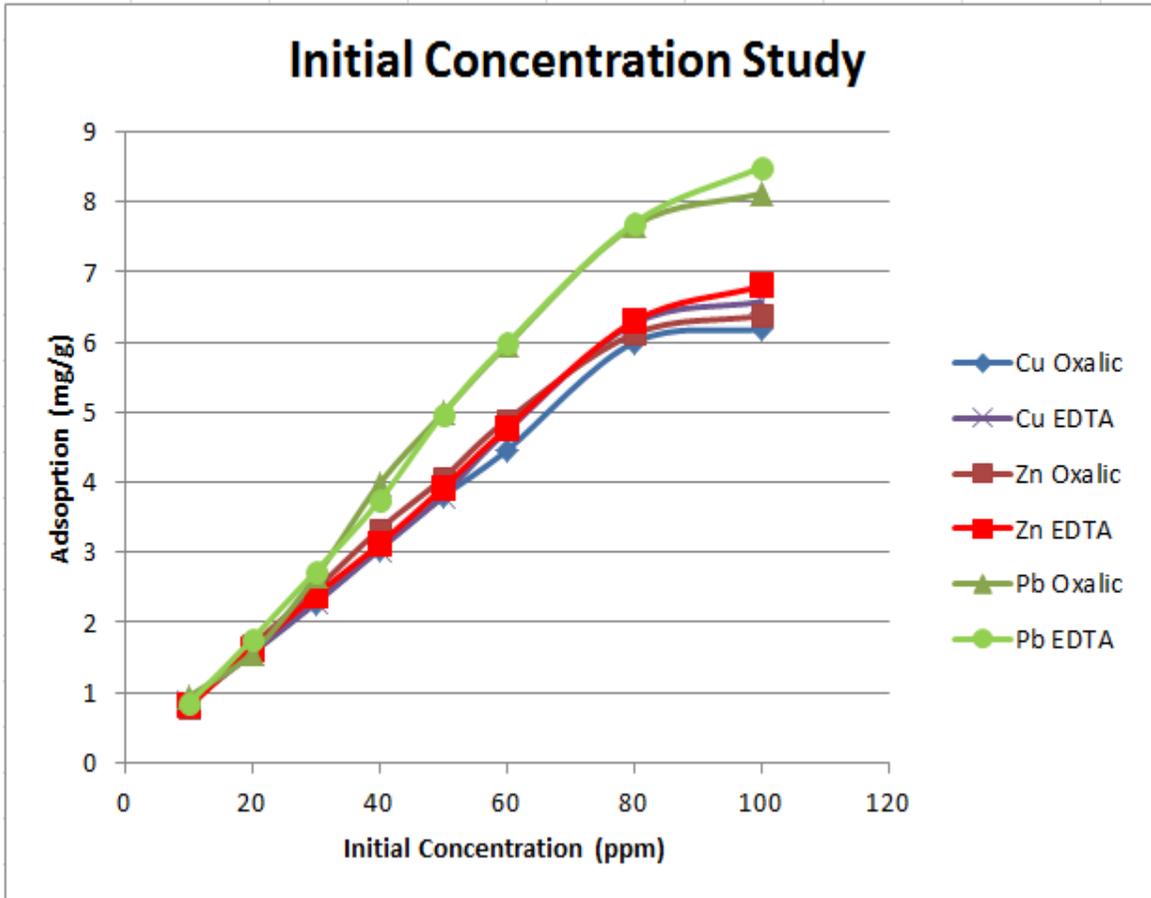

Figure 15. Adsorption of heavy metals with different initial metal ions concentration.

4.2.3 PH Study

PH is another variable that can significantly affecting the adsorption isotherm of metals in cellulose as well as the degree of ionization of different solutes. The effect of pH is studied by varying it from 4.0 to 8.0, with results are shown in the diagrams below. From the graphs, the uptake amount of metals is low at pH 4.0 for all metals. When the pH is increased by adding Sodium Hydroxide, the adsorption capacity is increasing as well. However, the metal uptake is start to equilibrate and reduced at high pH. Copper uptake is highest at pH 7.0 using Cellulose EDTA and pH 8.0 with Cellulose Oxalic. In case of Zinc adsorption, pH 6.0 gives highest uptake for both EDTA and Oxalic before the adsorption is decreasing at higher pH. The same case applied for Lead, where the optimum adsorption is at pH 6.0. The reason of this observation is because at low pH, the concentration of H^+ is high, and the carboxylic acid functional groups of the adsorbent is easier to be protonated. As a consequence, the electrostatic interaction between the adsorbent and the metal ions made them to be in mutual repulsion, causing the adsorption to be low. At higher pH value, the concentration of H^+ is reduced. The electrostatic interaction between adsorbent functional group and solution achieve mutual affinity, thus allowing more metal ions to bind at the active sites. However, when the pH is above the optimum, the tendency of metal ions to hydrolysis and polymerize will overwhelm the diffusion rate to the active sites.
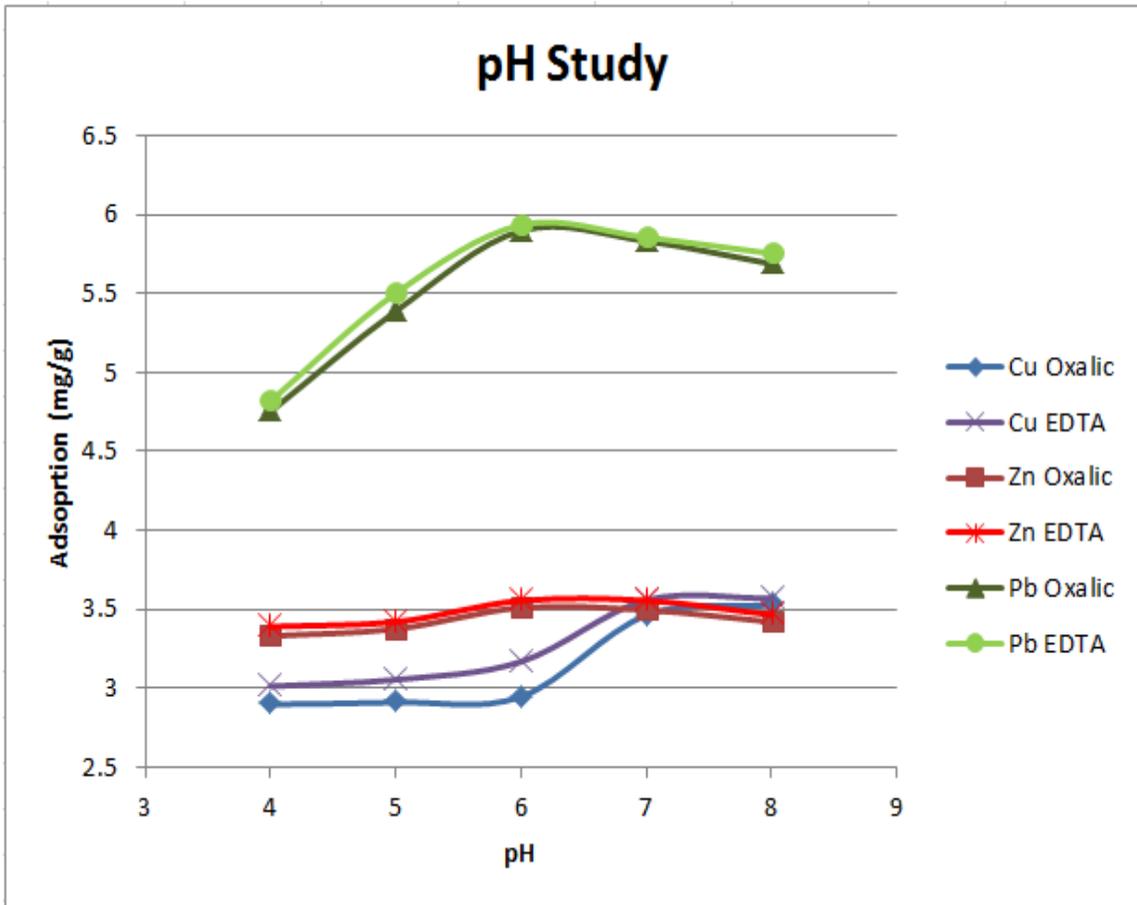
Figure 16. Adsorption of heavy metals at pH.

4.3 Adsorption Isotherms

To quantify the adsorption capacity of OPEFB modified cellulose for the removal of copper, zinc and lead ions from aqueous solutions, the Langmuir, Freundlich and Temkin isotherm models were used.

4.3.1 Langmuir model

This model assumes that the adsorptions occur at specific homogenous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The data of the equilibrium studies for adsorption of all metal ions onto modified cellulose may follow the following linear form of Langmuir model:

$$\frac{C_e}{q_e} = \left(\frac{1}{b}\right)(C_e) + \left(\frac{1}{b}\right)\left(\frac{1}{K_L}\right)$$

where C_e is the equilibrium concentration (mg/L) and q_e is the amount adsorbed per specified amount of adsorbent (mg/g), K_L is the Langmuir equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of C_e/q_e versus C_e should be a straight line with a slope ($1/b$) and an intercept as ($1/bK_L$) as shown in Figure 17. The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hint towards the conclusion that the surface adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect to adsorption phenomenon. The correlation coefficient (R^2) values of 1 indicated that the adsorption data of heavy metal ions onto OPEFB cellulose acetate was well fitted to the Langmuir isotherm.
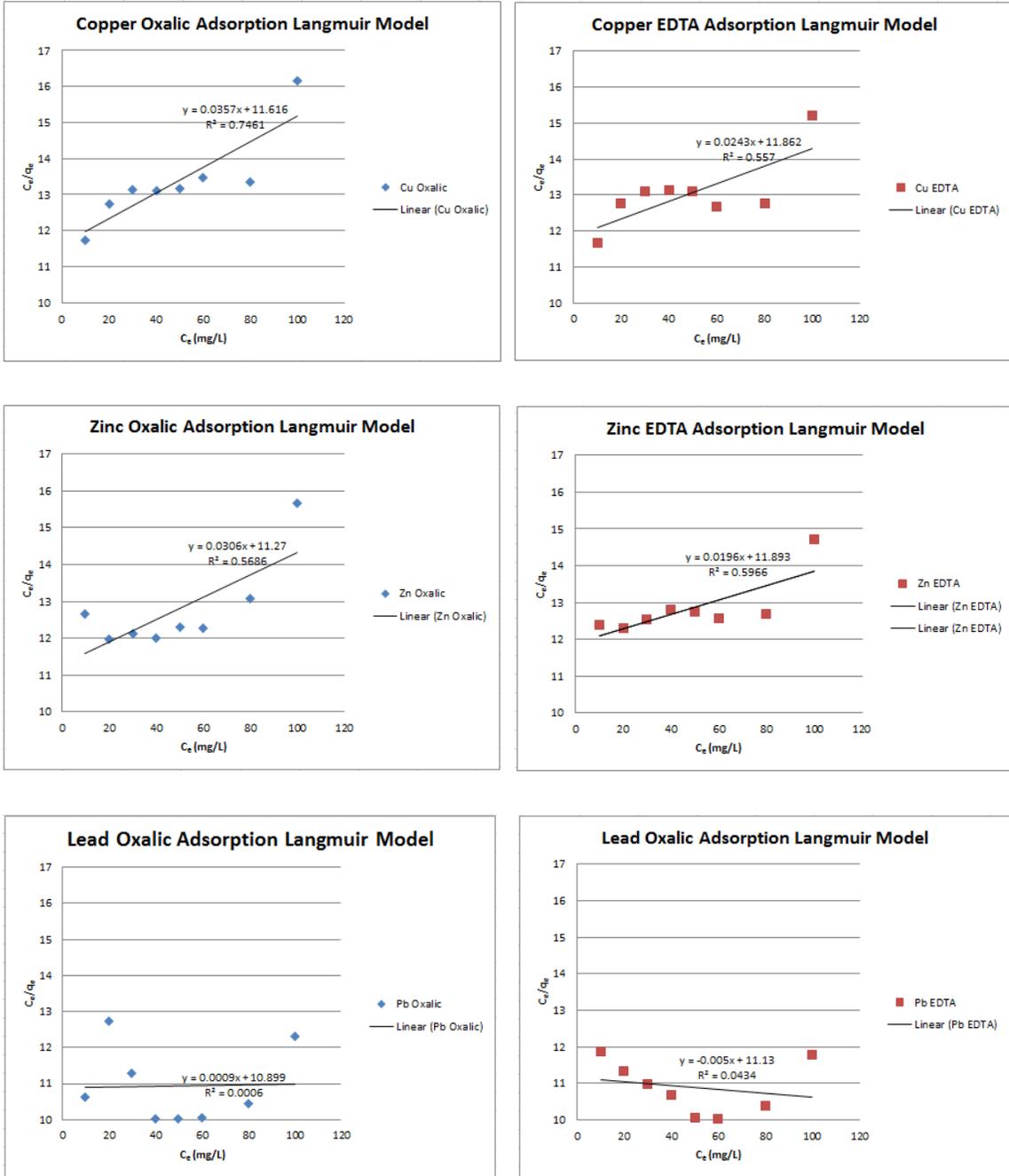
Figure 17. Langmuir Models for all metal ions adsorption onto cellulose modified with oxalic acid and EDTA.

The calculations of constants are as follows:

(For copper (II) ions in cellulose oxalic)

$$\frac{C_e}{q_e} = \left(\frac{1}{b}\right)(C_e) + \left(\frac{1}{b}\right)\left(\frac{1}{K_L}\right)$$

$$y = mx + c$$

$$y = 0.0357x + 11.616$$

$$\left(\frac{1}{b}\right) = 0.0357 \,, b = 28.0112$$

$$\left(\frac{1}{b}\right)\left(\frac{1}{K_L}\right) = (0.0357)\left(\frac{1}{K_L}\right) = 0.730, K_L = 0.003073$$

$$\therefore b = 28.0112 \,, K_L = 0.003073$$

The related parameters for all metal ions adsorption were reported in Table 2.

4.3.2 Freundlich model

The Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. According to this model:

$$q_e = (K_F)\left(C_e^{\,1/n}\right)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$$

where K_F is Freundlich equilibrium constant, n is an empirical constant and the rest if the terms have the usual significance. Thus, a plot of $\ln q_e$ versus $\ln C_e$ should be a straight line with a slope $1/n$ and an intercept of $\ln K_F$ as shown in Figure 18.
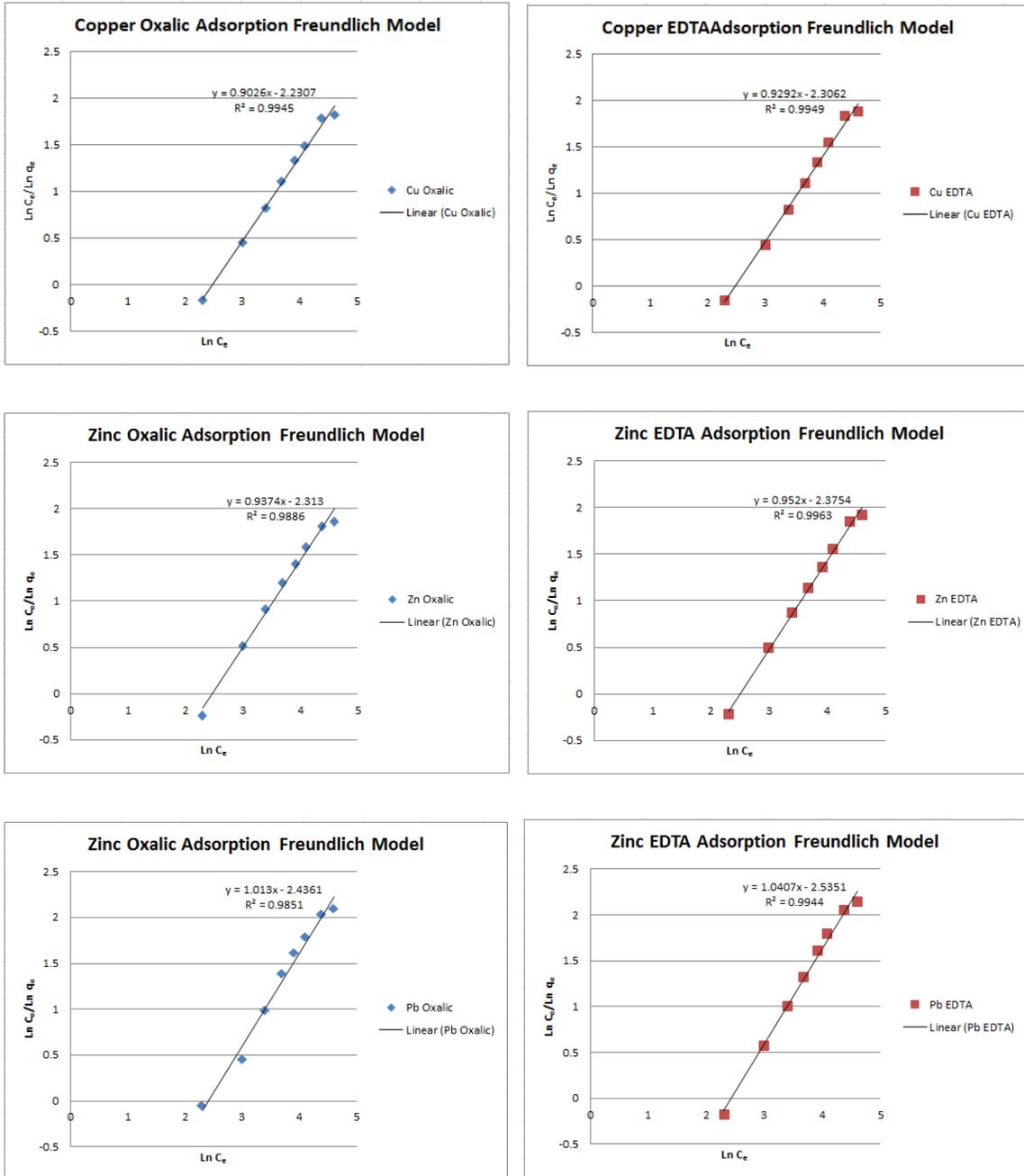
Figure 18. Freundlich Models for all metal ions adsorption onto cellulose modified with oxalic acid and EDTA.

(For copper (II) ions in cellulose oxalic)

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

$$y = 0.9026x - 2.2307$$

$$\frac{1}{n} = 0.9026 \, , n = 1.108$$

$$\ln K_F = -2.2307 \, , K_F = 1.107$$

The parameters for all metal ions adsorption were reported in Table 2.

4.3.3 Temkin model

Temkin and Pyzhev(1940), considered the effects of indirect adsorbate-adsorbate interactions on adsorption isotherms. The Temkin isotherm has been used in the linear form as follows:

$$q_e = \left(\frac{RT}{b}\right) \ln(K_T C_e)$$

$$q_e = B \ln K_T + B \ln C_e$$

where B=(RT/b), a plot of q_e versus $\ln C_e$ yielded a linear line, as shown in Figure 19 and 20, enables the determination of the isotherm constants K_T and B. K_T is the Temkin equilibrium binding constants (L/mg) corresponding to the maximum binding energy and constant B is related to heat of adsorption. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbate interactions.
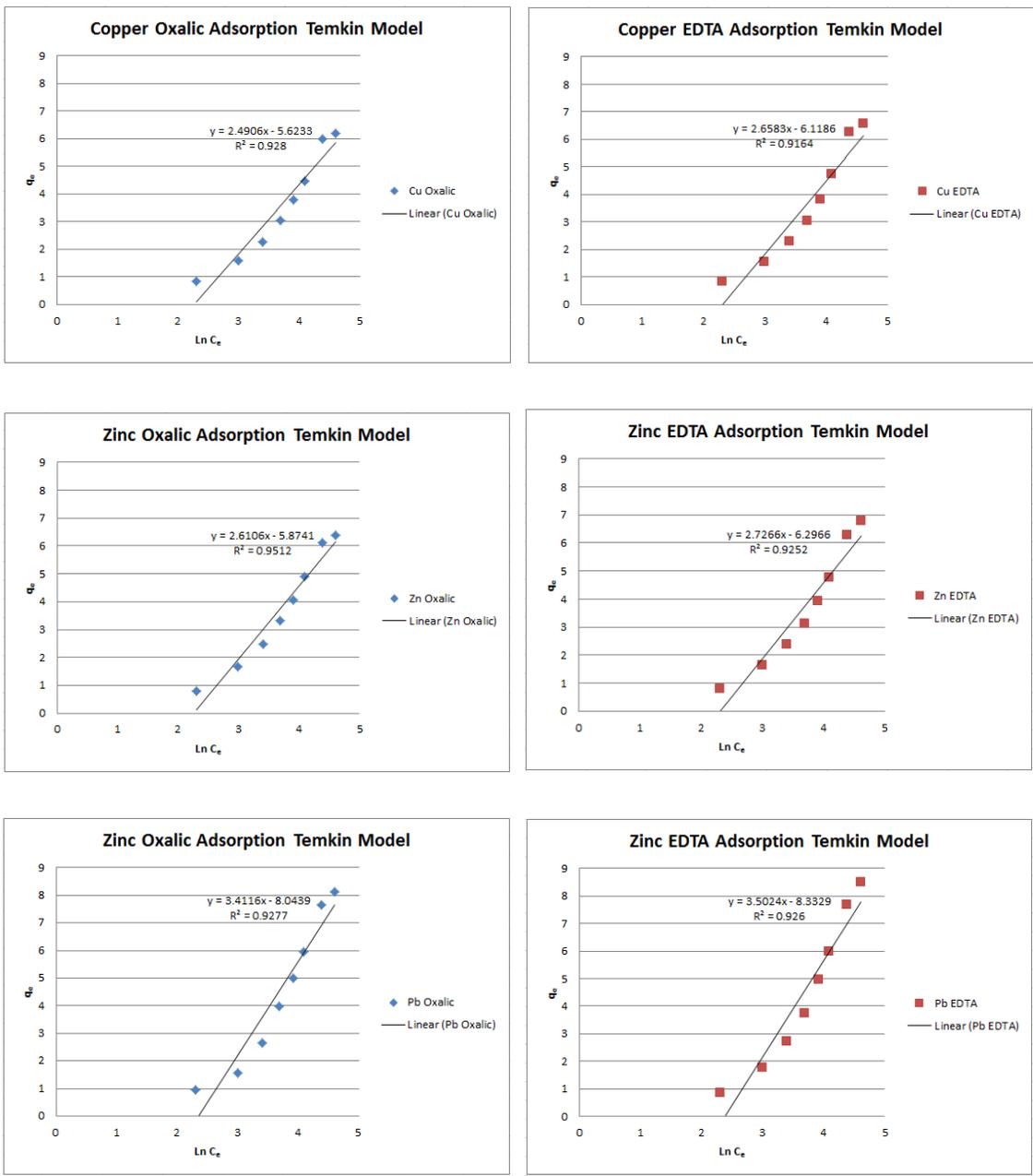
Figure 19. Temkin Models for all metal ions adsorption onto cellulose modified with oxalic acid and EDTA.

Table 2(a) Isotherm Constants for heavy metal ions adsorption in cellulose oxalic

Adsorption isotherms and its constants	Copper (II)	Zinc (II)	Lead (II)
Langmuir adsorption isotherm constants			
b (mg/g)	28.011	51.020	1111.111
K_L (L/mg)	0.0031	0.002	0.000
R^2	0.746	0.569	0.001
Freundlich adsorption isotherm constants			
K_F (mg/g)(L/mg)$^{1/n}$	0.107	0.099	0.088
n	1.108	1.067	0.987
R^2	0.995	0.989	0.985
Temkin adsorption isotherm constants			
K_T (L/mg)	0.105	0.105	0.095
B	2.491	2.611	3.412
R^2	0.928	0.951	0.928

Table 2(b) Isotherm Constants for heavy metal ions adsorption in cellulose oxalic

Adsorption isotherms and its constants	Copper (II)	Zinc (II)	Lead (II)
Langmuir adsorption isotherm constants			
b (mg/g)	41.152	32.680	-200
K_L (L/mg)	0.002	0.003	0.000
R^2	0.557	0.597	0.043
Freundlich adsorption isotherm constants			
K_F (mg/g)(L/mg)$^{1/n}$	0.100	0.093	0.079
n	1.076	1.050	0.961
R^2	0.995	0.996	0.994
Temkin adsorption isotherm constants			
K_T (L/mg)	0.100	0.099	0.093
B	2.658	2.727	3.502
R^2	0.916	0.925	0.926

From Table 2, the Freundlich adsorption isotherm model yielded best fit as indicated by the highest R^2 values for all heavy metal ions compared to the Langmuir and Temkin adsorption isotherm models. This result suggested heterogeneous binding sites on the cellulose layer.

4.4 Kinetic studies

The modeling of the kinetics of adsorption of copper, zinc, and lead ions on OPEFB cellulose acetate was investigated by two common models, namely, pseudo-first-order model and pseudo-second-order model. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

4.4.1 Pseudo-first-order model

The pseudo-first-order rate model of (Lagergren, 1898) is based on solid capacity and generally expressed as follows:

$$\log(q_e - q) = \log q_e - \left(\frac{k_1}{2.303}\right) t$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant. This is the most popular form of pseudo-first-order kinetic model. Values of k_1 were calculated from the plots of $\log(q_e-q)$ versus t (Figure 20) for copper, zinc, and lead ions. Constant k_1 and correlation coefficients (R^2) have been calculated and summarized in Table 3. The correlation coefficients (R^2) values were relatively low, it showed that this model have very poor correlation coefficients (R^2) for best fit data.

4.4.2 Pseudo-second-order model

The kinetic data were analyzed using the pseudo-second-order model which can be expressed as:

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t$$

$$h = k_2 q_e^2$$

Where h is the initial sorption rate (mg/min). The plot of t/q versus t should give a linear relationship, from which, q_e and k_2 can be determined from the slope and intercept of the plot (Figure 21). The k_2 and q_e determined from the model are presented in Table 3 along with the corresponding correlation coefficient (R^2) values. The values of the calculated and experimental q_e are presented in table 3.
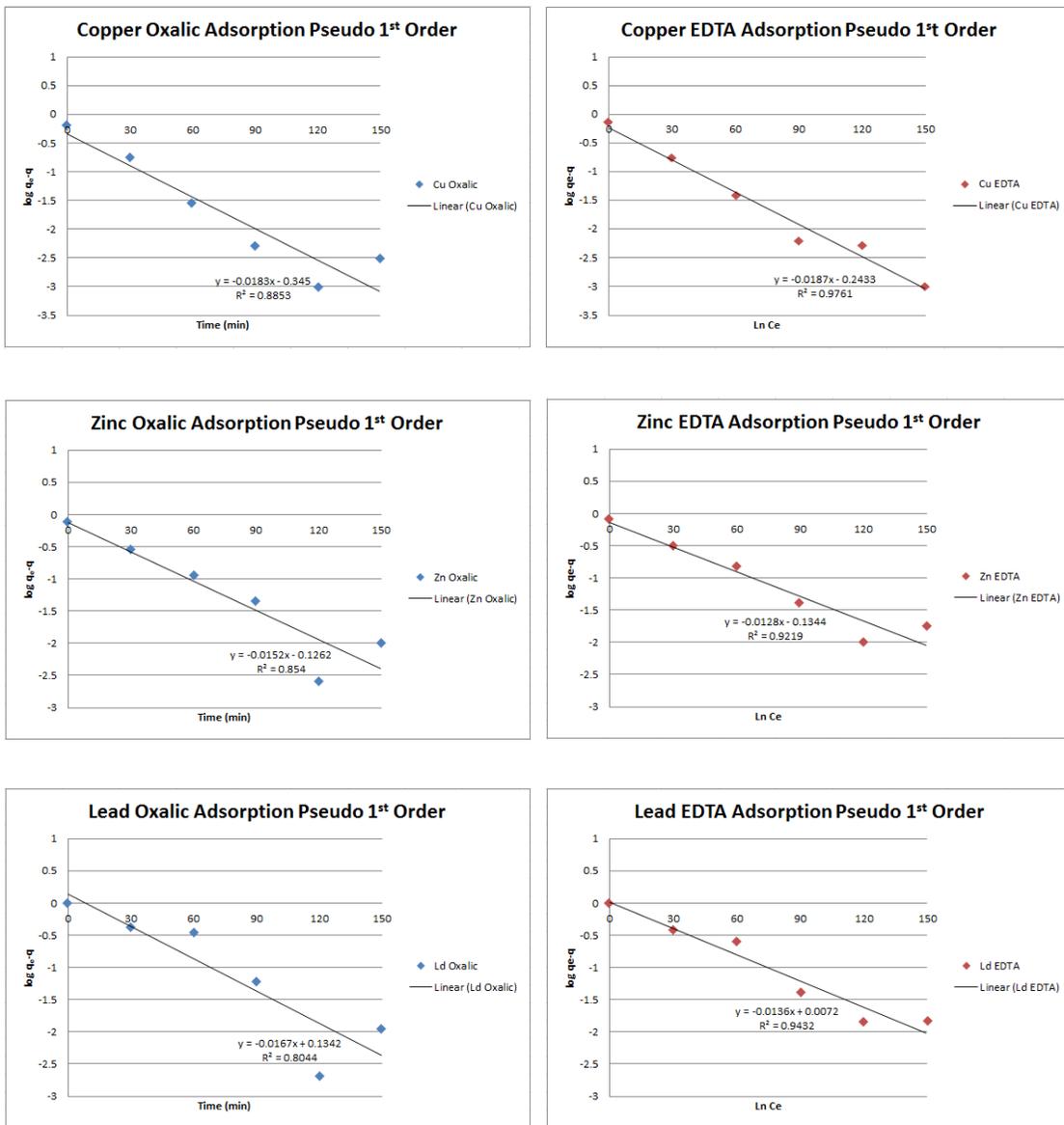
Figure 20. Pseudo 1st Order models for all metal ions adsorption onto cellulose modified with oxalic acid and EDTA.
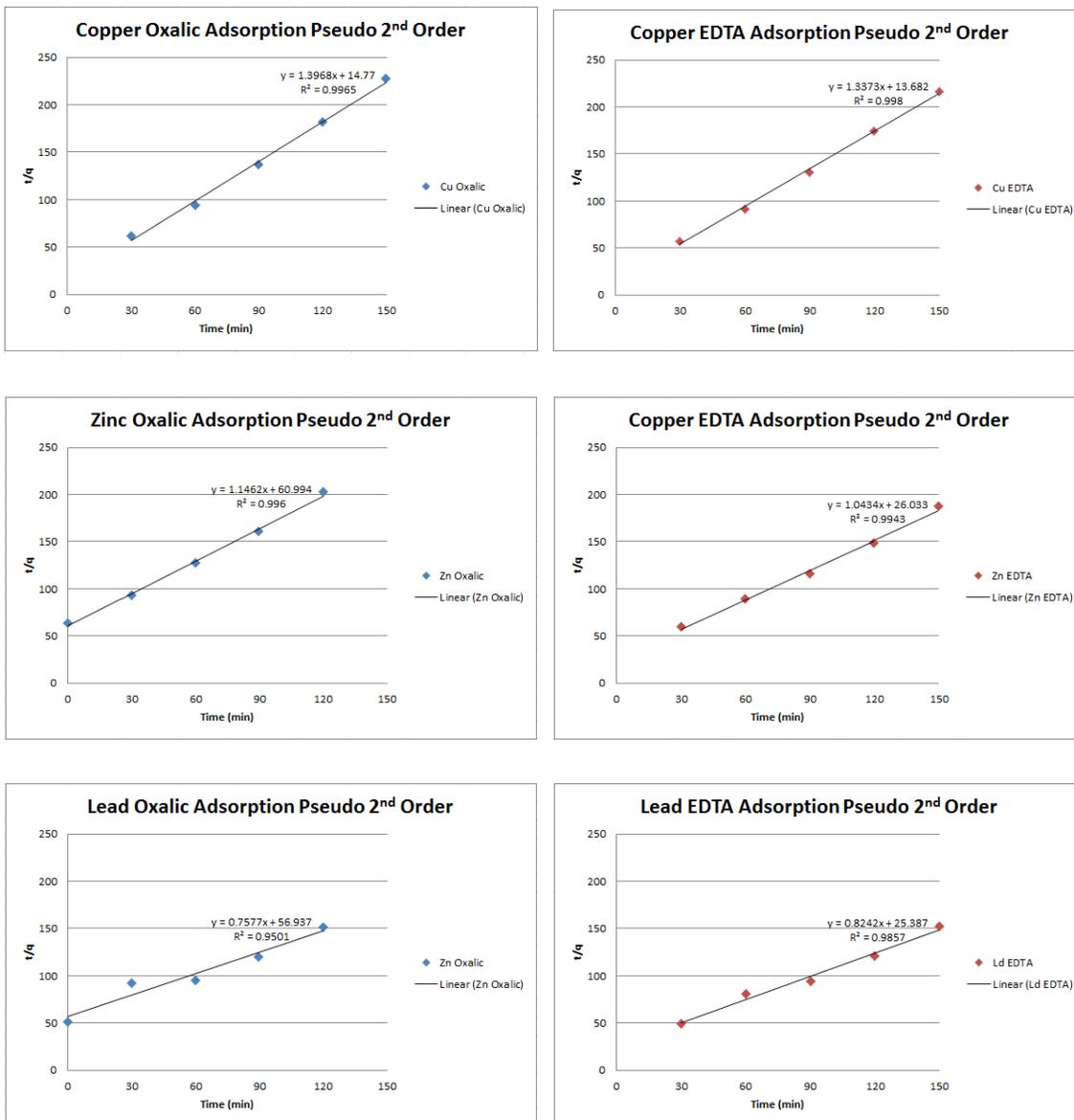
Figure 21. Pseudo 2nd Order models for all metal ions adsorption onto cellulose modified with oxalic acid and EDTA.

Table 3(a). Pseudo 1st Order and Pseudo 2nd Order parameters for heavy metal ions adsorption in cellulose oxalic.

Kinetic model and its parameter	Copper (II)	Zinc (II)	Lead (II)
$q_{e,exp}$ (mg/g)	0.662	0.750	1.000
Pseudo-first-order kinetic model			
q_e (mg/g)	0.452	0.748	1.362
k_1 (min^{-1})	0.042	0.035	0.038
R^2	0.885	0.854	0.804
Pseudo-second-order kinetic model			
q_e (mg/g)	0.716	0.872	1.320
k_2 (g mg^{-1} min^{-1})	0.132	0.022	0.010
h (mg g^{-1} min^{-1})	0.067	0.016	0.018
R^2	0.997	0.996	0.950

Table 3(b). Pseudo 1st Order and Pseudo 2nd Order parameters for heavy metal ions adsorption in cellulose EDTA.

Kinetic model and its parameter	Copper (II)	Zinc (II)	Lead (II)
$q_{e,exp}$ (mg/g)	0.694	0..820	1.000
Pseudo-first-order kinetic model			
q_e (mg/g)	0.571	0.734	1.017
k_1 (min^{-1})	0.043	0.029	0.031
R^2	0.976	0.922	0.943
Pseudo-second-order kinetic model			
q_e (mg/g)	0.748	0.958	1.213
k_2 (g mg^{-1} min^{-1})	0.131	0.042	0.027
h (mg g^{-1} min^{-1})	0.073	0.038	0.039
R^2	0.998	0.994	0.986

It can be seen from this table that the adsorption of all heavy metal ions followed the pseudo-second-order kinetic model due to highest R^2 value.

4.5 Sulphur Removal Process

4.5.1 CHNS Analyzer

The sulphur removal experiment had been conducted by contacting treated cellulose and metal loaded cellulose with 1:10 weight to volume ratio of diesel. The value of adsorption of sulphur is investigated by CHNS Analyzer that display the amount of Carbon, Hydrogen, Nitrogen, and Sulphur molecules exist in the liquid.
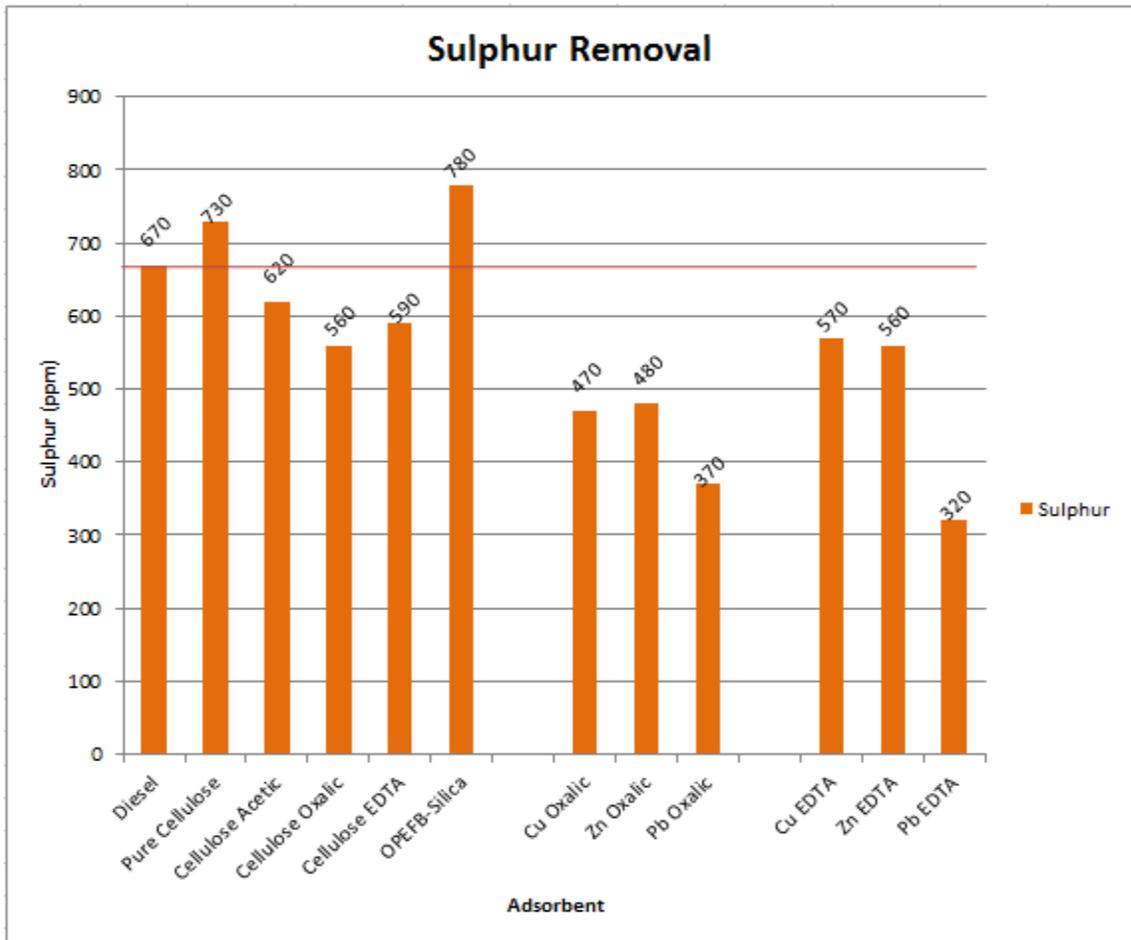

Figure 22. Sulphur content in diesel after treatment.

From the graph above, maximum sulphur removal is done by cellulose EDTA Lead loaded with 350 ppm sulphur reduction (52.2%). Metal ions loaded celluloses are capable to remove the sulphur due to the present of cation from the metal ions that bind to anion from sulphur compared to cellulose without metal ions loading.
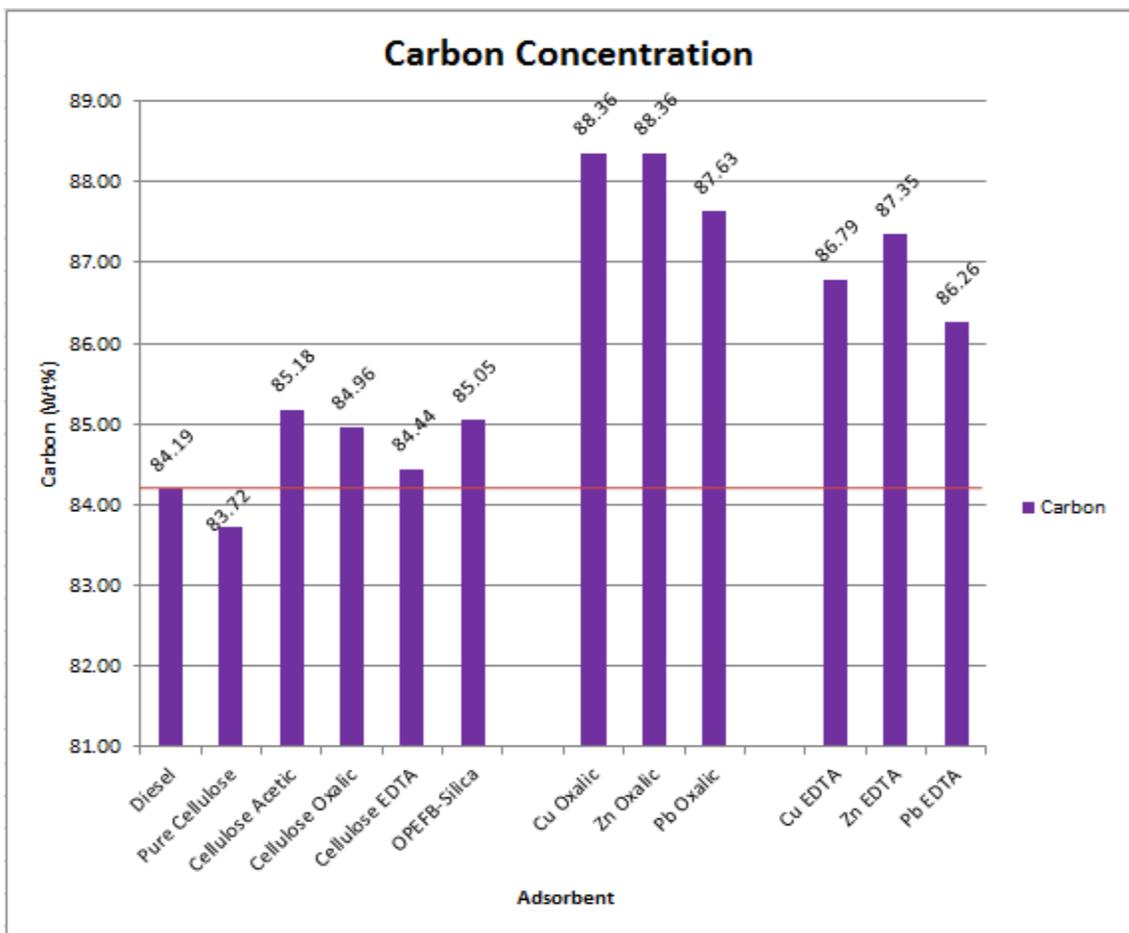
Figure 23. Carbon content in diesel after treatment.

From figure 23, carbon element has shown increments in weight percentage after the treatment with cellulose loaded with metal ions. The possible reason is due to large portion of impurities such as dibenzothiophene and other organosulphur compound that has been removed, thus increasing the percentages of hydrocarbon left in the diesel.

CHAPTER 5: CONCLUSION

The sulphur removal process by cellulosic fiber sounds to be an easy way of desulphurization; however, it takes a lot of considerations to investigate the best parameter to be used. A thorough and detail study have to be conducted to analyze the structure of cellulose and possible ways of modification to enhance sulphur adsorption process. Modification of –OH group with –COOH from acetic acid, oxalic acid, and EDTA change the hydrophobic properties of cellulose to hydrophilic, enabling adsorption process in water and most solvent. Treatment with EDTA provides most porous structure and active sites for metal ions loading. The process of loading metal into the cellulose structure is manipulated by three parameters; contact time, initial concentration of metal, and pH of solution. Lead has shown highest adsorption among all the metals at 8.1 mg/g using 100 ppm initial concentration after 120 minutes of treatment. The sorption process follows Freundlich isotherm and Pseudo 2nd order kinetic model.

Treated cellulose with metal ions loading will create polar structure of cellulose that capable of absorbing slightly polar organosulphur DBT in diesel composition. As a prove, 52,2% of sulphur is removed by treatment with cellulose EDTA loaded with Lead. The treatment also has shown increasing percentage of hydrocarbon, which remarks to better diesel specification. Optimization on sulphur removal process can be done by varying the batch treatment time and increasing metal ions concentration in the treated cellulose. For the future works, it is recommended to treat the cellulose with other functional group such as Aldehyde and Peroxide group. Both of them are green and can be purged out of stream without releasing carbon contaminate. In term of equipment, it is suggested to test the sulphur content using standard ASTM D5453 instead of depending on CHNS Analyzer. ASTM D5453 will require the use of TDS 3000 machine that work on UV Spectroscopy principles and used widely in refinery laboratory for testing sulphur content in hydrocarbon.

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