Surface Engineering Of Cellulose For Heavy Metal And Pesticide Removal

by

Muhammad Faizal Izuany Bin Zailani

Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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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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MUHAMMAD FAIZAL IZUANY BIN ZAILANI

ABSTRACT

The main objective of this research is to study the feasibility of heavy metals (zinc, copper and lead) and 2,4-Dichlorophenoxy acetic acid(2,4-D) removal through adsorption using surface modified cellulose. The current methods for removal of heavy metal and pesticide from aqueous solution are uneconomical and cellulose has the potential to become an effective biosorbent. However, cellulose lack of certain properties such as what to make it effective biosorbent and therefore surface engineering through chemical modification were investigated. Oxalic acid and ethylenediamminetetraacetate (EDTA) solution were used to modify the surface of cellulose. The resultant adsorbents (oxalic acid treated cellulose and EDTA treated cellulose) were characterized by Field Emission Scanning Microscope (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), and Thermogravimetric Analysis (TGA).

Batch adsorption process was carried out to test the suitability of the treated celluloses for removal of the heavy metals and 2,4-D. The amount of metal ions removed depended on the contact time, initial metal ion concentration and initial pH value. The adsorption equilibrium time for copper is 90 min while for zinc and lead is 120 min. The adsorbed amount of lead was the highest among the three heavy metals. However, the adsorption capacities of both of the treated celluloses were still low compared to previous similar research using other modifying agent to remove the heavy metals. Improvisation need to be done to increase its adsorption capacity. For adsorption of 2,4-D, the results in this study showed that it was not feasible to remove the pesticide using treated celluloses as the adsorbent. Pure cellulose adsorbed the highest amount of 2,4-D at 3.9844 mg/g.

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CHAPTER 1

1.1 Background of Study

Pollution by heavy metal and pesticide in waste water is a global major concern. Heavy metals such as zinc (Zn), copper (Cu) and lead (Pb) can bring harmful effects if present in high doses in any living organisms. Zinc is associated with nephrotoxic effects particularly at high exposure levels as long-term exposure may cause bone damage. High copper concentrations may lead to weakness, apathy, anorexia, and damage to the gastrointestinal tract. Lead poisoning can cause severe health problems to adults such as high blood pressure and damage to the brain, nervous system, stomach, and kidneys (O'Connell et. al., 2008).

A common type of pesticide used extensively in agricultural industry is 2,4-dichlorophenoxyacetic acid (2,4-D). It used as a broadleaf herbicide (weed killer) in commercially-available products and also applied to some recreational-use lakes to control weed growth. International Agency for Research on Cancer has reported that 2,4-D (and the entire family of phenoxy herbicides) is classified as potentially carcinogenic. When low doses of a commercial 2,4-D herbicide are fed to pregnant laboratory animals, an average size is reduced by about 20 percent. Exposure to 2,4-D causes serious eye and skin irritation, nausea, weakness, fatigue and in some cases neurotoxic effects. Maximum allowable concentration of 2-4-D in drinking water is 100 µ/L (Salman et al, 2011).

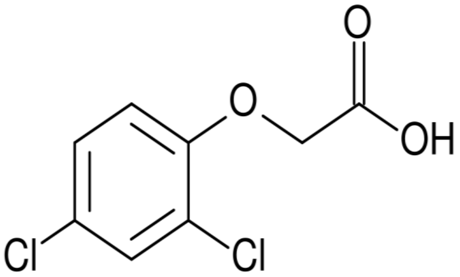


Figure 1 : Chemical Structure of 2,4-D (Salman et al.,2011)

Some of the methods of removing heavy metals from aqueous solution as shown in Table 1 are ion exchange, neutralization, reverse osmosis, precipitation, solvent extraction and adsorption (Zhou et al, 2012). Due to its easy handling, and high efficiency in removing heavy ions especially at medium to low ion concentrations from wastewaters, adsorption is considered as an economic choice.

Photocatalytic degradation, ultrasound in combination with photo-Fenton treatment, advanced oxidation processes, aerobic degradation, electrodialysis membranes, ozonation and adsorption are several methods currently used to remove pesticides from water according (Salman et al., 2011). Adsorption by activated carbon (AC) is also by far the most common methods to remove organics from aqueous solution (Khoshnood et al., 2012). This is due to its physicochemical properties including good mechanical strength, chemical stability in diverse media, and large pore size distribution in addition to its extensive specific surface area.

Table 1: Treatment Technologies for the removal of Heavy Metals from Wastewaters and associated Advantages and Disadvantages (O'Connell et al., 2008)

Technology	Advantages	Disadvantages
Chemical precipitation	Process simplicity Not metal selective Inexpensive capital cost	Large amount of sludge containing metals Sludge disposal cost High maintenance costs
Ion exchange	Metal selective Limited ph tolerance High regeneration	High initial capital cost High maintenance cost
Coagulation-flocculation	Bacterial inactivation capability Good sludge settling and dewatering characteristics	Chemical consumption Increased sludge volume generation
Floatation	Metal selective Low retention times Removal of small particles	High initial capital cost High maintenance and operation costs
Membrane filtration	Low solid waste generation Low chemical consumption Small space requirement Possible to be metal selective	High initial capital cost High maintenance and operation costs Membrane fouling Limited flow-rates
Adsorption	Wide variety of target pollutants High capacity	Performance depends on type of adsorbent Chemical derivatisation to

	Fast kinetics Possibly selective depending on adsorbent	improve its sorption capacity

Cellulose is a polysaccharide with the formula $(C_6H_{10}O_5)_n$. It is an organic compound consisting of linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. Cellulose is considered one of the most abundant components on earth. As basic structural component of plant cell walls, cellulose comprises about one third of all vegetable matter (Encyclopædia Britannica, 2012).

Commercially available ACs are generally expensive because of running costs thereby limiting its use. Therefore, cellulose can perhaps provide the alternative in replacing current ACs as the interest in a low cost adsorbent from renewable sources is growing for the removal of heavy metals and pesticide. Cellulose is a suitable because of its abundance and low cost as compared to commercial ion-exchange sorbent. However, unmodified cellulose lack properties to be used directly as an effective adsorbent such as low heavy metal adsorption capacity and variable physical stability (O’Connell et. al, 2008). The uniqueness of the chemical structure and macromolecules configurations make cellulose rigid, highly crystalline material which is difficult to dissolve in common organic solvents (Salameh, 2009). For these reasons, cellulose needs to be chemically modified to give it adequate structural durability and efficient adsorption capacity for heavy metal ions (O’Connell et. al, 2008).

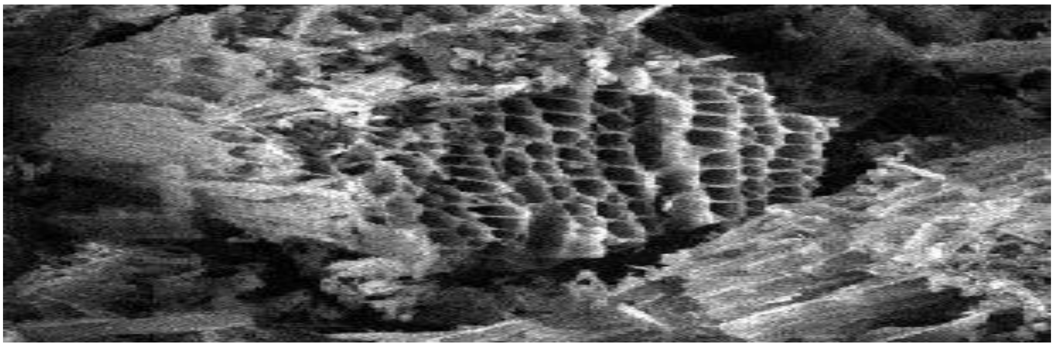


Figure 2 : Activated carbon, as viewed by an electron microscope (Cox, 2006)

Surface engineering is one of the techniques to help engineer cellulose surface to durable properties. As the sub-discipline of materials science, it deals with the surface of matter. It has applications to chemistry, mechanical engineering, and electrical engineering (Thakur et al., 2011). The surface which is confined to the bulk material is called the surface phase. It represents as an interface to the surrounding environment. The interaction between the surface phase of a matter with the surrounding environment can degrade the surface phase over time. This is due to corrosion, wear, fatigue and creep. Surface engineering involves modifying the properties of the surface phase to reduce the degradation over time and enhance other specific physicochemical properties of the material. This is achieved by introducing new functional groups to the surface phase. The diverse nature of the field of surface engineering includes plating technologies, nanotechnology biotechnology, characterization and testing. In biotechnology, cell surface engineering can lead to more effective catalyst, biosensor or increasing efficiency of of biomedicine (Thakur et al., 2011).

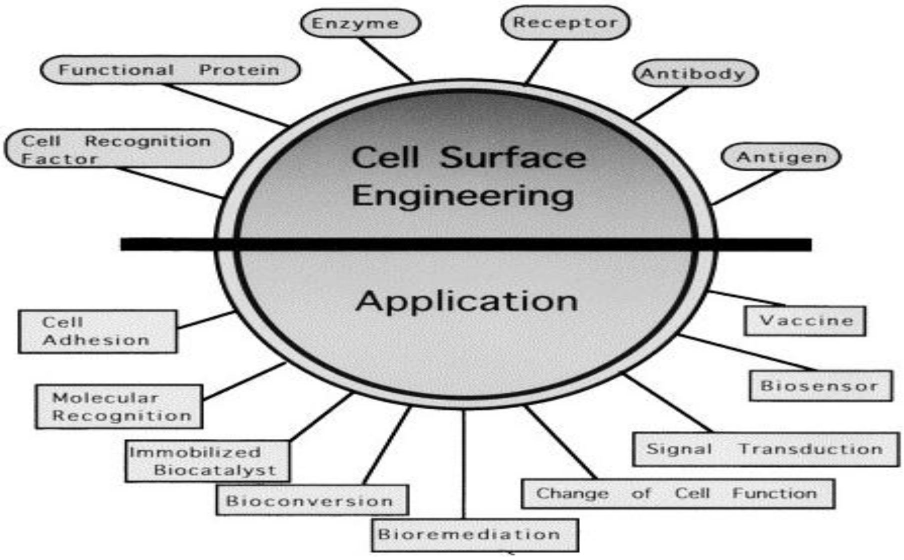


Figure 3 : Application of Surface Engineering (Ueda et al., 2000)

INTRODUCTION

1.2 Problem Statement

1.2.1 Problem Identification

The current methods to remove heavy metal ions and pesticide such as chemical precipitation, chemical oxidation/reduction, reverse osmosis, electrodialysis, and ultrafiltration from aqueous solutions have disadvantages such as low efficiency, high cost, and generation of toxic wastes (Zhou et. al, 2012). Biosorbents from renewable sources have characteristics such as economical, biodegradable, and potential for industrial applications. Cellulose as one of the most abundant renewable polymers can be explored through surface engineering to develop biosorbent with durable properties to capture heavy metals or pesticides.

1.2.2 Significance of the project

This project could promote cost-effective environmental remediation in Malaysia and brings improvement to waste water engineering through the development of more efficient and effective type of adsorbent. The project can also help to develop reuse and recycling of wastes especially those generated from palm oil industry. This can lead to biomass conversion into value-added products.

1.3 Objectives and Scope of study

The objectives of this study were:

a) To apply surface chemistry for the modification of cellulose for heavy metals and 2,4-Dichlorophenoxyacetic acid removal
b) To study the feasibility of the modified cellulose for heavy metals and 2,4-Dichlorophenoxyacetic acid removal from aqueous solution

The scopes of this study were:

- To develop adsorbent material from the modification of cellulose

- To perform surface characterization study on the modified cellulose
- To study the effects of concentration, contact time and pH for the adsorption process

1.4 Relevancy of the project

This project will apply the knowledge of chemical engineering especially separation technique which is adsorption, and organic chemistry which is very much relevant in the context of multi-disciplinary approach to problem-solving.

1.5 Feasibility of the project

The feasibility of this project is to complete the project within the allocated time frame, while maintaining the consistency of this project.

During the first semester (FYP I), the scope and task covered are:

a) Research on the different methods of modification of cellulose

b) Differentiate ion of each method

In the second semester (FYP II), the scope and task covered are:

a) Performing the experiments to verify the theory.

b) Analyzing the findings from the experiment.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical Structure of Cellulose

Cellulose is a linear homopolymer of β-(1→4)-D-glucopyranose units in $^4C_1$ conformation. The monomer of cellulose is anhydroglucose and its dimer is cellobiose. The basis of the cellulose structure is the chair-conformed anhydroglucose unit (D-glucopyranose) whose number determines the degree of polymerization (Kontturi, 2005).

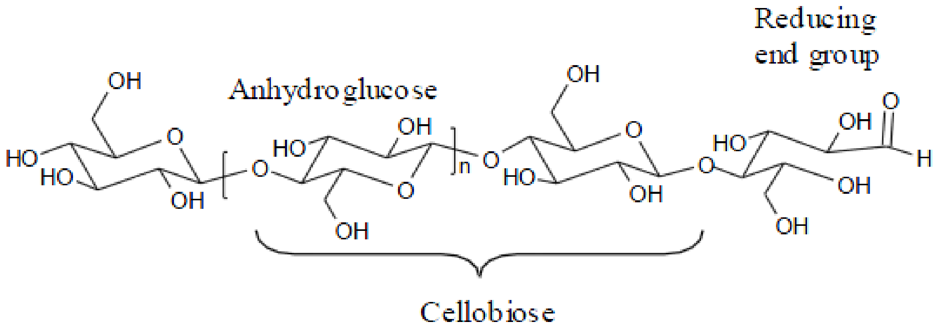


Figure 4 : Molecular Structure of Cellulose (Kontturi, 2005)

Each of the anhydroglucose units in cellulose takes the shape of 6-membered rings, called pyranoses or glucopyranoses. The monomers are connected to each other by a single oxygen atom (acetal linkages) between the C_1 of one ring and the C_4 of the next ring. A molecule of water is given off during the chemical reaction forming the acetal linkage and hence the term anhydroglucose units (AGU). The spatial arrangement of these acetal linkages is crucial (Magali, 2006). When the hydroxyl group at C_3 is on the same face of the ring as the C_6 carbon, it is said to be in the β configuration where all functional groups are in equatorial positions. This causes an extended conformation cellulose molecular chain (a semi rigid conformation), making it a good fibre-forming polymer.

2.2 Surface Engineering of Cellulose

The reactive sites on cellulose, which may be derivative, are the three-hydroxyl groups as shown in Figure 5 indicated as C-2, C-3 and C-6 (Gardner, 2008). C-6 is the primary hydroxyl, which is the most reactive position for esterification reactions while C-2 is the more acidic of the two secondary hydroxyl groups and is the more reactive site for etherification. Because of these reactions, a lot of cellulose derivatives, such as methylcellulose (-CH3 groups substitute –OH groups), can be obtained (Magali, 2006).

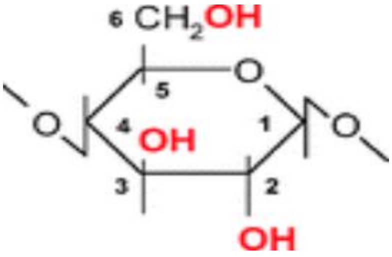


Figure 5 : Location of the hydroxyl groups (Gardner, 2008)

Although celluloses have great potential, the difficulty of dispersing the highly polar celluloses in non-aqueous mediums or in polymers is one of the main challenges to overcome (Jonoobi et al., 2010). The uniform dispersion of nano-sizes in materials and liquids as well as in polymers is difficult due to their high energy surface, and to be able to improve the dispersion, the surface characteristics of cellulose must be changed from hydrophilic to more hydrophobic. The hydrophilicity can be reduced by different chemical modifications.

Chemical modification of natural or synthetic polymers is an elaborate experimental task that results in improvements of the original surface properties of the materials for uses in technological applications (Gurgel et al., 2009). This includes modified cellulose for the removal of heavy metal in waste water treatment. Chemical modification of cellulose can be carried out to achieve adequate structural durability and efficient adsorption capacity of heavy metal ions, and to vary properties such as its hydrophilicity or hydrophobicity, elasticity, water sorbency, resistance to microbial attack and thermal resistance.

2.3 Cellulose Modifications

The β-D-glucopyranose units which make up the cellulose chain contain one primary hydroxyl group and two secondary hydroxyl groups. Functional groups may be attached to these hydroxyl groups through a variety of chemistries. Esterification, etherification, halogenations and oxidation are the four main routes of direct cellulose modification in the preparation of adsorbent materials (O'Connell et. al, 2008).

2.3.1 Esterification

Esters are produced when carboxylic acids are heated with alcohols in the presence of an acid catalyst. The esterification reaction of the primary and secondary hydroxyl groups of cellulose is basically similar to that of other alcohols, the only difference being in the macromolecular structure of cellulose.

Possible esterification reagents are acids, acid chlorides and acid anhydrides for the three hydroxyl groups in each glucose unit.

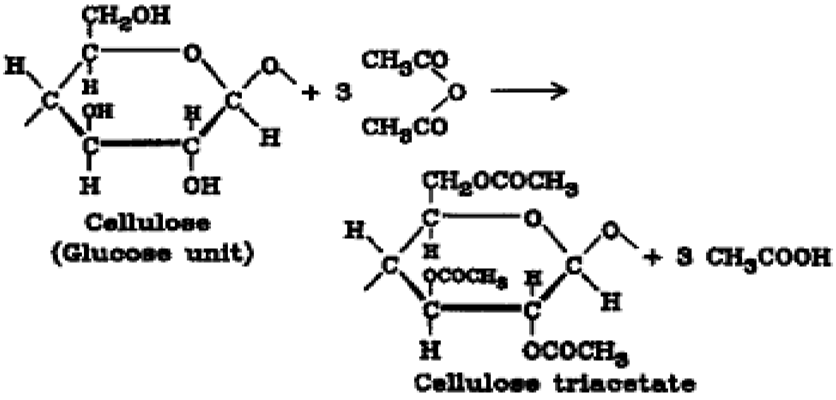


Figure 6 : Esterification process to produce cellulose acetate (Weetall, 1995)

The most common cellulose ester in the world at the moment is cellulose acetate, using acetic acid anhydride as the reactant. Theoretically, 3 mol of anhydride per unit of glucose are used and 3 mol of acetic acid are formed as shown in Figure 6. Cellulose acetate can be used for textile yarn and cigarette filter tow. The degree of esterification primarily determines the solubility and compatibility with softeners, resin, varnish, etc. and ultimately influences the mechanical properties.

Low et al. (2004) utilize heat to convert citric acid to citric acid anhydride, which is further reacted with the cellulosic hydroxyl groups in wood pulp to form an ester linkage. The Cu(II) and Pb(II) adsorption capacities for the modified wood pulp are 24 mg g $^{-1}$ and 83 mg g $^{-1}$, respectively. Chemically modified wood pulp using succinic anhydride through a similar esterification process, in the presence of a number of catalysts, leading to the introduction of carboxyl groups has been reported (Marchetti et al., 2000). The cadmium(II) binding capacity of the modified sawdust is directly related to the acid value estimated by titration and could reach uptakes of up to 169 mg g $^{-1}$.

2.3.2 Halogenation

Halogenation is a chemical reaction that integrates a halogen atom into a molecule. It is considered to be another type of cellulose modification. A number of methods are described for halogenating cellulose (O'Connell et. al, 2008).

The most general technique is to form an ester of a strong acid such as p-toluenesulfonic acid, methanesulfonic acid or nitric acid and later displaced the acid by halide ion. Pyridinium chloride in pyridine, and sodium iodide in acetone or in 2,5-hexadione (acetylacetone) give the chloride and iodide, respectively. Concentrated aqueous solutions of sodium halides halogenate methanesulfonic esters of cellulose if buffered, to neutralize the acid formed. Some halogenation occurs if the temperature is too high while making p-toluenesulfonyl esters from p-toluenesulfonyl chloride. In general, because displacement reactions are used to make the halide, halogenation occurs mainly at primary hydroxyls (Weetall, 1995).

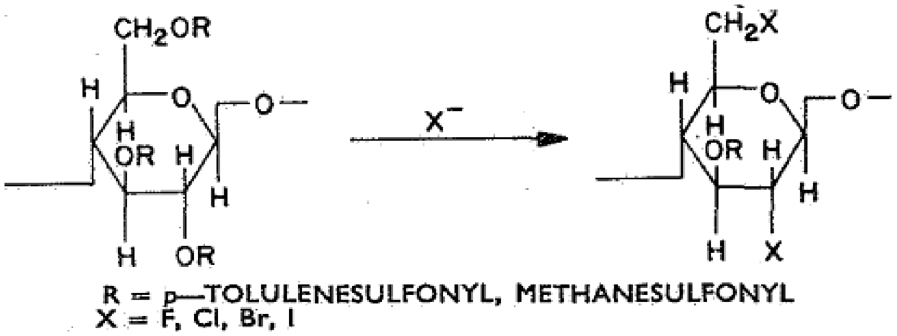


Figure 7 : Displacement of the acid by halide ion (Weetall, 1995)

For cellulose modified by halogenation to adsorb heavy metal**,** Aoki et al., (1999) synthesize 6-deoxy-6-mercaptocellulose and its s-substituted derivatives from 6-bromo-6-deoxylcellulose. The reactivity of cellulose and bromine as compared to cellulose and chlorine is higher. Carboxyl, amino, isothiouronium, mercapto and additional hydroxyl groups are introduced to cellulose and their adsorption behavior for metal ions is examined .The derivatives containing carboxyl groups due to the reaction with 2-mercaptobutanedioic acid show an adsorption capacity for Cu(II), Ni(II) and Pb(II) of 36 mg g^{-1}, 93 mg g^{-1} and 105 mg g^{-1}, respectively. The derivatives with amino and carboxyl groups due to the reaction with cysteine show adsorption capacity for Cu(II), Ni(II) and Pb(II) of 22 mg g^{-1}, 8 mg g^{-1} and 28 mg g^{-1} respectively (O'Connell et. al, 2008).

2.3.3 Etherification

Ethers are a type of organic compounds that contain an ether group — an oxygen atom connected to two alkyl or aryl groups. The general formula of ether is R–O–R'.

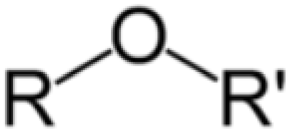


Figure 8 : Chemical Structure of ether

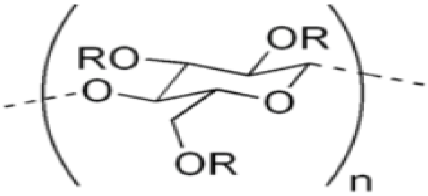


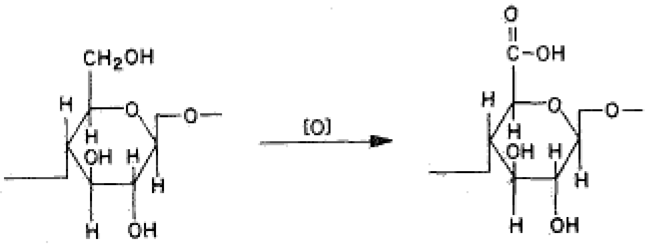
Figure 9: General Structure of Hydroxyethl cellulose (HEC)

Carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and ethyl hydroxyethyl cellulose (EHEC) are some examples of cellulose ethers. Cellulose can be etherified to block unwanted hydroxyl groups, to couple on a reactive group that may be used as an intermediate for coupling other groups, or for coupling desired molecules directly to cellulose. Ethers are among the most stable derivatives of cellulose and may be counted upon to remain intact under most conditions that will degrade or depolymerize the cellulose itself (Weetall, 1995).

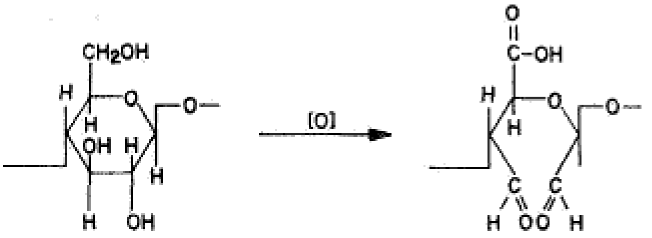
Most cellulose ethers are prepared by reacting alkali cellulose with organic halides. Navarro et al. (1996) modify porous cellulose carriers by initially reacting the cellulose, which is subsequently reacted with the organic halide, epichlorohydrin, yielding reactive epoxy groups for further functionalisation with polyethyleneimine as a chelating agent. The prepared adsorbent shows metal uptake affinities for Co(II), Cu(II) and Zn(II), respectively, of 2.5 mg g^{-1}, 38 mg g^{-1} and 12 mg $g^{-1.}$ Chemically modified sawdust with amidoxime groups has been developed by reacting acrylonitrile with the sawdust through an etherification reaction in order to add cyano groups to the cellulose structure (Saliba et al., 2005). These cyano groups are then amidoximated by reaction with hydroxylamine The amidoximated sawdust shows high adsorption capacity for Cu(II) of 246 mg $g^{-1}$and for Ni(II) of 188 mg g^{-1} (O’Connell et. al, 2008).

2.3.4 Oxidation

Cellulose can be oxidized to products with acidic properties. At the same time, aldehydic (reducing) groups are formed to a greater or lesser extent. Periodate, which oxidizes vicinal hydroxyl groups (glycols) to aldehydes or acids, and nitrogen dioxide which oxidizes mainly 6-hydroxy groups to form glucuronic acids, are both reported to attack the amorphous and crystalline regions of cellulose without causing so much degradation, that the material loses its fibrous form. With the commoner types of oxidants, the reaction is virtually confined to the amorphous regions and the surfaces of the crystallites, and the material falls to a powder at comparatively low degrees of oxidation (Weetall, 1995).



OXIDATION TO GLUCURONIC ACID



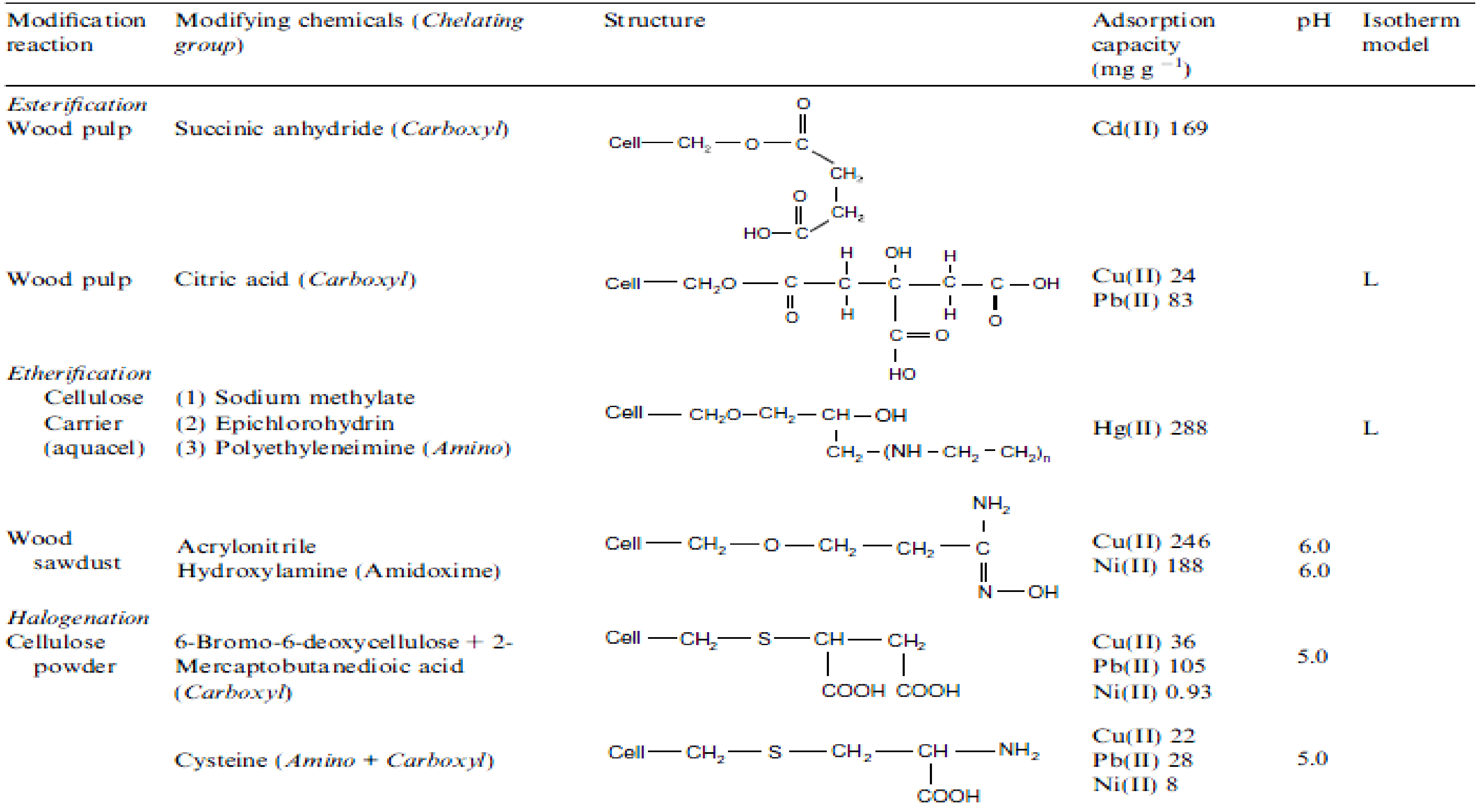
OXIDATION TO ACIDIC AND ALDEHYDIC GROUPS

Figure 10: Some of the cellulose derivatives produced by oxidation (Weetall, 1995)

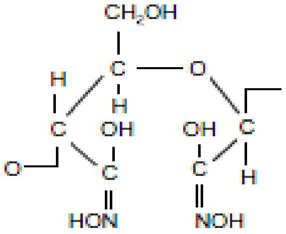
Maekawa and Koshijima (1984) prepare dialdehyde cellulose by periodate oxidation of cellulose. The aldehyde cellulose is further oxidised using mildly acidified sodium chlorite. The 2,3-dicarboxy cellulose oxidised to nearly 100% oxidation level, is completely soluble in water, but the 2,3-dicarboxy cellulose of 70% oxidation is largely insoluble. The latter is assessed for heavy metal adsorption capability and the uptake levels of 184 mg g^{-1} and 236 mg g^{-1}were achieved for Ni(II) and Cu(II), respectively. Subsequently, Maekawa and Koshijima (1990), synthesise cellulose-hydroxamic acid derivatives from dialdehyde cellulose obtained by the previous periodate oxidation method and the heavy metal adsorption capacity for Cu(II) from aqueous solutions has been reported at 246 mg g^{-1} (O’Connell et al., 2008).

Table 2 shows the summary of cellulose modification for heavy metal removals.

Table 2 : Cellulose modification method with various chemical reagents and associated functional groups (O'Connell et al., 2008)



Modification reaction	Modifying chemicals (*Chelating group*)	Structure	Adsorption capacity (mg g^{-1})	pH	Isotherm model
Esterification Wood pulp	Succinic anhydride (*Carboxyl*)	$\mathrm{Cell{-}CH_2{-}O{-}C({=}O){-}CH_2{-}CH_2{-}C({=}O){-}OH}$	Cd(II) 169		
Wood pulp	Citric acid (*Carboxyl*)	$\mathrm{Cell{-}CH_2O{-}C({=}O){-}CH_2{-}C(OH)(COOH){-}CH_2{-}C({=}O){-}OH}$	Cu(II) 24 Pb(II) 83		L
Etherification Cellulose Carrier (aquacel)	(1) Sodium methylate (2) Epichlorohydrin (3) Polyethyleneimine (*Amino*)	$\mathrm{Cell{-}CH_2O{-}CH_2{-}CH(OH){-}CH_2{-}(NH{-}CH_2{-}CH_2)_n}$	Hg(II) 288		L
Wood sawdust	Acrylonitrile Hydroxylamine (Amidoxime)	$\mathrm{Cell{-}CH_2{-}O{-}CH_2{-}CH_2{-}C(NH_2){=}N{-}OH}$	Cu(II) 246 Ni(II) 188	6.0 6.0	
Halogenation Cellulose powder	6-Bromo-6-deoxycellulose + 2-Mercaptobutanedioic acid (*Carboxyl*)	$\mathrm{Cell{-}CH_2{-}S{-}CH(COOH){-}CH_2(COOH)}$	Cu(II) 36 Pb(II) 105 Ni(II) 0.93	5.0	
	Cysteine (*Amino + Carboxyl*)	$\mathrm{Cell{-}CH_2{-}S{-}CH_2{-}CH(COOH){-}NH_2}$	Cu(II) 22 Pb(II) 28 Ni(II) 8	5.0	

Modification reaction	Modifying chemicals (*Chelating group*)	Structure	Adsorption capacity (mg g^{-1})	pH	Isotherm model
Oxidation					
*Cellulose powder	Sodium metaperiodate (*Carboxyl*)		Ni(II) 184 Cu(II) 236		
*Cellulose powder	Sodium metaperiodate Hydroxamic acid (*Amino*)		Cu(II) 246		

The structure of cellulose can therefore be modified by esterification, halogenation, etherification and oxidation to produce modified cellulose as an adsorbent to remove heavy metals. However for pesticide, there have been no report on its removal by modified cellulose, though activated carbon (AC) generated by lignocellulosic fibres has been reportedly used as shown in Table 2. Thus, this project is significant in investigating the feasibility of cellulose removal of heavy metals and pesticide from aqueous solution.

Table 2 : Comparison of 2,4-D adsorption capacities of various activated carbons (Salman et al., 2011)

Activated carbon type	**Adsorption capacity (mg g^{-1})**
Modified coal-based granular activated carbon F400	11.76-16.25
Date stone-based activated carbon	238.10
Banana stalk-based activated carbon	196.33

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

A correct methodology is very crucial in guaranteeing the successfulness of a project. For this project, the research methodology is shown in Figure 11 below.

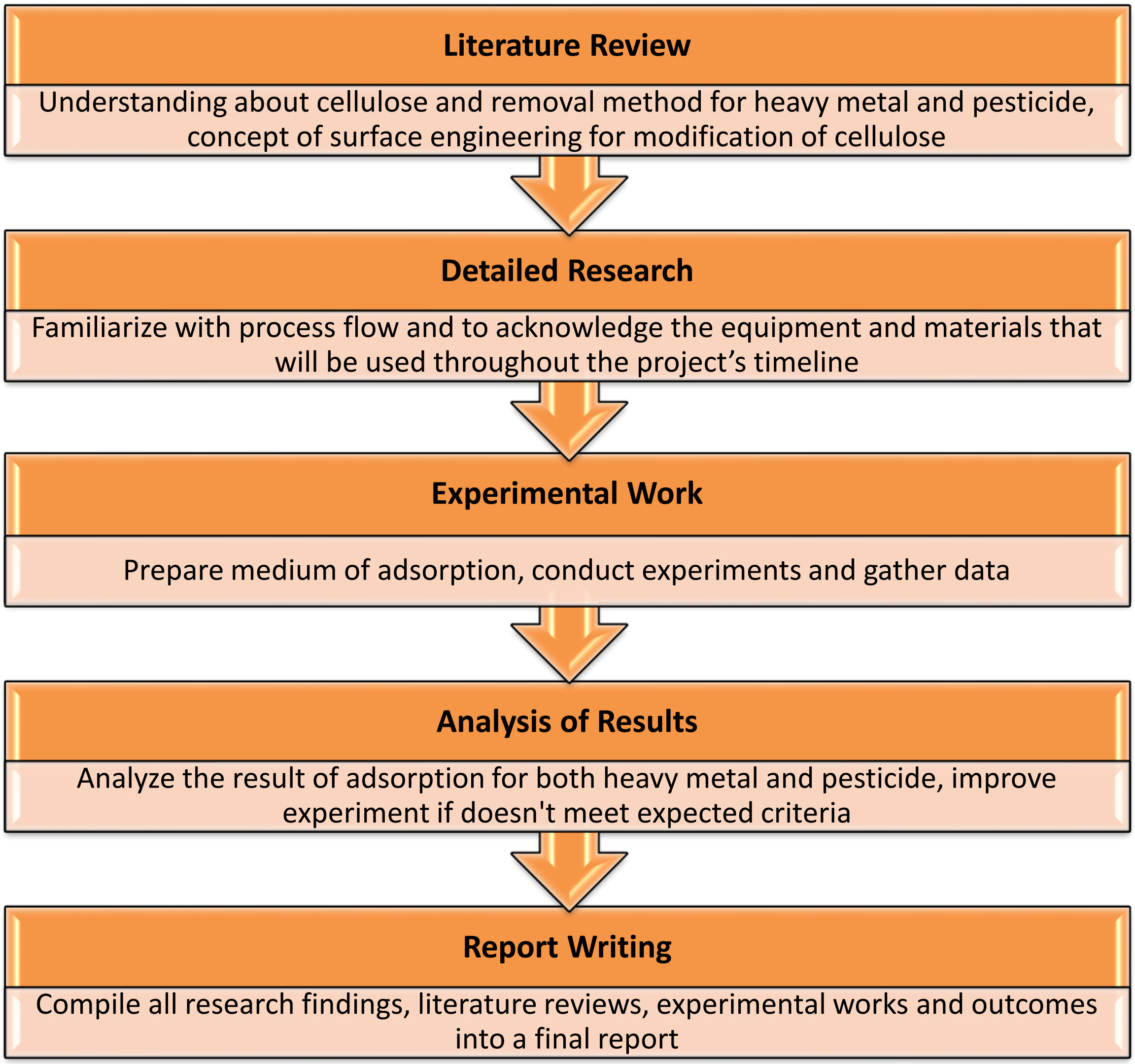


Figure 11: Project Methodology

3.2 Project Activities

The summary of the project activities/experimental work that will be conducted to achieve the objective of the project stated earlier is shown in Figure 12 below.

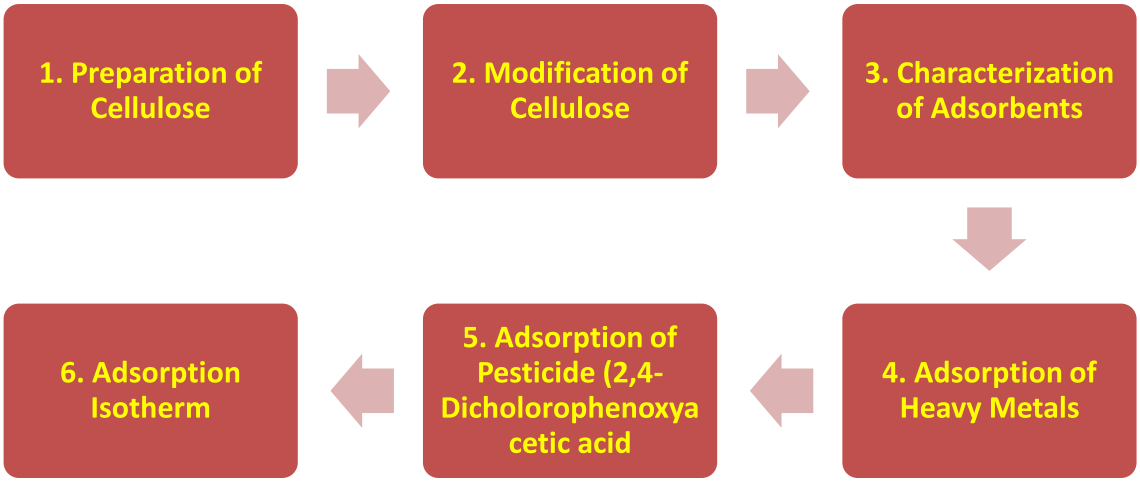


Figure 12 : Summary of project activities

3.2.1 Cellulose Preparation

Before modification process can be conducted on cellulose, cellulose first need to be mercerized, this means removal of impurities in cellulose. Mercerization can be done by treating in NaOH solution. The OH groups of NaOH will remove all the impurities that might interact with metal ions during adsorption process. Standard method of mercerization is used in this process, which is ASTM D1695. Cellulose (100g) was treated with 1L of 0.1 M NaOH solution at room temperature for 4 hours with constant magnetic stirring (350 rpm). The solution was filtered using filter paper and the filtered cellulose was dried in fume chamber and weighed.

3.2.2 Modification of cellulose

In this project, carboxylic group was chosen as modifying group. Two reagents containing carboxylic group have been selected:

i. Oxalic Acid (2 COOH groups)
ii. Ethylenediaminetetraacetic acid, EDTA (4 COOH groups)

Oxalic acid (10wt%) and EDTA (10wt%) solution at 0.1M were prepared in 250mL conical flask. Twenty grams of dried mercerized cellulose was placed in 250 mL round bottom flask and 200mL of 0.1M oxalic acid was added. The ratio of the mercerized cellulose treated with the reagent was 1:10 (Mercerized cellulose: Oxalic acid = 1:10). The flask was plugged to soxhlet apparatus, set at 105^{o}C and refluxed for 6h. The solution was filtered and the filtered cellulose was dried in oven at 105^{o}C for 1 hour. The modified cellulose was obtained and stored in a desiccator until use. The same procedure was applied for EDTA solution.

3.2.3 Characterization of cellulose before and after modification

The IR spectrum of the samples prepared by mixing 1 mg of each material with 100 mg of spectroscopy grade KBr was recorded from 4,000 to 400 cm^{-1} using a Perkin Elmer FTIR Spectrometer. Surface morphlogy of samples was studied by using a Zeiss Supra 55 VP Field-Emission Scanning Electron Microscope (FESEM). Thermogravimetric analysis (TGA) was recorded using a Mettler-Toledo TGA instrument in the temperature range from 25 to 700^{o}C at a rate of 10^{o}C min^{-1} under nitrogen flow. The samples are also tested with particle size analyzer (Sciroco 2000).

3.2.4 Preparation of metal ions stock solutions

Metal ions stock solutions containing Cu(II), Zn(II) and Pb(II) ions were prepared from $CuSO_4$, $ZnCl_2$ and $PbSO_4$. 1000 ppm stock solutions of each of the salts were prepared. Other cencentrations (10ppm-100ppm) were obtained from this stock solution by serial dilution. The concentration of metal ions was analyzed by Atomic Absorption Spectrometer (Z-5000, Hitachi).

3.2.5 Batch adsorption of heavy metal

Batch adsorption studies were carried out by shaking 0.5 g of treated cellulose with 50mL of the aqueous solutions of Cu(II), Zn(II) and Pb(II) ions in different Erlenmeyer flask using an orbital shaker. The solution–adsorbents mixtures were stirred at 140rpm and at the end of pre-determined time interval the reaction mixtures were filtered out and analyzed for its metal ion concentrations using Polarized Zeeman Atomic Absorption Spectrometer (Z-5000, Hitachi). The adsorption experiments were also conducted to determine the equilibrium contact time (10–150 min.), initial metal concentrations (10–100 ppm) and initial pH of metal solution (4–8) for maximum adsorption. The initial pH values of the solutions were adjusted with diluted CH_3COOH (0.01 M) or NaOH (0.01 M) using a pH meter. The amount of metal ions adsorbed at adsorption equilibrium, q_e (mg/g), was calculated according to Eq 1, where C_0 and Ce are the initial and equilibrium metal ion concentrations (mg/L) obtained from atomic absorption spectrophotometer, respectively. V is the volume of metalion solution (L), and W is the weight of bioadsorbent (g).

Equation 1: Adsorption Capacity at Adsorption Equilibrium

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

3.2.6 Batch adsorption of 2,4-dichlorophenoxyacetic acid

Stock solutions of 1000 ppm of 2,4-D was prepared by dissolving appropriate amounts in distilled water. Solutions of different initial concentrations of the pesticide were prepared by serial dilution of the stock solutions. Batch adsorption studies were performed by shaking 50 mL of known initial concentrations of pesticide with 0.5 g of adsorbent in 100 mL Erlenmeyer flasks ar 140 rpm. The adsorption were carried out using three three different adsorbent; untreated cellulose, oxalic acid treated cellulose and EDTA treated cellulose. The adsorption experiments were also conducted to determine the equilibrium contact time (6–12 h.) and initial 2,4-D concentrations (10–60 ppm) for maximum adsorption. The concentrations of 2,4-D in the solutions before and after adsorption were determined using a double beam UV–VIS spectrophotometer (UV-3150, Shimadzu) at its maximum wavelength of 284 nm. The amount of 2,4-D adsorbed at adsorption equilibrium, q_e (mg/g), was calculated according to Eq 1.

3.3 Project Gantt's Chart

Table 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	🟨	🟨																										
Literature Review and detailed research			🟨	🟨	🟨	🟨																						
Preparation of cellulose							🟨	🟨																				
Modification of cellulose structure									🟨	🟨	🟨	🟨																
Characterization of untreated and treated cellulose													🟨	🟨	🟨													
Adsorption of heavy metal																🟨	🟨	🟨	🟨									
Adsorption of pesticide																				🟨	🟨	🟨						
Adsorption Isotherm																							🟨	🟨				
Result analysis and report writing																									🟨	🟨	🟨	

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 cellulose modification process and removal of heavy metal and pesticide						🟪																						
Modify cellulose structure												🟪																
Characterization of materials															🟪													
Adsorption of heavy metal																			🟪									
Result analysis																									🟪			
Complete report writing																											🟪	

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Cellulose Before and After Treatment

4.1.1 FESEM

Field Emission Scanning Electron Micrographs presented in Figure 13 (a), (b), and (c), show the surfaces of cellulose before and after being treated with oxalic acid and EDTA respectively. Compared to the cellulose before treatment, the surface of modified cellulose is more irregular and rough. This could be because of the swelling effect after grafted with carboxyl group. Due to heterogeneous grafted surface, the specific surface area of the treated cellulose could have increased indicating a higher possibility for adsorption process.

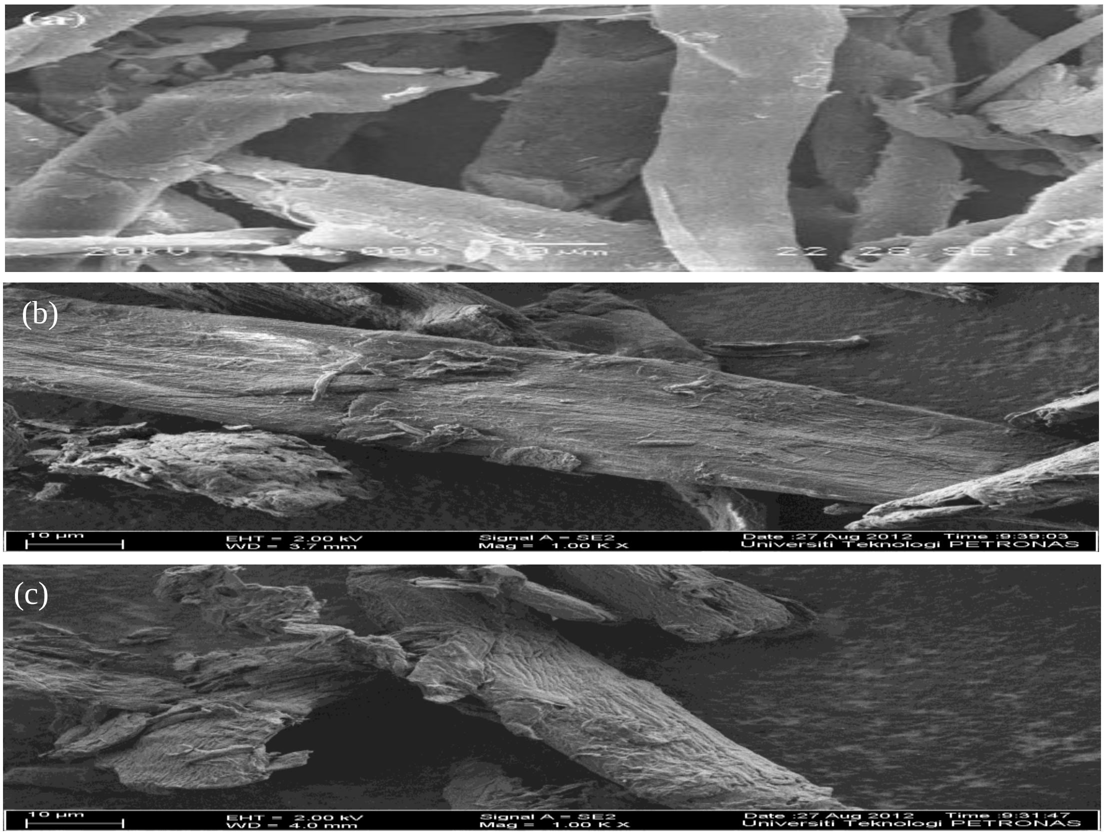


Figure 13 : FESEM micrograph (1000x magnification) of a) Pure cellulose - before treatment, b) after treatment with Oxalic acid c) after treatment with EDTA

4.1.2 FTIR

Figures 14(a), (b), and (c) show the FTIR spectrum of cellulose before and after being treated with oxalic acid and EDTA, respectively. The transmittance peaks at 3277, 3273 and 3278 cm^{-1} are due to hydroxyl groups (-OH) stretch. Peaks at 2889, 2890 and 2893 cm^{-1} are related to the C-H vibration of -CH_2 groups. The significant change is observed in the spectra at 1732 cm^{-1} and 1736 cm^{-1}. The appearance of these peaks signify the presence of carboxyl groups (-COOH). This could indicate the modification process was successful. High absorption peaks at 1051 and 1054 cm^{-1} indicate the presence of β-glucosidic linkage in the cellulose (Zhou et al., 2012).

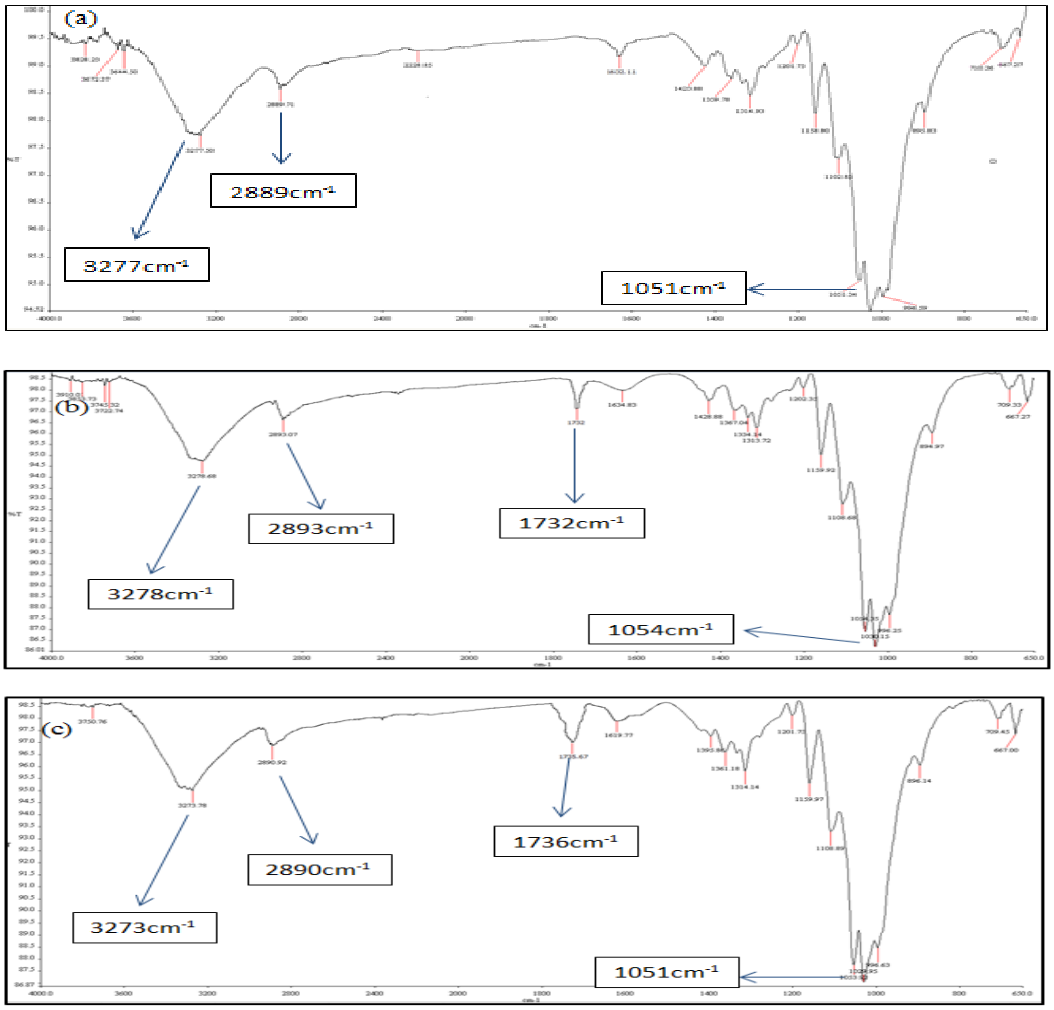


Figure 14 : FTIR spectra of a) Pure cellulose - before treatment, b) after treatment with Oxalic acid c) after treatment with EDTA

4.1.3 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.

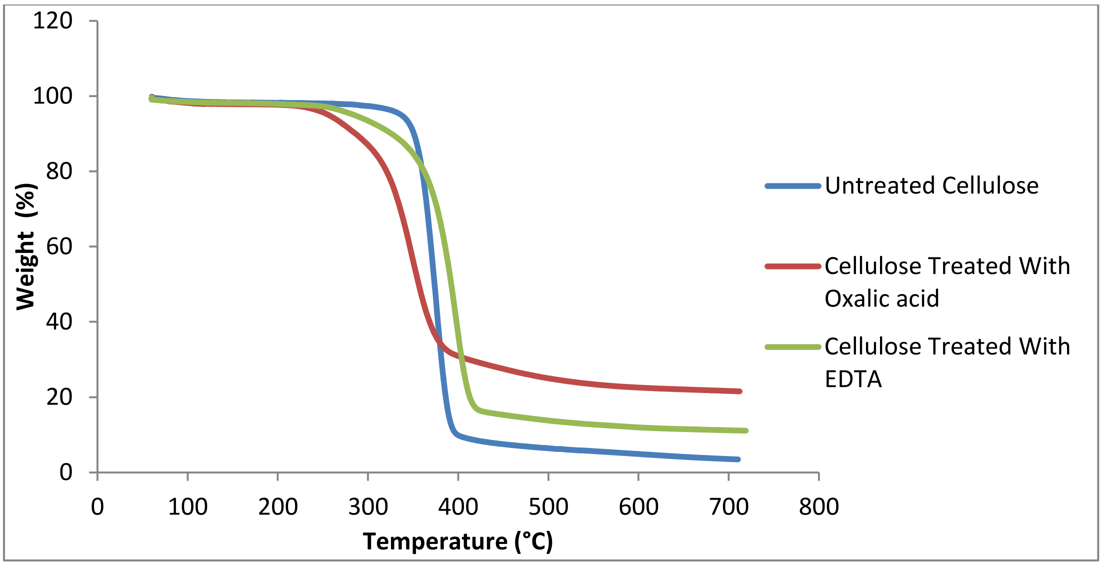


Figure 15 : TGA Curve for Cellulose Before and After Treatment

TGA curves for cellulose before and after treatment are shown in Figure 16. The main differences in thermal behaviour of the three samples are the temperature of initial weight loss and the rate of the weight loss. The first mass loss for cellulose after treatment below 200°C in the TGA curve is due to a significant amount of water released. The second weight loss, which starts at about 270°C, is reflected in a slow weight decrease represented by a shoulder; this is the initial stage of thermal degradation (Zhou et al., 2012). As shown in Figure 16, the weight loss of untreated cellulose is more than 90% at 390°C, more than 80% for cellulose treated with EDTA, and more than 70% for cellulose treated with oxalic acid. The rate of weight loses for cellulose before modification is higher compared to cellulose after treated with oxalic acid and EDTA. These differences signify that cellulose after modification becomes much more thermally stable.

4.1.4 Particle Size Analyzer

The analysis of cellulose particle is carried out to justify modification of –OH group with –COOH groups. Figure 16(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.

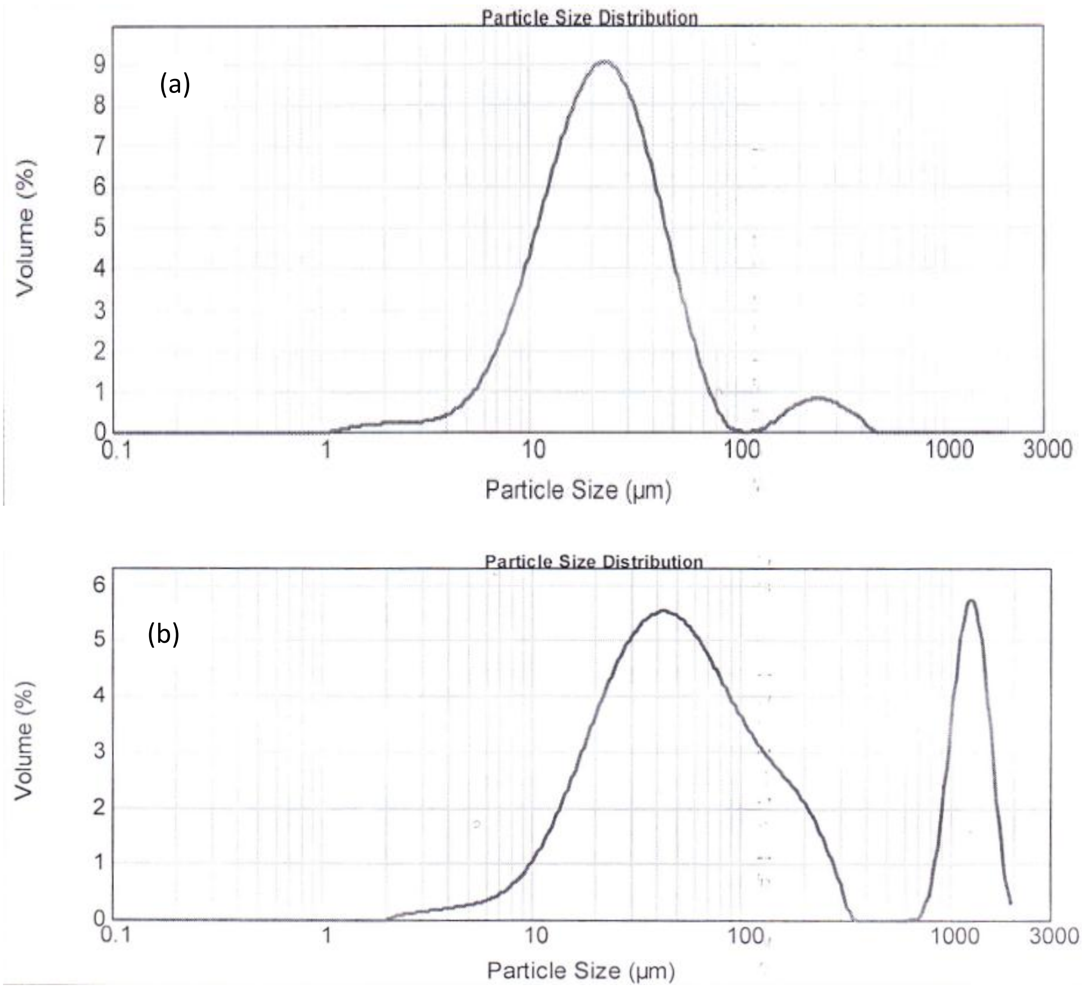


Figure 16 : Particle Analyzer (a)Pure Cellulose (b)Oxalic acid treated cellulose

In Figure 16(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.

4.2 Adsorption Experiment on Three Different Heavy Metals

4.2.1 Effect of contact time

Figure 17(a) and (b) show the effect of contact time on three different heavy metals adsorption. In this experiment, the initial metal concentration was maintained at 10 ppm for all three metals. It is clearly shown that the amount of lead (II) ions adsorbed is much higher than the other two metals. This is due to difference in atomic weight of the metal ions and the mode of interaction between the metal ions and the adsorbent. The relative atomic mass of lead metal is 207.2 u, for zinc metal is 65.409 u and for copper is 63.546 u (Low, 2004). The level of the metal ions uptake followed the order of the decreasing relative atomic mass of the three metals Pb > Zn > Cu.

For both celluloses treated with EDTA and oxalic acid, all the three metals exhibit a similar scenario where after a certain amount of time the adsorption capacity of the modified cellulose achieve its peak and remain constant onwards after equilibrium is achieved. This is because during the initial stage, a large number of vacant surface sites are available for adsorption and after certain time the remaining vacant surface sites are fully occupied by the solute molecules. The adsorption of copper (II) ions reached equilibrium at 90 minutes while for zinc (II) ions and lead (ions), the equilibrium contact time are at 120 minutes. This is probably due to mode of interaction and chemical affinity of each metal towards the adsorbent. At these equilibrium contact time, the adsorption capacity of the adsorbent is at its highest. The subsequent adsorption studies are maintained at these optimum contact times for the three heavy metals.

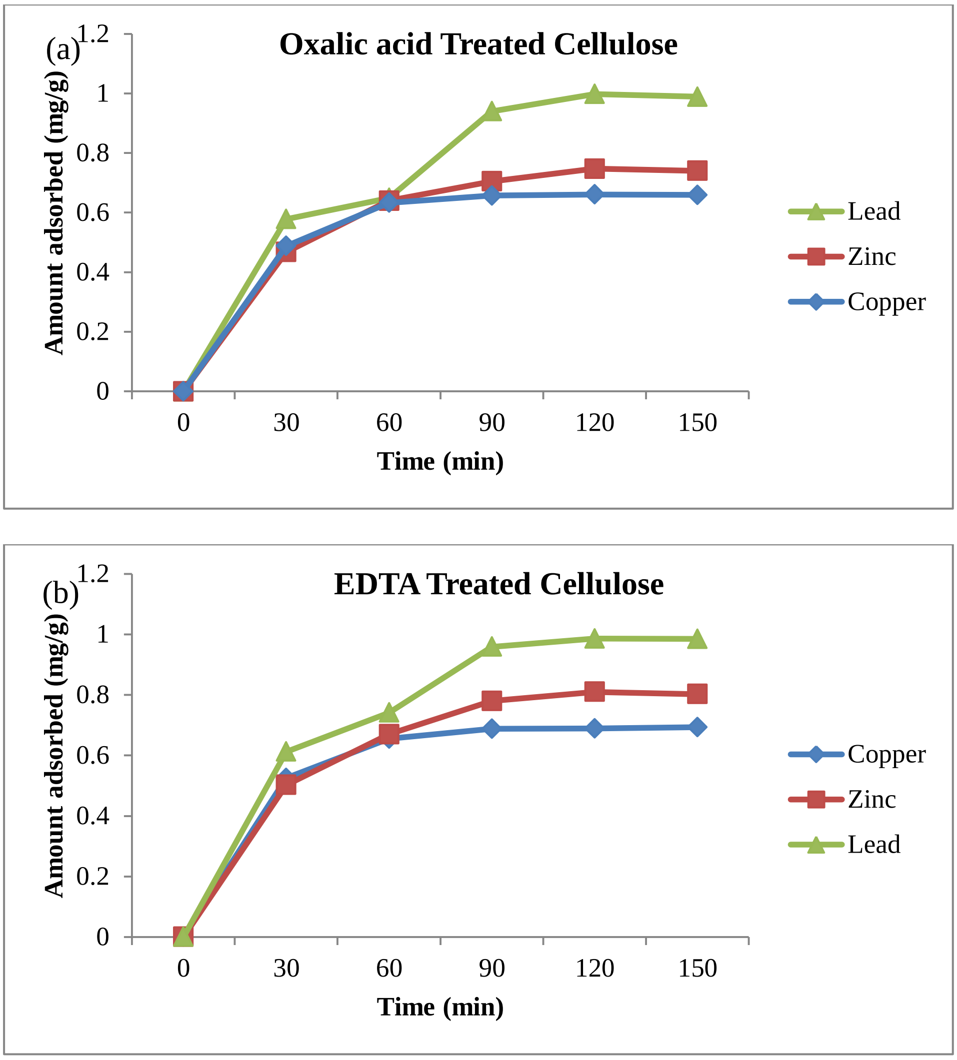


Figure 17: Effect of contact time on heavy metal adsorption with a) cellulose treated with Oxalic acid b) cellulose treated with EDTA

4.2.2 Effect of initial metal concentration

By varying the initial metal concentration, the rate of adsorption is affected. From Figure 18(a) and (b), the amount of lead (II) ions adsorbed are comparably higher that zinc (II) and copper (II) ions. From 10 ppm to 100 ppm, the amount of three metals adsorbed per unit mass of adsorbent increased with the increase in initial metal concentration.

It can be observed that with a higher initial metal concentration the rate of adsorption will increase because initial metal concentration provides a significant driving force of mass transfer. The affinity of the metal ions towards the active sites will increased at higher initial metal concentration (Egila et al., 2011).

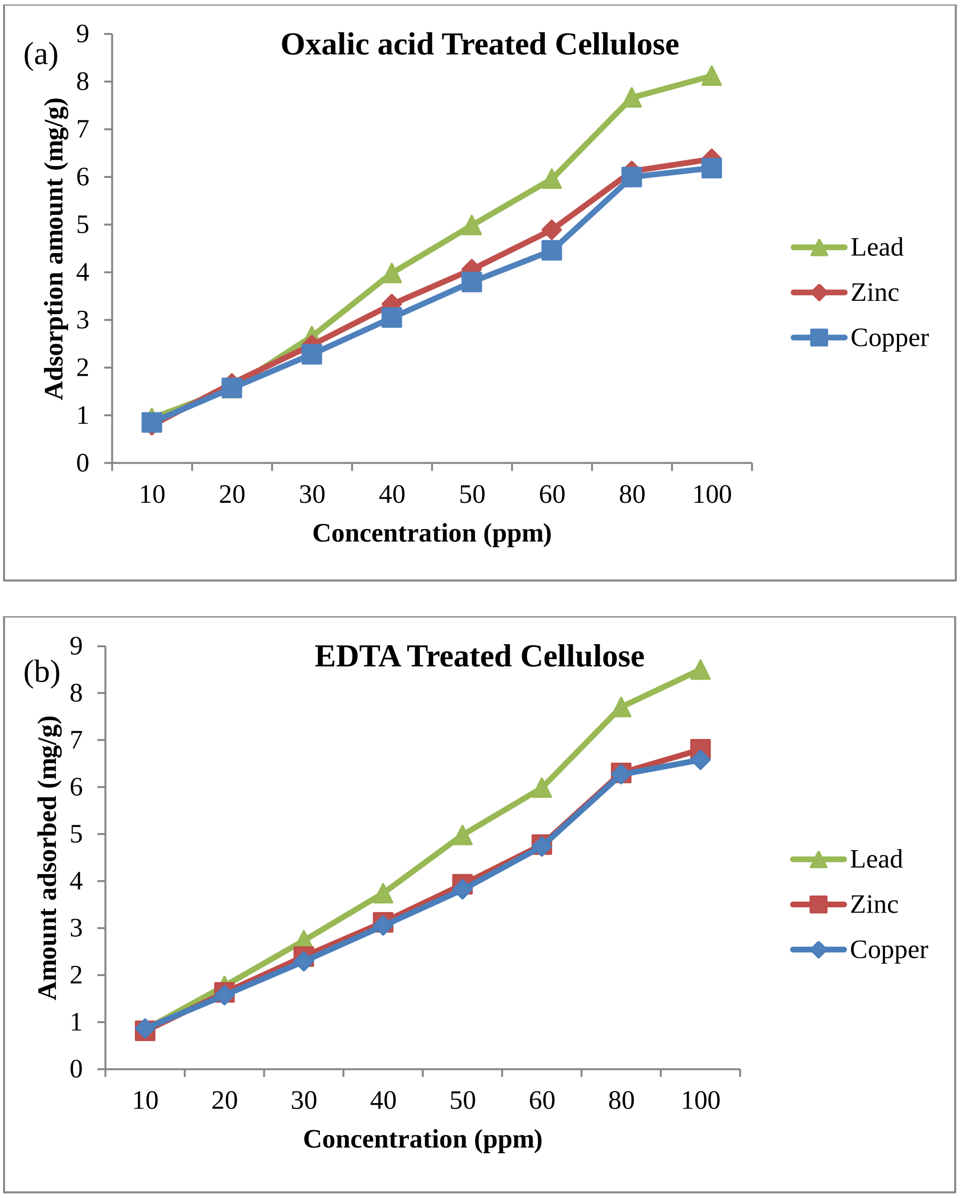


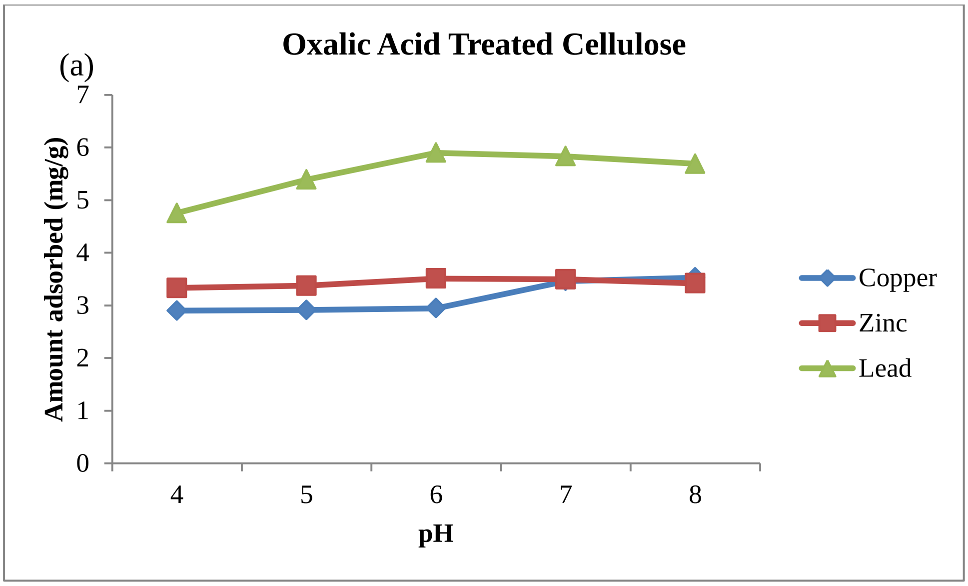
Figure 18: Effect of initial metal concentration on heavy metal adsorption with a) cellulose treated with Oxalic acid b) cellulose treated with EDTA

4.2.3 Effect of pH

Regulating pH can affect the surface charge of the adsorbent, speciation of the adsorbate and the degree of ionization. A series of experiment was conducted at different pH values to obtain optimum pH adsorption of Cu (II), Zinc (II) and Pb(II) ions and the results are presented in Figure 19 (a) and (b).

The adsorption capacities for all three metals are low at pH 4.0. This is because at lower pH the concentration of H^+ is high, which competes with metal ions for surface active sites. As the pH is increased, the adsorption capacity is increasing as well. However, at a certain pH value, the metal uptake starts to equilibrate. This pattern is similar to all three metals ions. At higher pH value, the concentration of H^+ is reduced and the carboxyl group become deprotonated (COO^-) and easily attract the positively charged metal ions. 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.

The equilibrium adsorption capacity of copper is at pH 7.0 using EDTA treated cellulose EDTA and pH 8.0 with oxalic acid treated cellulose. For zinc and lead, the optimal pH value is determined at pH 6.0 for both EDTA and Oxalic acid treated cellulose.



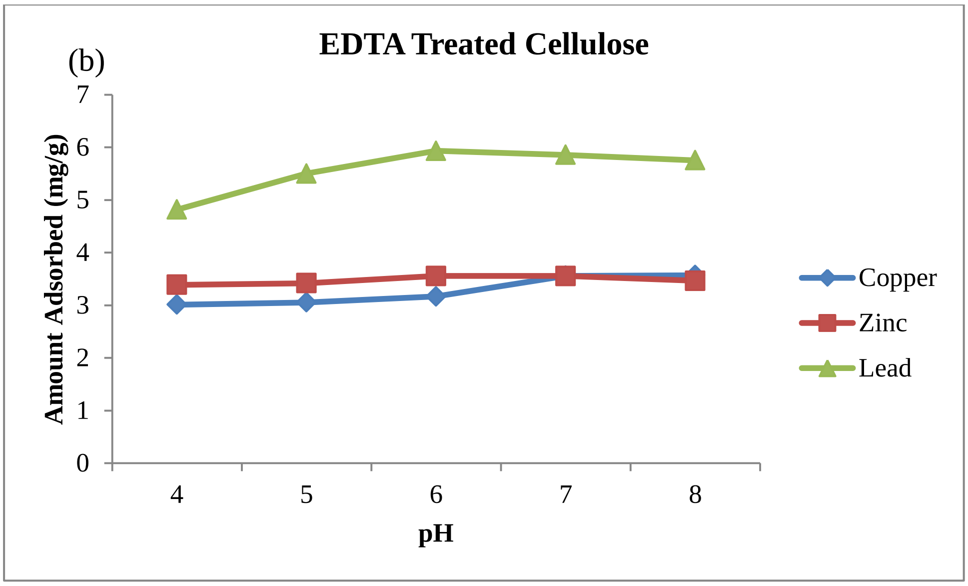


Figure 19: Effect of pH on on heavy metal adsorption with a) cellulose treated with Oxalic acid b) cellulose treated with EDTA

4.2.4 Adsorption Isotherm

4.2.4.1 Langmuir Model

This model assumes that a monolayer is formed when the solid surface reaches saturation and adsorptions occur at specific homogenous sites on the adsorbent (Salman et al, 2011). The Langmuir adsorption isotherm is often expressed as:

Equation 2 : Langmuir isotherm model (Salman et al., 2011)

$$q_e = \left(\frac{bK_L Ce}{1 + K_L Ce}\right)$$

Where:

C_e = Concentration of material remaining in solution when equilibrium(mg/L)

q_e = amount material adsorbed per specified amount of adsorbent (mg/g)

K_L= Langmuir equilibrium constant (L/mg)

b = amount of adsorbate required to form a monolayer (mg/g)

The linearized version of Langmuir Model is as follow:

Equation 3 : Linearized form of Langmuir Model

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

Hence, a plot of $1/q_e$ versus $1/C_e$ should be a straight line with a slope ($1/bK_L$) and an intercept as ($1/b$) as shown in Figure 20. Figure 20 (a) and (b) show the Langmuir isotherm plot for the three heavy metals for both adsorbent, oxalic acid treated cellulose and EDTA treated cellulose, respectively. The values of correlation coefficient (R^2) and other constants are summarized in Table 3.

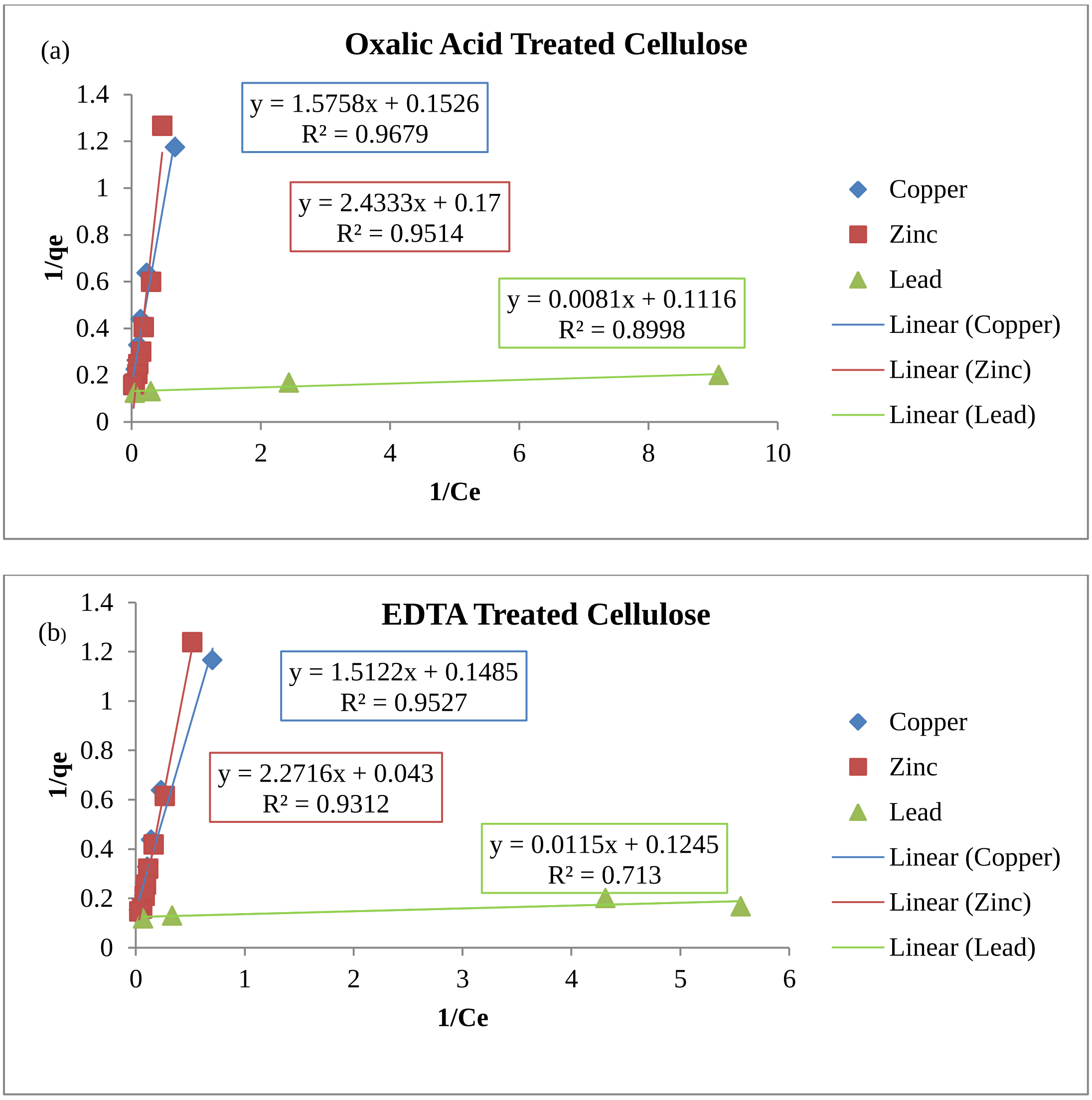


Figure 20: Langmuir isotherm plots for all the three heavy metals for both (a) oxalic acid and (b) EDTA treated cellulose

4.2.4.2 Freundlich model

The Freundlich model is based on non-ideal adsorption on heterogenous surfaces and multilayer adsorption (Salamatinia et al., 2007). The Freundlich isotherm is expressed as:

Equation 4: Frendlich Isotherm Model (Salman et al., 2011)

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

Where:

C_e = Concentration of material remaining in solution when equilibrium (mg/L)

q_e = amount material adsorbed per specified amount of adsorbent (mg/g)

K_F=Freundlich equilibrium constant (L/g)

n = empirical constant

The linearized version of Freundlich Model is as follow:

Equation 5 : Linearized form of Freundlich Model

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

Therefore, 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 21 (a) and (b).

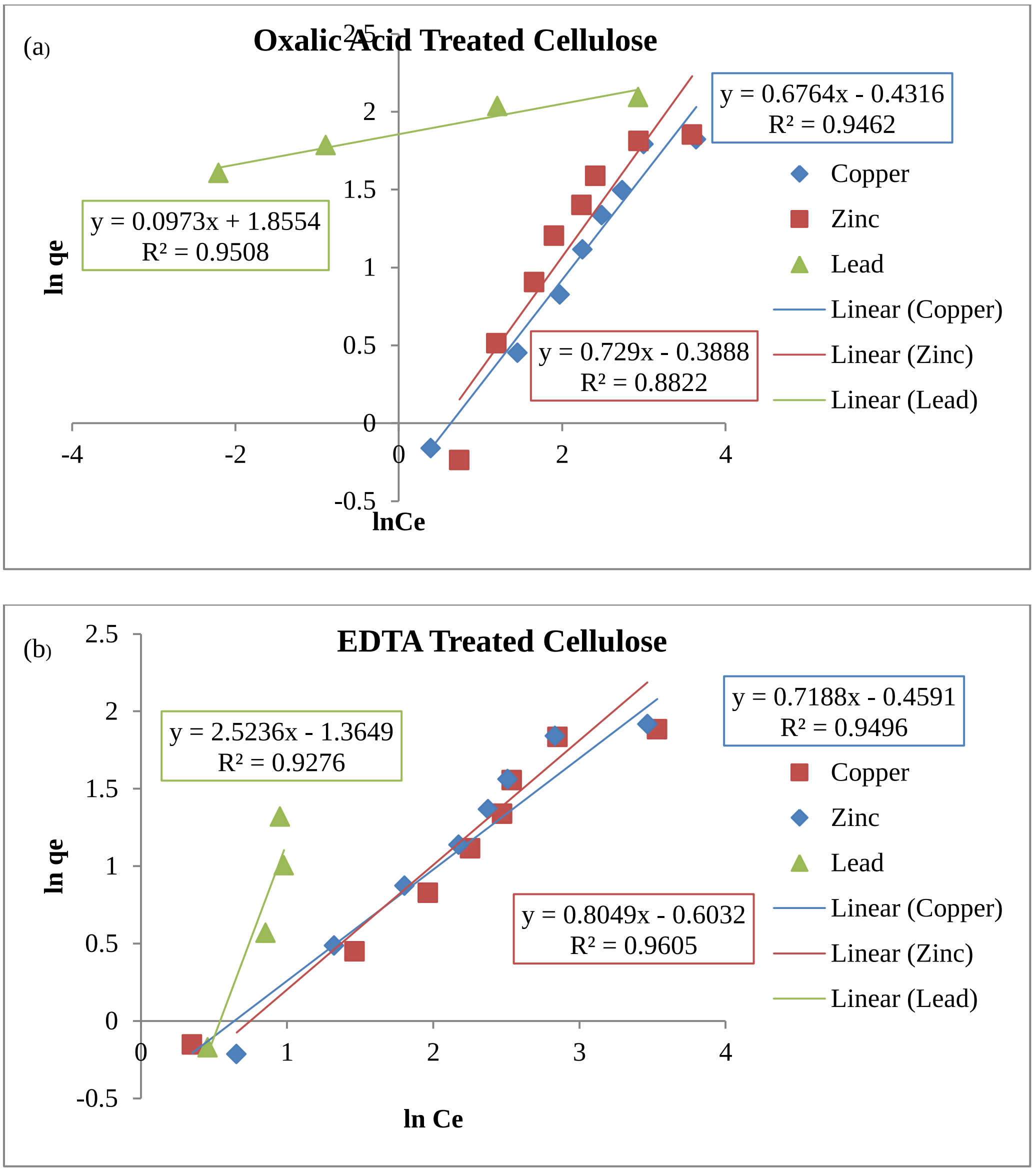


Figure 21 : Freundlich isotherm plots for all the three heavy metals for both (a) oxalic acid and (b) EDTA treated cellulose

Table 4: R^2 and isotherm constants of different adsorbent for Langmuir and Freundlich isotherms for three heavy metals

Adsorbent	**Heavy Metal**	**Isotherm Models**	**R^2**	**Langmuir Constants**		**Freundlich Constants**	
				b	**K_L**	**K_F**	***n***
Oxalic acid Treated Cellulose	Cu(II)	Langmuir	0.9679	6.553	0.0967	-	-
		Freundlich	0.9462	-	-	0.649	1.484
	Zn(II)	Langmuir	0.9514	5.882	0.0699	-	-
		Freundlich	0.8822	-	-	0.678	1.372
	Pb(II)	Langmuir	0.8998	8.961	13.777	-	-
		Freundlich	0.9508	-	-	6.394	10.27
EDTA Treated Cellulose	Cu(II)	Langmuir	0.9527	6.734	0.0982	-	-
		Freundlich	0.9605	-	-	0.547	1.242
	Zn(II)	Langmuir	0.9312	23.26	0.0158	-	-
		Freundlich	0.9496	-	-	0.632	2.178
	Pb(II)	Langmuir	0.713	8.032	8.3001	-	-
		Freundlich	0.9276	-	-	0.255	0.396

From Table 4, for oxalic acid treated cellulose, it is shown that Langmuir isotherm showed better fit to the adsorption process for copper and zinc metal indicated by a higher R^2 values. This result showed the adsorption process occurs in a monolayer form. For lead metal, Freundlich isotherm fits better, thus, multilayer adsorption was achieved here. The difference of adsorption isotherm for lead compares to the other two metals can be explained in terms of chemical affinity and mode of interaction between the metal ions and the substrate.

For EDTA treated cellulose, the Freundlich adsorption isotherm model yielded best fit for all the three metals as indicated by the higher R^2 values compared to the Langmuir adsorption isotherm model. The good fit obtained with Freundlich model suggests that the adsorption of the three heavy metals onto EDTA treated cellulose may involve multi-layer adsorption with interactions between the heavy metals ions and the heterogeneous nature of EDTA treated cellulose.

4.3 Adsorption of 2,4-dichlorophenoxyacetic acid

4.3.1 Effect of Initial 2,4-D Concentration

In this experiment, the adsorption process was carried out with three different adsorbent; pure cellulose (untreated cellulose), oxalic acid treated cellulose and EDTA treated cellulose. The initial concentration of 2,4-D was varied between 10-60ppm and the contact time was maintained for 24 hours. The result is shown in Figure 20. The amount of 2,4-D adsorbed by pure cellulose is the highest among the three adsorbent. The highest adsorption capacity for pure cellulose is recorded at 60 ppm which is 3.9844 mg/g. The trend of the adsorption process with pure cellulose is that by increasing the initial pesticide concentration, the amount of 2,4-D adsorbed is also increased. This is due to initial adsorbate concentration provides a significant driving force of mass transfer.

For oxalic and EDTA treated cellulose, the amount of 2,4-D adsorbed with these two adsorbents are very low compared with pure cellulose. Varying the initial concentration of adsorbate does not increase the adsorption amount onto the treated cellulose. The highest adsorption capacity of 2,4-D for oxalic acid and EDTA treated cellulose is 1.1303 mg/g and 0.7861 mg/g, respectively. This can be explained by the existence of carboxyl group (-COOH) and also chlorine groups (–Cl) in 2,4-D which have more pronounced electron withdrawing properties. In pure cellulose, the existence of hydroxyl grops (-OH) can be replaced by the carboxyl groups (-COOH).

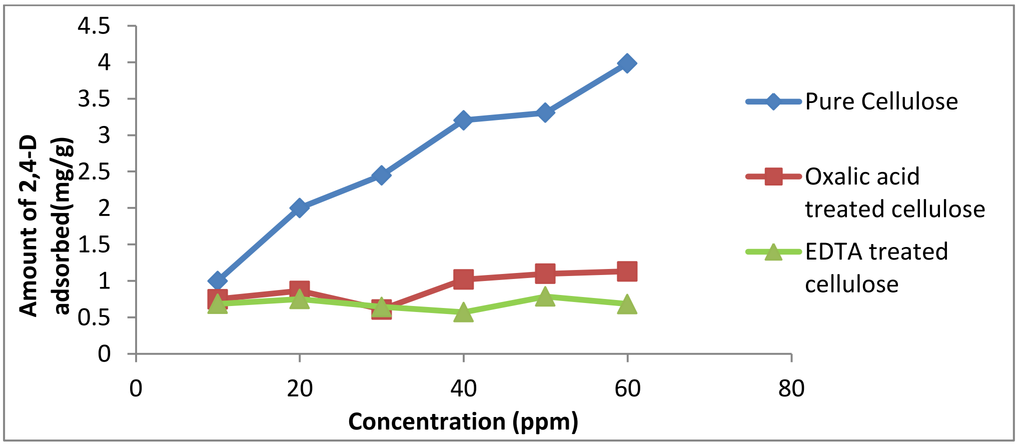


Figure 22 : Effect of varying the initial concentration of 2,4-D on the three type of adsorbent

4.3.2 Adsorption Isotherm

Just like heavy metal, the adsorption process on 2,4-D for the three adsorbents is characterized by using the adsorption isotherm of Langmuir and Freundlich model. The result of the adsorption isotherm plot is shown in Figure 23 (a) and (b). The R^2 and isotherm contants are summarized in Table 4.

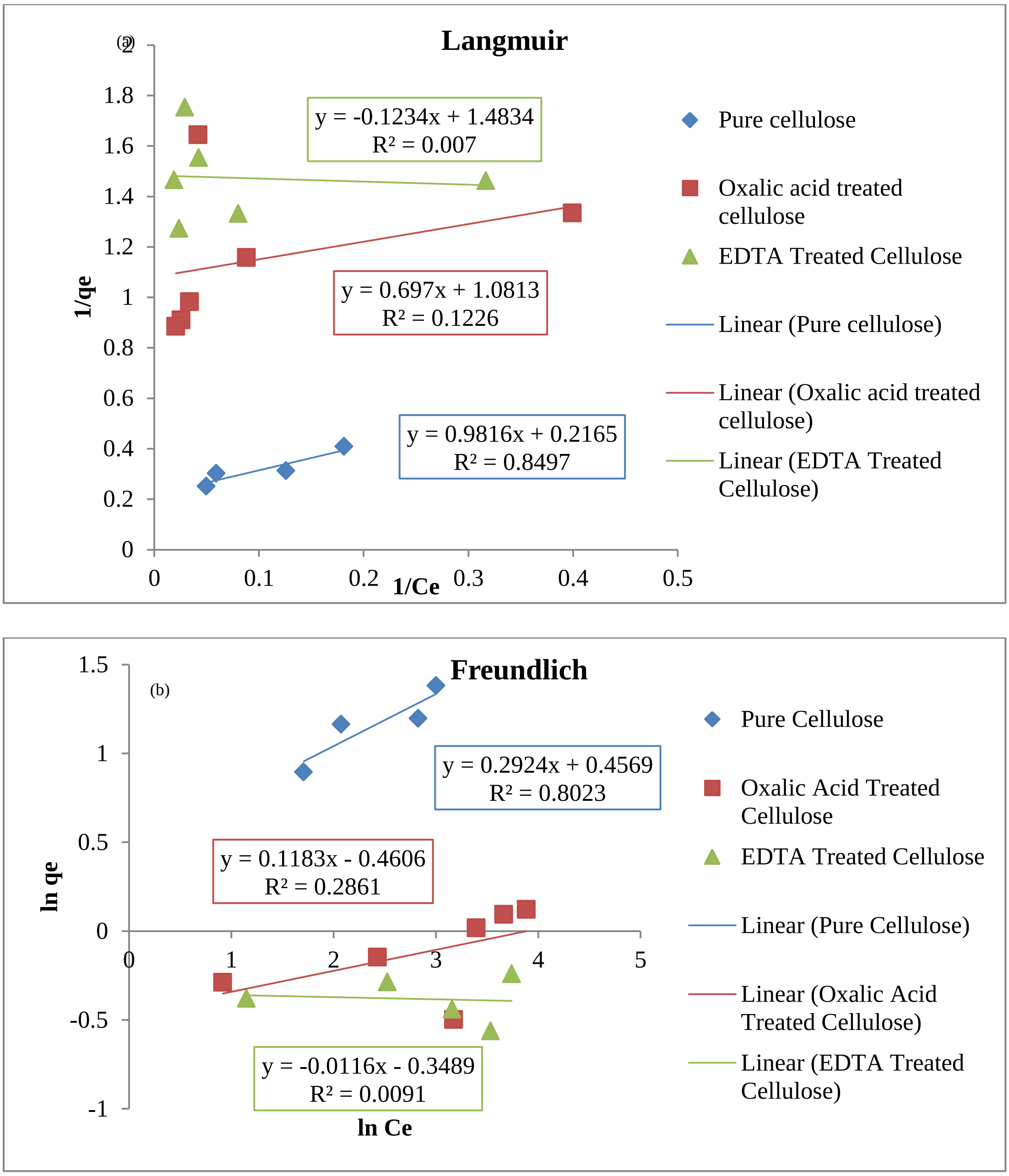


Figure 23 : (a) Langmuir and (b) Freundlich isotherm plots for the adsorption of 2,4-D with three type of adsorbent

Table 5 : R^2 and isotherm constants of different adsorbent for Langmuir and Freundlich isotherms for 2,4-D adsorption

Adsorbent	Isotherm Models	R^2	Langmuir Constants		Freundlich Constants	
			b	K_L	K_F	n
Pure Cellulose	Langmuir	0.8497	4.619	0.221	-	-
	Freundlich	0.8023	-	-	1.579	3.420
Oxalic acid Treated Cellulose	Langmuir	0.1226	0.924	1.553	-	-
	Freundlich	0.2861	-	-	1.126	-2.171
EDTA Treated Cellulose	Langmuir	0.0007	0.674	-12.02	-	-
	Freundlich	0.0091	-	-	0.9885	-2.866

Table 5 shows that values for both of the treated cellulose are very bad. This indicates that the adsorption process of 2,4-D cannot be represented by both Langmuir and Freundlich model as the R^2 values are very low. Thus, conforming that it is not suitable to use the treated cellulose to capture 2,4-D.

Fore pure cellulose, the Langmuir model yield the better fit compared to Freundlich model suggesting a monolayer adsorption of 2,4-D on a homogeneous surface of the pure cellulose. The highest adsorption capacity for pure cellulose which is represented by constant *b* is 4.619 mg/g which is comparable to the experimental data of 3.9844 mg/g. However, this value is actually still very low compared to the adsorption process by using activated carbon (AC) as the adsorbent to capture 2,4-D as reported earlier. Thus, it is proved that is it not feasible and economical to use cellulose as the adsorbent in order to remove 2,4-D from aqueous solution.

CHAPTER 5

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

In this project, two different chemicals are used in modifying the cellulose which is oxalic acid and EDTA. The concentration of carboxyl groups in these two chemicals is different from each other. After modification process, FESEM micrographs showed that the treated cellulose becomes more irregular indicate that adsorption process is likely to occur. Modification of hydroxyl group (–OH) with carboxyl group (–COOH) from oxalic acid and EDTA change the hydrophobic properties of cellulose to hydrophilic, enabling adsorption process in water and most solvent.

The process of adsorption of heavy metals 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 8.5 mg/g using 100 ppm initial concentration after 120 minutes of treatment. The optimal pH value for lead is 6. However, this amount of adsorption capacity is still low compared to previous study and research using similar type of adsorbent. Thus, improvisation needs to be done on the modification process of cellulose. It is suggested to use the anhydride of oxalic acid and EDTA to modify the structure of cellulose so that more carboxyl group will be attached to the surface of cellulose, thus increasing the adsorption capacity. Other parameter that may affect the adsorption process such as temperature is also highly recommended. It is also suggested that in future work that the treated cellulose to adsorb the three heavy metals at the same time.

For removal of 2,4-D, this study showed that it is not suitable to remove 2,4-D by treated cellulose. Activated carbon (AC) is still the best adsorbent to capture 2,4-D in aqueous solution as shown in Chapter 2.

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