Surface Engineering of Cellulose for Phenols and 2,4-Dichlorophenoxyacetic Acid (2,4-D) Removal

By

Low Wan Lin

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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Assoc. Prof. Dr. Mohd Azmuddin Abdullah

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

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.

LOW WAN LIN

ABSTRACT

The cellulose was extracted from abundantly available oil palm agrowaste in Malaysia. The cheap sorbents were prepared by modification of cellulose with carboxylic acids such as EDTA, fumaric and maleic acid. Modifications of cellulose are carried out using soxhlet apparatus. The carboxylic acids 0.1M of fumaric acid, maleic acid and EDTA each was substituted on the cellulose O-H group at carbon position C-2, C-3 and C-6. The metal, phenol and phenol derivative 2,4-dichlorophenoxy acetic acid are the main pollutant obtained from industrial and agricultural sources. This study was conducted for the purpose of determining the usage of cellulose in removing phenol and 2,4-D in water. Analysis on surface engineered cellulose onto phenol, 2,4-D and metal ions are carried out in this study. Metal loading onto the modified cellulose was studied using lead ion. Cellulose-malate gives the highest lead ion removal (98%) with adsorption capacity, q_e of 62.8 mg/g. For 2,4-D removal, cellulose-malate (Pb-loaded) showed the highest sorption of 2,4-D compared to other modified cellulose, with sorption percentage of 85.2% and q_e of 42.6 mg/g. On the other hand, cellulose-EDTA (Pb-loaded) gives the highest sorption percentage of phenol at 79.2% and adsorption capacity, q_e of 39.6 mg/g. The results show that modified cellulose has higher sorption capacity for divalent metal ions and phenol and 2,4-D. The adsorption of 2,4-D and phenol is found to be more effective in acidic condition (pH=5) compared to alkali condition (pH=10). The adsorption process follows Freundlich adsorption isotherm and pseudo second-order, which is based on chemical adsorption mechanism.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

2,4-Dicholorophenoxyacetic acid (2,4-D) is being commonly used as herbicide and plant growth regulator against broad-lead weeds in cereal crops, about 0.2-2.0 kg active ingredients (acid equivalent) are used per hectare. It constitutes 75.1% of total agrochemical used in Malaysia (Akma, Samsuri, Ainie, & Rosenani, 2009). The approval of 2,4-D usage have been debated constantly. The United States Environmental Protection Agency evaluated it for re-registration during 2005, but implemented changes in labeling of the chemical to mitigate risk. (Council, 2012)

A study revealed that herbicides are detected more frequently compared to other pesticides in water (such as insecticides and fungicides). This is because herbicides are directly applied to soil, while pesticides are being sprayed onto the plants. The herbicides can be leached into the ground immediately during rainy seasons.

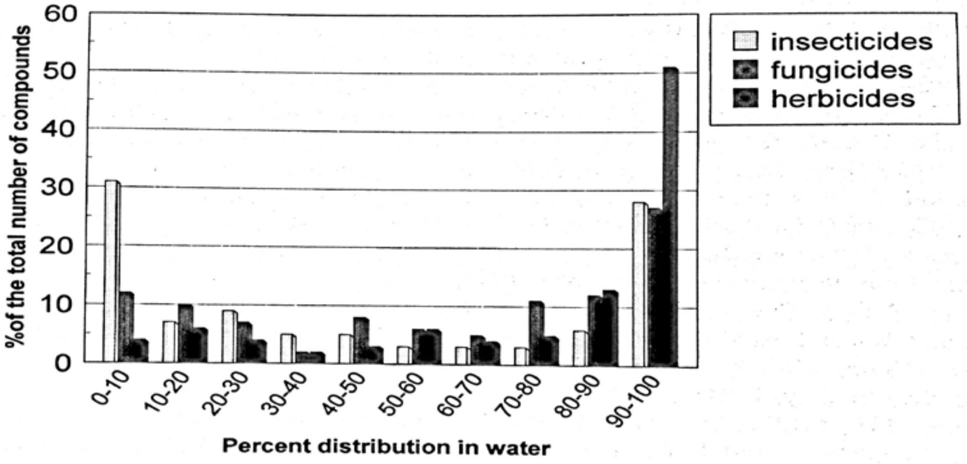


Figure 1.1.1: Percent distribution of herbicides, insecticides and fungicides in water. (Vighi & Funari, 1995)

Case reports and observational studies provide the majority of information regarding the toxicological effects of 2,4-D in incidents involving human poisonings. Researchers compiled the medical cases of 69 people who ingested 2,4-D and other cholorophenoxy herbicides; 23 of these patients died. Ingestion led to vomiting, abdominal pain, diarrhea, and development of hypotension. Peripheral neuromuscular effects including muscle twitching, weakness and loss of tendon reflexes have been reported. Neuromuscular effects have lasted several weeks to months and have been permanent in some cases (Gervais, Luukinen, Buhl, & Stone, 2008).

An investigation was carried out by researchers, and it was found that if there were more than 1000mg 2,4-D per kg of body weight detected in any mammals, it will start affecting its body central nervous system (Aydın, Özdemir, & Uzunören, 2005). Other than that, 2,4-D is specifically linked to non-Hodgkin's lymphoma and soft-tissue sarcoma in people (Gervais et al., 2008).

Phenol is widely used in the industry; the production rate of phenol exceeds 1.23 billion kgs worldwide. It is used in reagents in laboratories, iron and steel industries, medical products, phenolics resins and so on. However, it is among the list of priority organic pollutants proposed by the U.S. Environmental Protection Agency (Aravindhan, Rao, & Nair, 2009). Phenols are classified as endocrine disrupters, and associated with breast cancer. (Barlow & Johnson, 2007). A study was conducted and it was proved that low dose exposure to Bisphenol A (50ppb per day) can affect puberty in young females (Honma et al., 2002). The EU set a safety limit of 0.5 micrograms per litre of drinking water as phenol is potentially carcinogenic (Mahugo Santana, Sosa Ferrera, Esther Torres Padrón, & Juan Santana Rodríguez, 2009).

Researchers are constantly looking for cheaper alternatives for water treatment solutions. Biotreatments are highly sought after compared to the conventional methods because most biotreatment make use of waste materials to treat toxic substances. During 2009, it is reported that Oil Palm Empty Fruit Bunch (OPEFB) is generated 6.93 million tons on a dry basis in Malaysia (Foo, Foong, Yusof, & Kalyana, 2011). A extraction method was carried out and it was found that α-cellulose can be extracted from OPEFB with a yield of up to 64% of OPEFB (Nazir, Wahjoedi, Yussof, & Abdullah, 2013). Cellulose is an interesting research material as the vast availability of cellulose in plants or woods means that it is a low cost raw material. This study will determine whether surface engineered cellulose will be able to successfully bind with 2,4-D, phenols and heavy metal ions.

1.2 Problem statement

The hazardous effect of heavy metals, 2,4-D and phenol pose serious environmental threat. The sorbent used for heavy metals, phenol and its derivatives are costly and non-green. Raw Oil Palm Empty Fruit Brunch (OPEFB) is the potential source for cheap, biodegradable and renewable biosorbent, but it has its limitations to capture pollutants due to steric hindrance of exposed functional group. Adsorption is an economical and practical technique for pollutants removal over the existing ones. The extracted cellulose from OPEFB is selected as the potential candidate for removal of heavy metals, phenol and 2,4-D. The types of carboxylic acid modifiers such as fumaric, maleic and ethylene-diaminetetraacetic acid (EDTA) for cellulose which furthers optimize sorption are studied based on parameters such as pH, initial concentration and equilibrium contact time in batch study.

1.3 Objectives and scope of study

1.3.1 Objectives

i. To modify and characterize the OPEFB-cellulose.
ii. To study the removal of heavy metals, phenol and 2,4-D in batch system.
iii. To optimize adsorption parameters such as initial concentration, contact time and pH.

1.3.2 Scope of study

The scope of study is the synthesis of cheap, renewable and biodegradable sorbent for the removal of heavy metals, phenol and 2,4-D effectively. The surface engineered cellulose, using 0.1M EDTA, fumaric acid and maleic acid is investigated. Other than that, this study also covers the adsorption effects of lead ions, in the range of 200ppm to 500ppm per 0.2g of cellulose, by OPEFB-extracted cellulose and modified cellulose. Subsequently, the adsorption effects of phenol at 1000ppm and 2,4-D at 1000ppm respectively, by 0.1 gram of heavy metal-loaded cellulose. The optimum pH is analyzed at pH 5 and pH10. On the other hand, the equilibrium contact time studied is up to 240 minutes, using time interval of 30 minutes. The effects of pH, initial concentration and contact time are established to improve 2,4-D and phenol sorption. The adsorption isotherm and kinetic study of 2,4-D and phenol sorption are studied as well.

CHAPTER 2

LITERATURE REVIEW

2.1 Phenol and 2,4-D

Phenolics are organic compound that are characterized by a hydroxyl (-OH) group attached to a carbon atom that is part of an aromatic ring. From figure below, phenol has a molecular formula of C_6H_5OH, while the molecular formula of 2,4-D is $Cl_2C_6H_3OCH_2COOH$. Both compounds are soluble in water; hence it is dangerous as people would not know the presence of these compounds in the water.

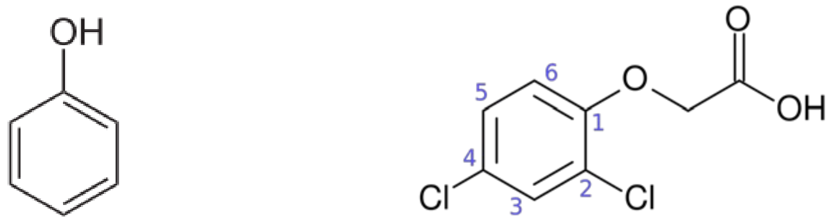


Figure 2.1.1: Molecular Structure of phenol (left) and 2,4-D (right).

In the market, phenol is available in white or clear acicular crystal form or aqueous form. At 41°C (105°F), phenol coagulates into a solid, it can be liquefied by mixing a very small amount of water (2 parts water: 23 parts phenol). On exposure to air and light, phenol assumes a pinkish or reddish discoloration. In the presence of impurities or alkalinity, the discoloration is accelerated. Phenol has a characteristic sweet, medicinal, or tar-like odor. (OSHA, 1996b)

NIOSH (NOES Survey 1981-1983) has statistically estimated that in the United States, 584,372 workers (120,977 of these are female) are potentially exposed to phenol. Phenol is used as a general disinfectant. It is used for the manufacture of colorless or light-colored artificial resins, and many industrial and medical organic compounds and dyes and as a reagent in chemical analysis. Aqueous phenol solutions have therapeutic characteristic, it is also used in the veterinary.

Occupational exposure to phenol may occur through inhalation and dermal contact with phenol at workplaces where phenol is produced or used. There are a number of possible ways to be exposed; via inhalation and dermal absorption of phenol-containing wastewater, emissions and disinfectants or solvents. Monitoring data indicate that the general population may be exposed to phenol via inhalation of ambient air, ingestion of food and drinking water, and dermal contact with consumer or medicinal products containing phenol. Dermal absorption of phenol may also occur from contact with decomposing organic matter than may contain phenol. (Budavari, 2001; NOES, 1983)

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for phenol is 5 parts per million (ppm) (19 milligrams per cubic metre) as an 8-hour time-weighted average (TWA) concentration. The National Institute for Occupational Safety and Health (NIOSH) has established a short-term exposure limit (STEL) of 15.6 ppm (60 milligrams per cubic metre) for periods not to exceed 15 minutes. (OSHA, 1996b)

2,4-D is an odorless, white to yellow crystalline powder. The solubility of 2,4-D is not as strong as phenol, but it is soluble in alcohol and in other organic solvents. Worker exposures to 2,4-D could be during manufacture, formulation, and transportation of 2,4-D, through inhalation of dust and dermal contact. The risk of exposure is higher for workers working in plantations or farms because it is an herbicide, fungicide, fruit drop control and also used to increase latex output of old rubber. It is possible that the general population could be exposed through ingestion of food and drinking water as well. The current OSHA PEL for 2,4-D is 10 milligrams per cubic meter (mg/m(3)) of air as an 8-hour TWA concentration. (OSHA, 1996a)

Phenolic compounds are resistant to decomposition due to their high stability in water. Several methods were introduced for removal of phenolic compounds from water. Some methods cause impact to the environment such as biological degradation and chemical oxidation. Some examples of methods that do not affect the environment are solvent extraction and adsorption.

2.2 Adsorption

Adsorption is one of the useful techniques in separation process utilized commercially. Dabrowski (1994) described the adsorption process into 2 regions, first involves the surface layer of the solid (adsorbent) and then the bulk fluid that flows across the adsorbent (adsorption space). Adsorption occurs when the molecules accumulate in the adsorption space.

Table 2.2.1: Worldwide sales of adsorbents(Yang, 2003)

Activated carbon	$1 billion
Zeolites	$100 million
Silica gel	$27 million
Activated alumina	$26 million

The table above shows the worldwide sales of four sorbents which are the top four adsorbents used commercially. Activated carbon has been used as an all-purpose sorbent, where it can adsorbs chemical agents in air or even phenols and certain compounds in the water. Unfortunately, regeneration of activated carbon could be expensive and time-consuming. Mattson, Mark Jr, Malbin, Weber Jr, and Crittenden (1969) indicated that phenol and its derivates adsorb on activated carbon via a “donor-acceptor complex” mechanism that involves carbonyl surface-oxygen groups acting as electron donor, and the aromatic ring of the solute acting as an acceptor (as cited in Aravindhan et al, 2009).

Table 2.2.2: Various methods used in removing phenol from aqueous solution.

Removal Method	Contact time	Optimum concentration of phenol adsorbed
Gas Membrane (Hasanoğlu, 2013)	150 mins	700 mg/L
Liquid Membrane (Hasanoğlu, 2013)	100 mins	800 mg/L
Electrocoagulation using aluminium cathode and anode (Abdelwahab, Amin, & El-Ashtoukhy, 2009)	120 mins	12 mg/L
Oxidation using nickel hydroxide catalyst at 60 ^{o}C (Saeed & Ilyas, 2013)	90 mins	400 mg/L
Tyrosinase with chitosan solution (Bevilaqua, Cammarota, Freire, & Sant'Anna Jr, 2002)	20 hours	350 mg/L
Marine seaweed (Navarro, Portales, Sun-Kou, & Llanos, 2008)	4 hours	35 mg/L
Olive wood/ethanol (El-Sheikh, Newman, Said, Alzawahreh, & Abu-Helal, 2013)	24 hours	25 mg/L
Activated sludge (Tay, Tay, Liu, Show, & Ivanov, 2006)	Up to 40 hours	1500 mg/L

The table above shows various methods used in phenolics removal. Chemical methods are effective and fast compared to most biotreatment methods. However, they are more costly than in terms of operating cost and maintenance cost. Methods such as reverse osmosis and ultrafiltration become in efficient when contaminants are present, even at a slight trace. It is not economically feasible because of their relative high cost. So the need to look into more effective and economical alternatives exists. Adsorption is a good option as it is highly effective, the design is also simple and low in cost.

Metals can be accumulated onto living or nonliving biomass. This mechanism was defined "bioaccumulation" by Means and Hinchee (1994), involving transfer of a metal from a contaminated matrix to biomass. Activated biomass uses mechanism such as ion exchange and complexation reactions. On the other hand, the primary mechanism taken by inactivated biomass is adsorption. The metals are adsorbed to the ionic groups either on the cell surface or in the polysaccharide coating found on most forms of bacteria. The metals are bound by exchange of functional groups or by sorption. The binding sites on the cell surface typically are carboxyl residues, phosphate residues, S-H groups and hydroxyl groups.

2.3 Polymeric resins

Polymeric resins are used in the water treatment industry as they can remove certain organics to lower concentration levels than activated carbon. Besides, they are used in other fields such as chromatographic analytical separation as well.

According to (Yang, 2003), these macroporous polymers are developed by emulsion polymerization of the monomers in the presence of a solvent which dissolves the monomers but which is a poor swelling agent for the monomer. One advantage for using polymeric resins in water treatment is the ability to regenerate. This will reduce maintenance cost. However, the cost price of resin is much higher compared to activated carbons, so resins are only being selected under long term circumstances.

2.4 Zeolite

Zeolites are highly porous aluminosilicates with different cavity structures. The price for zeolite is about RM0.09~0.36/kg, depending on the quality of the mineral. Zeolites have been investigated as an absorbent in removing phenol from aqueous solution. Zeolites can adsorb phenol selectively from water as zeolite has high Si/Al ratio and it is hydrophobic. The adsorption capacity is found to be slightly higher at low phenol concentration (<1.6 g/L) when compared to using activated carbon (Ahmaruzzaman, 2008).

2.5 Bioadsorbents

Bioadsorption makes use of biological material to concentrate and remove pollutants from aqueous solution. For the case of phenolic compounds removal, biological materials such as chitin, chitosan, fungi, or yeasts are used as chelating and complexing adsorbents. These bioadsorbents contain their own functional groups that can complex phenolic compounds.

One of the example is using sea-shells, where the clam or mussel shells are simply poured over the wastewater. These sea shells are made of aragonite, a form of calcium carbonate that can convert the metal ions in acid-laden water into solid form easily (Oilgae, 2008). One example of commercial biosorbent used in metal ions removal is BIO-FIX, as mentioned by Means and Hinchee (1994). It is developed by U.S. Bureau of Mines and licensees, it mainly consists of peat moss, *Spirulina* and supported by polysulfone polymer. The advantage of BIO-FIX is that it can tolerate low pH and high temperatures.

Researchers are highly interested in the usage of bioadsorbent in wastewater treatment due to a few advantages. The bioadsorbents are mostly recycled materials or waste, such as OPEFB and discarded clam shells. This advance in technology attracts the market as it is low cost and at the same time, decreasing the amount of waste in the world. However, there are still constraints in using bioadsorbents, such as the equilibrium time for sorption using activated sludge method, which is up to 40 hours (Tay et al., 2006). There could be less flexibility in the design and operation as well, as it could need a large land area for the contaminants to interact with the bioadsorbents, such as sea-shells.

2.5.1 Algae

Algae is being used in wastewater treatment to remove heavy metal ions such as copper, zinc and many more. Some of the advantages of using algae over traditional methods are the low cost of algae, low energy requirement and reduction in waste formation. Algae have the characteristic of being able to react even in low pH conditions. (Means & Hinchee, 1994).

Aravindhan et al. (2009) successfully used modified green macro alga (*Caulerpa scalpelliformis*) to remove phenols. The maximum uptake capacity was found to be 20mg of phenol per gram of green macro algae. Biosorption was found to be optimum at pH level 6 to 7. The effect of initial pH could change the degree of ionization of the biosorbent and sorbate (Rubín, Rodríguez, Herrero, & Sastre de Vicente, 2006). The algal surface has a pK_a of 3.85 and it is neutral at low pH conditions. As the pH increases, the overall surface charge becomes negative. Phenol has a pK_a of 9.90 and behaves as an anion at high pH values. Therefore, at pH values less than 6, acidic phenols are present and the neutral/undissociated phenol compounds get preferably adsorbed on the surface of the macro alga in their molecular form. On the other hand, at pH range of 6-10, the biosorption of phenol decreases because of the higher electrostatic repulsion when the sorbent and sorbate are both negatively charged.

2.5.2 Cellulose

Cellulose sparked the interest in the scientific world; many works regarding cellulose have been published. Cellulose chemistry started since the middle of 19th century, where artificial silk is obtained by dissolving water-insoluble cellulose in a suitable chemical according to Klemm et al.(1998). One of the many reasons is because cellulose is the most abundant organic polymer in the world. Every cell wall of a plant contains fibers of cellulose.

Zugenmaier (2008) stated that cellulose is harvested commercially from the seed hairs of cotton (over 94% cellulose) as bast fibers or as wood (40-55% cellulose). The isolation of cellulose from woody plants is explained by Klemm, Philipp, Heinze, Heinze, & Wagenknecht (1998), where it has been done by large-scale chemical digestion processes in the industry. The lignin and hemi-cellulose is dissolved using chemicals, and the cellulose will be in solid form. The process is somewhat similar to digestion as the lignin is digested into acid or alkali. At the end of the digestion process, bleaching steps are taken to remove the lignin completely.

Cellulose is an organic polymer with the formula $(C_6H_{10}O_5)n$, composed of D-anhydroglucopyranose units (AGU), which are linked together by β-(1→4)-glycosidic bonds. The pure cellulose has this long and rigid cellulose chain, connected by strong intermolecular forces. From the chemical structure based on figure 1 below, it is shown that C-2, C-3 and C-5 are bonded to one hydroxyl group each. These hydroxyl groups are open to substitution reach and this is how cellulose possesses the versatility in chemical changes. (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998; Zugenmaier, 2008)

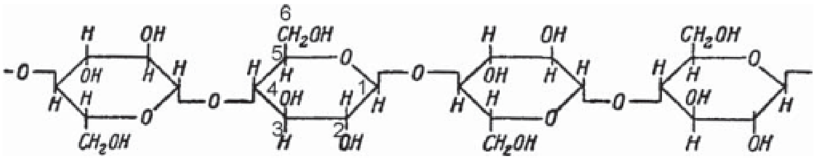


Figure 2.5.2: Chemical constitution of cellulose and numbering of carbon atoms (Zugenmaier, 2008)

Mercerization

Mercerization, or referred as caustic treatment, can loosen the structure of the structure of the cellulose fibers. Sodium hydroxide is most often used reagent for mercerization. Gurgel and Gil (2009) described that mercerization can increase the fibers specific surface area, making the hydroxyl groups attached to the cellulose structure more accessible to solvents. The alkali treatment decreases the degree of polymerization and crystallinity of the cellulose. (Morgado & Frollini, 2011).

2.6 Factors affecting sorption

2.6.1 Initial concentration

From most of the literature reviews, it was found that initial concentration of phenol samples does not improve nor inhibit the adsorption capacity.

2.6.2 pH

The pH of the phenol sample is important as phenol needs to be kept in the undissociated form. The pH value of phenol has to be remained under 10 for a strong interaction with adsorbent, as this will maintain the hydroxyl group protonated (neutral). Phenol compound has a pK_a value of 10.0 (Carey, 2000) while 2,4-D has a pK_a value of 2.87 (Qin, Wei, & Li, 2002).

Two types of phenol-biosorbent interactions are postulated; first is electrostatic, which is similar to metallic ions. This first type of interaction could be due to the hydroxyl group and other hydrophobics that exists in phenol structure. The adsorption could also occur due to the presence of phenoxide anion and alginates in the phenol solution that is under pH 10 (Navarro et al., 2008).

2.7 Kinetic and modeling of sorption process

2.7.1 Kinetic modeling for removal of heavy metal ions using cellulose acetate/zeolite composite fibers

Composite fibers made up of zeolite particles and cellulose acetate (CA) were used to adsorb copper and nickel ions from aqueous solution (Ji et al., 2012). Zeolite has high ion exchange capacity, makes heavy metal ions removal easier. However, it is difficult to remove zeolite from the solution after separation in large-scale treatment because the small particle size of zeolite. CA was chosen to form the composite as it can be easily molded into different forms, such as membranes, fibers and spheres. Other than that, CA has hydrophilic surfaces that will increase its accessibility for the aqueous solution. The composite fibers were found to have highly porous and sponge-like structures.

The experimental data shows that pure CA fiber has much lower efficiency (up to 15%) compared to CA/zeolite composite (up to 95%) in pH solution of 4-8. This can be explained with the fact that zeolite was highly selective for H^+ ions in acidic medium when H^+ ions concentration were high. Besides, the hydrolysis of the surface functional groups of zeolite (Si^{4+} and Al^{3+}) may have occurred at higher pH values, this increases the surface hydroxyl sites for metal ion adsorption.

It was analyzed that the adsorption isotherm that best fit the experimental data was Langmuir equation. The isotherm is expressed in terms of R_L, a dimensionless constant separation factor,

$$\boldsymbol{R_L} = \frac{\mathbf{1}}{\mathbf{1} + \mathrm{K_L C_0}}$$

Where C_0 (Mg/L) is the lowest initial concentration. Langmuir isotherm gave the plot that fits best, compared to other isotherms. The value of R_L was in the range of $0 < R_L < 1$, shows that the CA/zeolite fiber was favourable for adsorption of copper and nickel ions.

2.7.2 Kinetic modeling for removal of red phenol dye using OPEFB fibers

OPEFB fibers that are treated with polyethylenimine (PEI) were successfully to remove anionic phenol red from aqueous solutions in a previous study (Sajab, Chia, Zakaria, & Khiew, 2013). The PEI treated OPEFB were able to produce cationic adsorbents to adsorb anionic phenol red. The optimum pH is when the pH is less than 5 as in basic medium, the amount of OH^- ions competes with anionic phenol red molecules.

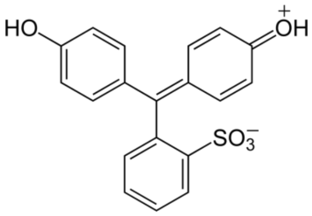


Figure 2.7.2: Molecular structure of anionic phenol red (PR)

It is found that Freundlich adsorption is the most favourable adsorption isotherm as it fits the model. This is due to the grafting of highly branched PEI onto the OPEFB fibers, which introduced a high amount of amine groups that can interact with phenol red.

CHAPTER 3

METHODOLOGY

3.1 Chemicals and materials

3.1.1 Preparation of cellulose

5g of OPEFB-extracted cellulose are mercerized in 100ml of 0.1M NaOH solution at room temperature for 4 hours with constant magnetic stirring (120rpm). The solution is filtered using filter paper (Whatman No.1) and dried in oven for 3 hours at 50^oC.

3.1.2 Preparation of heavy metal solution

$PbNO_3$ 1000ppm stock solution is prepared by diluting 1g of substance in 1L of deionized water. From the 1000ppm stock solution, further diluted to 200ppm, 300ppm, 400ppm and 500ppm using $M_1V_1 = M_2V_2$.

3.1.3 Preparation of phenol ion solutions

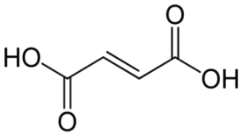
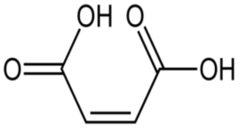
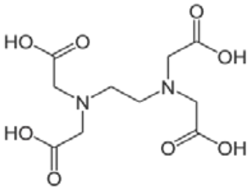
Stock solution of 1000pm of 2,4-D and phenol are prepared respectively, by diluting 1g of substance in 1L of deionized water. The solutions are adjusted to pH 5. Then another batch of 1000ppm stock solutions are prepared and adjusted to pH10. The pH of the solutions is adjusted using sodium hydroxide solution (to increase the pH) and acetic acid (to decrease the pH).

3.2 Experimental Work

3.2.1 Surface engineering of cellulose

Three compounds containing carboxylic groups are chosen to study the surface engineering of OPEFB-cellulose. Table 3.2.1 describes the structural formulae of the modifiers.

Table 3.2.1: List of modifiers used for surface engineering of cellulose

Name	**Molecular Formula**	**Molecular Structure**	**No. of Carboxylic Group**
Fumaric acid	$HO_2CCH{=}CHCO_2H$		2
Maleic acid	$HO_2CCHCHCO_2H$		2
EDTA	$(HO_2CCH_2)_2N$- CH2-CH2- $N(CH_2CO_2H)_2$		4

These reagents (each of them are 0.1M) are prepared by diluting with deionized water in a 250ml conical flask. 3g of dried mercerized cellulose are added to 50ml of the 0.1M fumaric acid. The flask is then plugged to soxhlet apparatus, set at 105°C and refluxed for 6h. The solution is filtered and the filtered cellulose is dried in oven at 50°C for 3 hours. The dried and modified cellulose is stored in a desiccator until further study. The same procedures are applied to the other reagents.

3.2.2 Batch adsorption of heavy metal

0.5g of the respective treated cellulose is mixed with 100ml of each metal ion solutions in conical flask using an orbital shaker. The concentration of the metal ion solutions are in a range of 200 to 500ppm for 4 hours. The mixtures are stirred at 120rpm. The mixtures are filtered out and stored as a sample. Samples are taken every 30 minutes to determine the equilibrium concentration. The samples are diluted to 100 times dilution to be within Atomic Absorption Spectrometer (AAS) detection range. The samples are analyzed for its metal ion concentrations using Shimadzu AA-6800 AAS. The equilibrium contact time, initial and final metal ion concentrations are recorded.

3.2.3 Batch adsorption of 2,4-D and phenol

50ml of the 1000ppm 2,4-D and phenol (adjusted to pH5) are taken in the 250ml conical flask working solution and added with 0.1g of every modified cellulose and metal-loaded modified cellulose. The flasks are placed on the orbital shaker and the speed of the shaker is set at 120rpm for 24 hours. 10ml of the test sample is filtered and stored for analysis. After that, 2,4-D and phenol sorption are repeated in pH 10 condition. The test samples are diluted to 10 times dilution to get the UV-VIS detection range. The concentrations of the samples are analyzed using Shimadzu UV-3150 UV-VIS spectrophotometer. Absorption spectrum 2,4-D and phenol are carried out in the range of 190 to 450nm. Two separate calibration graphs are plotted from their respective absorption peaks, $\lambda_{max.}$ The concentration of 2,4-D and phenol are reported at λ_{max} = 283nm (Kundu, Pal, & Dikshit, 2005) and λ_{max} = 270nm (Aravindhan et al., 2009) respectively.

3.3 Characterization of cellulose before and after modification

The functional groups of the mercerized cellulose and modified cellulose are analyzed using a Perkin Elmer FTIR Spectrum One/BX Spectrometer. The IR spectrum is recorded from 4000 to 450 cm^{-1}. Surface morphology of the samples is also studied using FESEM at 200x and 2000x magnification. The mean diameter was determined by selecting five fibers randomly from the image. Besides, TGA is carried out using Perkin Elmer Pyris 1 to study the thermal stability of the samples. The instrument is set to run from room temperature to 700^{o}C at a rate of 10^{o}C min^{-1} under nitrogen flow. The phase behaviors of the samples are also analyzed using wide angle XRD (Bruker-AXS D8 Advance) at 1.540^{o}A wavelength, with a scan speed of 2^o per second.

3.4 Adsorption isotherm and kinetic study

The phenol / 2,4-D sorption that gives highest sorption % are chosen to investigate the adsorption isotherm. The kinetics was determined by analyzing the adsorptive uptake of phenol derivatives from the aqueous solution at different time intervals.

3.5 Research methodology

Literature Review

Understanding the background of surface engineering, hazards and chemical structure of 2,4-D, phenol, and cellulose.

Pre-experimental Work

Determine the suitable amount of chemicals to be used and verify the factors that will determine the results.

Experimental Work

Carry out the methodology according to the gantt chart to achieve the research objective.

Results Analysis

Samples are analysed using suitable equipments. Then, the results are analysed according to determining factors, which are changes in concentration, pH and contact time.

Conclusion and Report Writing

Conclude the study according to objectives and compile the findings into a report.

3.6 Gantt chart

Week number	**FYP 1**															**FYP 2**													
Project activities	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
Literature Review	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				**ONE WEEK BREAK**														
Preparation of modified cellulose samples							▨	▨	▨	▨	▨																		
Characterization of modified cellulose samples											▨	▨	▨	▨		▨	▨												
Preparation of metal ion solutions										▨	▨																		
Adsorption of heavy metal ions											▨	▨	▨																
Characterization of adsorption for heavy metal ions												▨	▨	▨		▨	▨												
Adsorption of 2,4-D and phenol																▨	▨	▨											
Characterization of adsorption for 2,4-D and phenol																	▨	▨	▨	▨	▨	▨							
Result analysis and report writing																▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

3.7 Milestone

Milestone	June	July	Aug	Sept
1. Investigate the different types of modifier	■			
2. Study the effects of raw OPEFB, OPEFB-extracted cellulose and surface-engineered cellulose onto heavy metal ions.		■		
3. Study the effects of raw OPEFB, OPEFB-extracted cellulose and surface-engineered cellulose onto phenol and 2,4-D.			■	
4. Study the adsorption parameters such as initial concentration, contact time and pH.			■	
5. Completion of report writing				■

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of modified cellulose

4.1.1 FTIR spectra

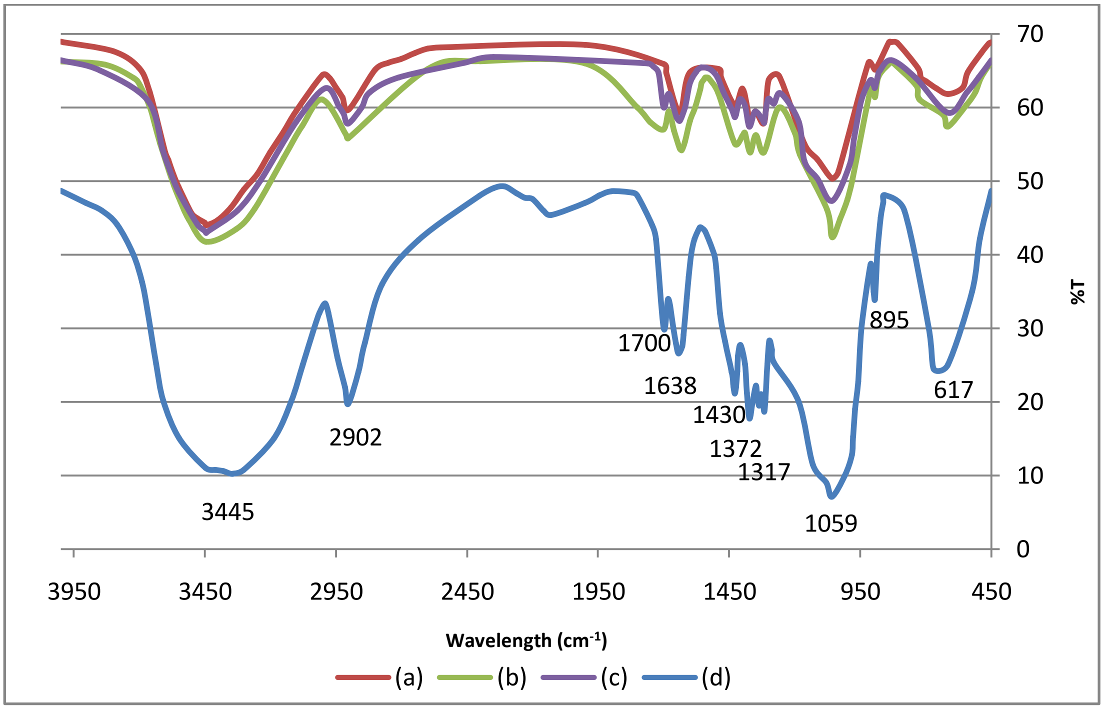


Figure 4.1.1: FTIR of (a) mercerized cellulose, (b) cellulose-EDTA, (c) cellulose-fumarate and (d) cellulose-malate

The transmittance peak at 3445cm^{-1} and 2902 cm^{-1} are due to the cellulose –OH and C-H groups stretching vibrations. The presence of in-plane bending vibrations by $-CH_2$ and C-O in cellulose is shown at 1430 cm^{-1} and 1317 cm^{-1}, while the C-H deformation vibration is at 1373 cm^{-1}. The –OH bending observed at 1638 cm^{-1} is due to water absorption (Nazir et al., 2013). The peak at 1059 cm^{-1} indicates presence of –CO group. The peak at 895 cm^{-1} is associated with the C-O-C, C-C-O and C-C-H deformation modes and stretching vibrations at the β-gycosidic linkage situated in C-5 and C-6 atoms (Oh et al., 2005). Aromatic rings –CH bending is indicated at 617 cm^{-1}. All these are characteristics of cellulose and they are observed in all the samples.

On the other hand, the peak at 1700 cm^{-1} is only observed in the modified cellulose samples. This peak indicates the presence of carboxylic acid and it signifies the –OH substitution reaction carried out by EDTA, fumarate and maleic acid.

4.1.2 Thermogravimetry analysis

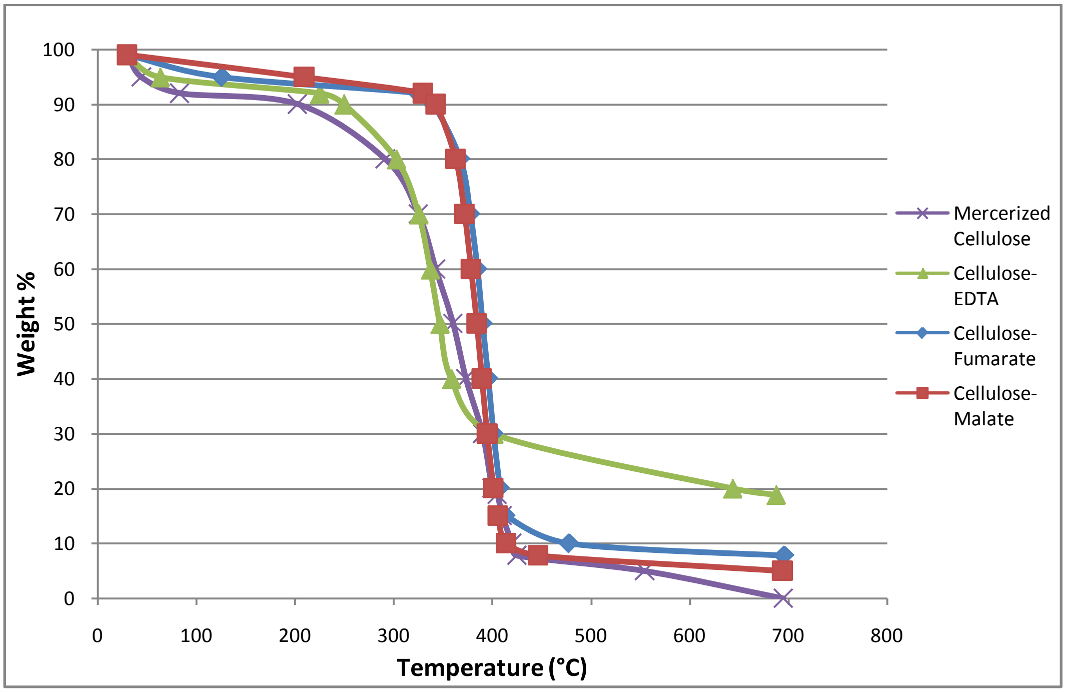


Figure 4.1.2: TGA Analysis of Mercerized Cellulose and Modified Cellulose

Table 4.1.2: TGA Results of Mercerized Cellulose and Modified Cellulose

Samples	Peak temperature (^{o}C)	% Degradation	% Residue at 690^{o}C
Mercerized cellulose	339.1	62.5	0
Cellulose-EDTA	343.3	55.0	18.9
Cellulose-fumarate	394.2	42.9	7.7
Cellulose-malate	387.9	42.9	5.2

The first stage of weight loss occurs below 200 ^{o}C due to moisture loss (Nazir et al., 2013). Cellulose degradation for mercerized cellulose starts at around 340 ^{o}C. However, for the cellulose-malate and cellulose-fumarate, cellulose decomposition starts at around 330^{o}C with a sharp drop in the weight percentage, and it continues onto around 390^{o}C. This may be due to stronger crystalline structure of the modified cellulose, the modification managed to improve thermal stability of the cellulose. The cellulose that is not modified has a weaker crystalline structure, thus it degrades at lower temperature. The residual char of remaining 5% may be due to aromatization, as it of fragmented cellulose C-C, C-O bonds at temperatures higher than 380^{o}C (Jahan, Saeed, He, & Ni, 2011). The higher amount of residual char by the modified cellulose also indicates better thermal stability compared to mercerized cellulose. There were no other degradation peaks; this concludes that the samples are very pure.

4.1.3 FESEM

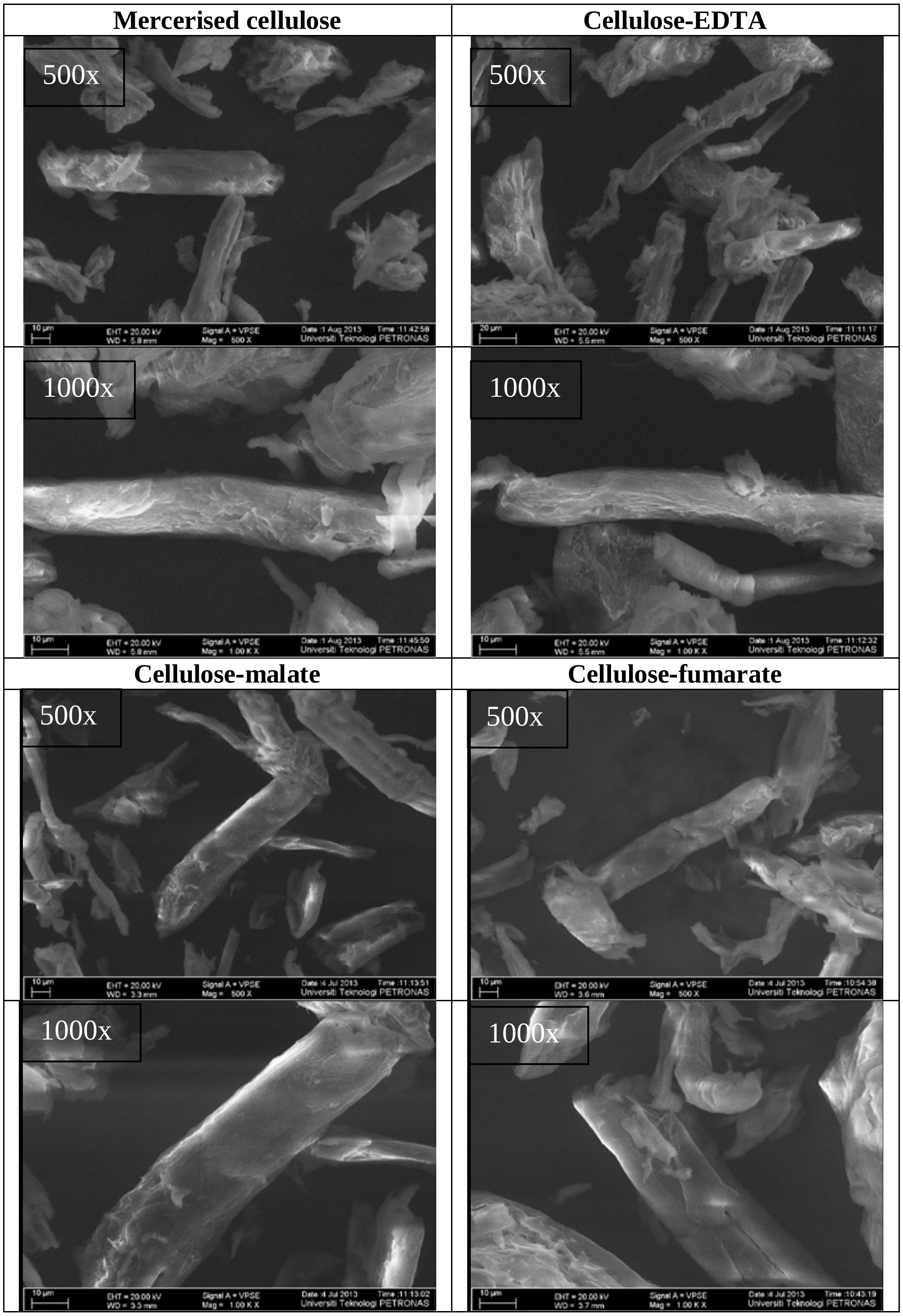


Figure 4.1.3: FESEM micrographs of cellulose samples at 500x and 1000x magnification

The fibers of the modified cellulose are more broken down and the surface are rougher and have more strains compared to the OPEFB-extracted cellulose (untreated state) by Nazir et al. (2013). The loosening of cellulose structure and the separated fiber bundles is similar with the cellulose pretreatment study carried out by Ariffin, Hassan, Umi Kalsom, and Abdullah (2008). This indicates the occurrence of delignification. The average sizes of the fibers are calculated by taking an average of five fibers.

Table 4.1.3: Average Fiber Size of Cellulose Samples

Samples	Average size
Mercerized cellulose	17.7µm
Cellulose-EDTA	15.4µm
Cellulose-fumarate	16.9µm
Cellulose-malate	16.6µm

4.1.4 XRD

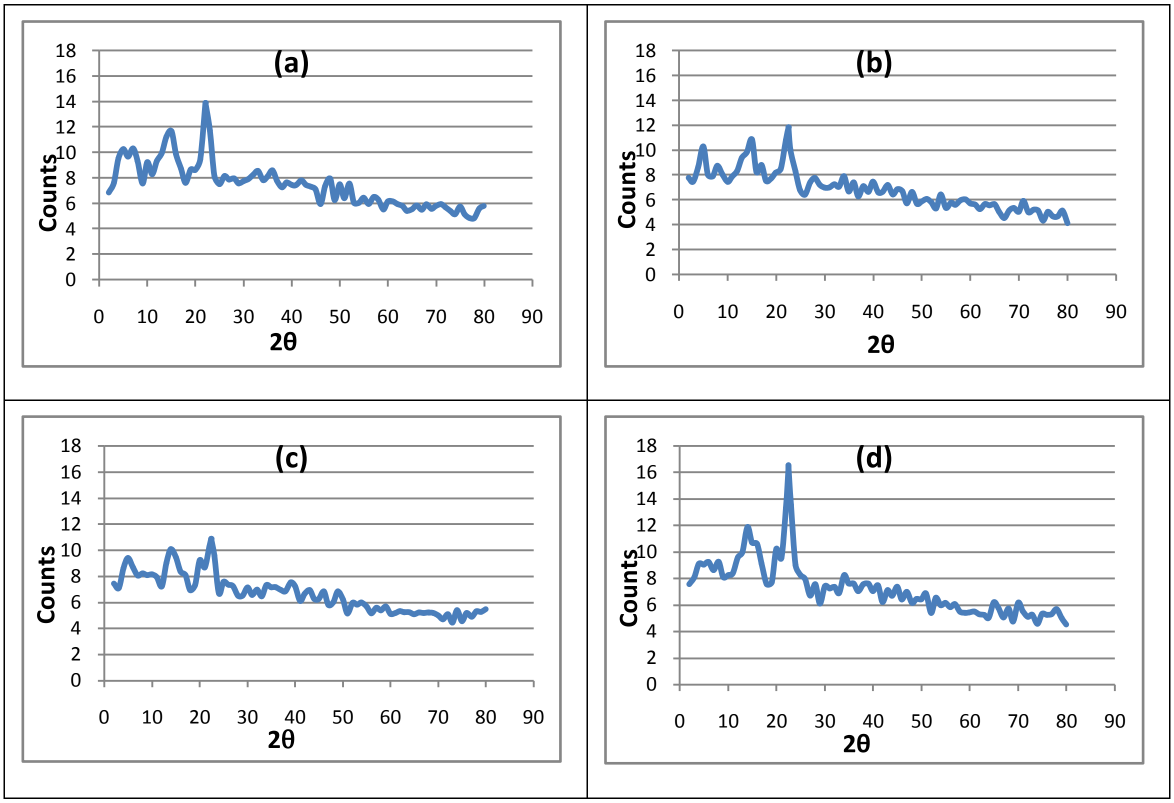


Figure 4.1.4: FTIR of (a) mercerized cellulose, (b) cellulose-EDTA, (c) cellulose-fumarate and (d) cellulose-malate

The measure of crystallinity is related to the number of intra-and intermolecular hydrogen bonds in cellulose. Cellulose crystallites contain both crystalline (ordered) and amorphous (less-ordered) regions. Higher C_{Ir} indicates that the cellulose is more ordered. (Park, Baker, Himmel, Parilla, & Johnson, 2010)

The crystallinity index, C_{Ir} was calculated using the XRD peak height method (Park et al., 2010):

$$C_{Ir} = [(I_{002} - I_{am})/I_{002}]\, x\ 100$$

Where I_{002} is the intensity reading from the highest peak (crystalline peak) and I_{am} is the intensity reading from the amorphous peak.

Table 4.1.4: Crystallinity index of the cellulose samples

Samples	Crystallinity Index. C_{Ir}
Mercerized cellulose	69.61
Cellulose-EDTA	60.99
Cellulose-fumarate	65.17
Cellulose-malate	63.66

The modification using carboxylic acid has changed the crystallinity of the mercerized cellulose. The modified cellulose has lower C_{Ir} than mercerized cellulose. Similar to the research carried out by Liu (2012), treated cellulose has lower C_{Ir}. In addition to that, research by Liu (2012) indicated that treated cellulose with lower C_{Ir} gives better adsorption result.

4.2 Batch adsorption of lead ions

4.2.1 Preparation of calibration curve

Stock solution of lead ion (1000ppm) was diluted in distilled water to obtain solutions in the range of 2 to 6ppm. The calibration curve obtained has a mean R^2 value of 0.998. The unknown concentrations of lead ion in the solutions are interpolated using this calibration curve.

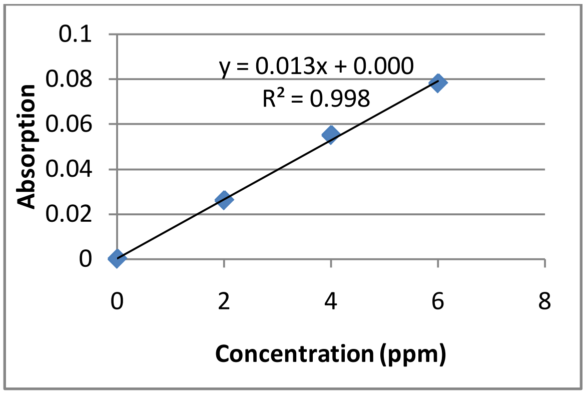


Figure 4.2.1: Calibration curve of lead ion

4.2.2 Lead ion sorption

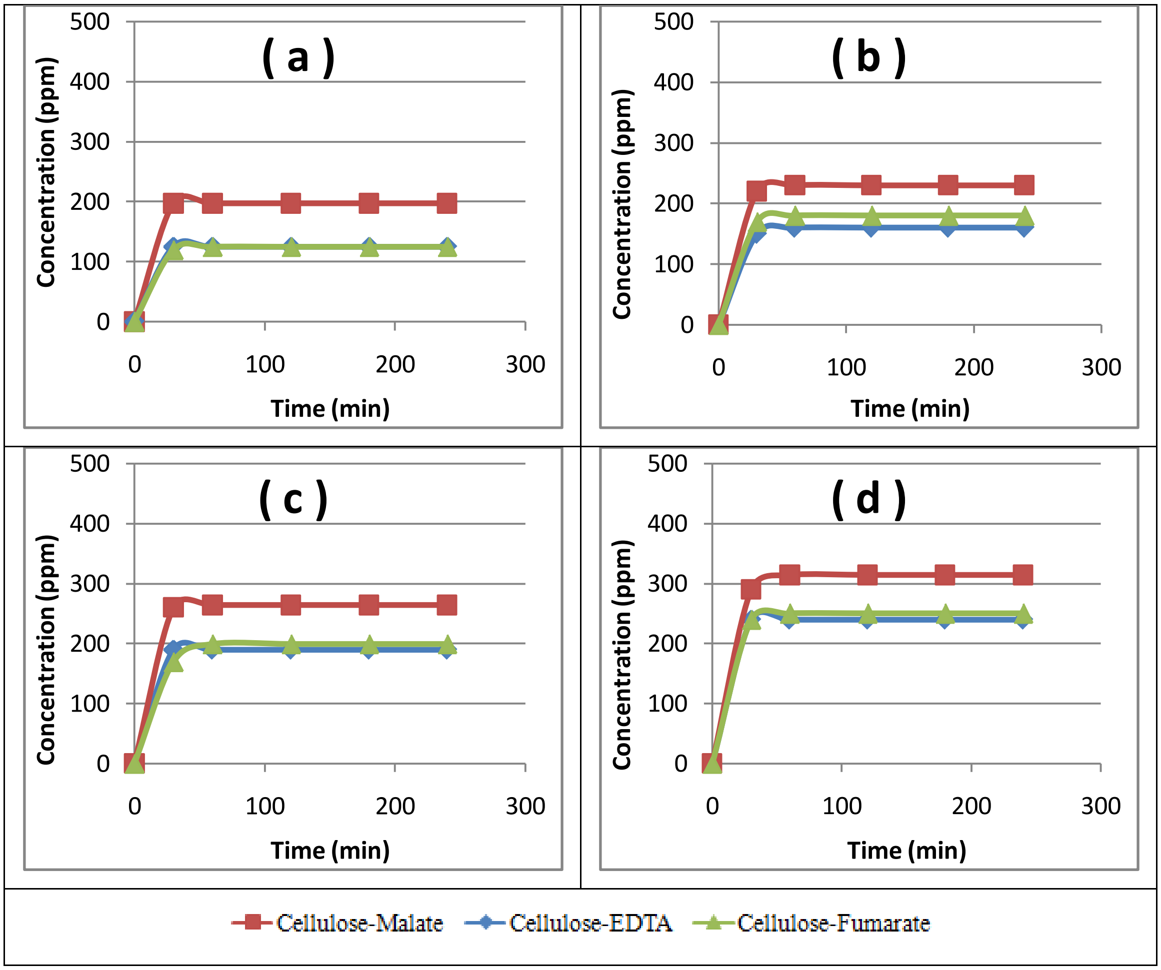


Figure 4.2.2: Lead ion sorption profiles by modified cellulose

Figure above shows the lead ion sorption by cellulose-malate, cellulose-EDTA and cellulose-fumarate. (a) is obtained by using initial concentration of 200ppm lead solution, followed by (b) with 300ppm lead solution, (c) with 400ppm lead solution and (d) with 500ppm lead solution.

From figure 4.2.2, sorption of lead ion onto the cellulose samples are observed to have attained equilibrium state after 50 minutes. The sorption occurred rapidly during the first hour. During this time, the lead ions are loaded onto the cellulose fibers. After 60 minutes, the maximum sorption capacity has reached as the active sites are fully loaded with lead ions.

The amount of lead adsorbed per unit mass of cellulose (q_e) was determined using the following equation (Sajab et al., 2013):

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

Where C_0 and C_e are the initial and equilibrium concentrations of lead ion (mg/l) repectively. V is the volume of the solution (l) and m is the mass of cellulose (g). The percentage of lead ion removal was calculated using the following equation:

$$\text{Percentage of lead ion removal (\%)} = \frac{(C_0 - C_e)}{C_0}\, x\ 100\%$$

Table 4.2.2: Amount of lead adsorbed per unit mass of cellulose

Samples C_0 **(ppm)**	**q_e (mg/g)**				**Lead ion removal (%)**			
	200	**300**	**400**	**500**	**200**	**300**	**400**	**500**
Cellulose-EDTA	25	32	38	48	62.5	53.3	47.5	48.0
Cellulose-fumarate	25	36	42	50	62.5	60.0	52.5	50.0
Cellulose-malate	39.4	46	52.8	62.8	98.5	76.7	66.0	62.8

Cellulose-malate has the highest adsorption capacity compared to other modified cellulose. The data shows that as the concentration of lead ion solution increases, the adsorption capacity of modified cellulose, q_e increases. However, the optimum adsorption occurs when the initial concentration of lead solution is at 200ppm, where cellulose-malate adsorbed 98.5% of the lead ion.

4.3 Batch adsorption of phenol and 2,4-D

4.3.1 Preparation of calibration curves

Stock solution of phenol was diluted in water to obtain phenol solutions at different concentrations. Absorption spectrum of phenol was run in the range of 190nm to 450nm. The equation obtained for phenol is $Abs = [0.005\, x\, C(ppm]) + 0.007$. On the other hand, calibration for 2,4-D is conducted in the same manner. The equation obtained for 2,4-D is $Abs = [0.017\ x\ C(ppm)] + 0.063$. The unknown concentrations can be determined by interpolation using these calibration curves.

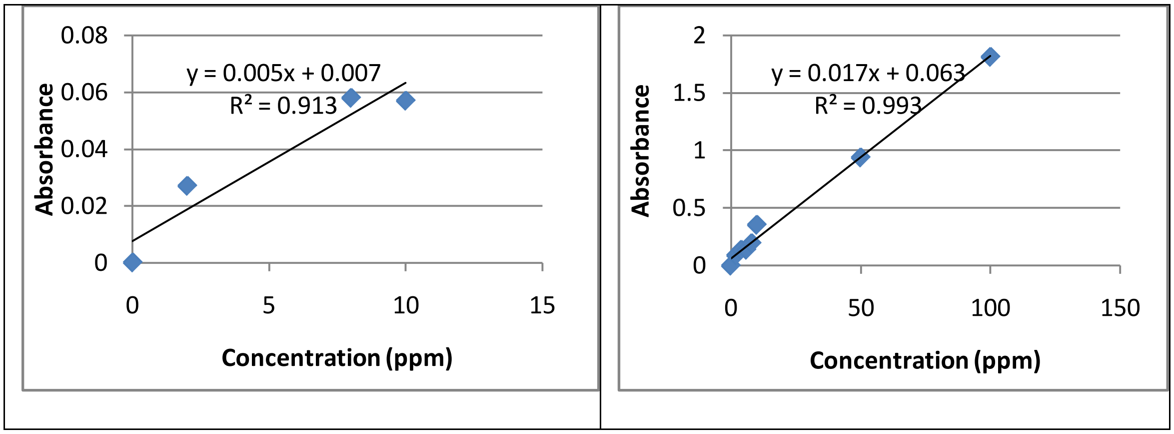


Figure 4.3.1: Calibration curve of phenol (left) and 2,4-D (right)

4.3.2 Batch adsorption of phenol

Phenol sorption could be affected in terms of the pH of the solution. Hence, the experiment is carried out in pH 5 solution and pH 10 solution separately. The initial concentration of phenol solution is 1000ppm.

Table 4.3.2a: Phenol sorption result in pH 5 solution

Cellulose samples	**C_e (ppm)**	**q_e (mg/g)**	**Phenol removal (%)**
Mercerized cellulose	350	32.5	65.0
Cellulose-EDTA (Pb-loaded)	208	39.6	79.2
Cellulose-fumarate (Pb-loaded)	326	33.7	67.4
Cellulose-malate (Pb-loaded)	242	37.9	75.8
Cellulose-EDTA	280	36.0	72.0
Cellulose-malate	208	39.6	79.2
Cellulose-fumarate	246	37.7	75.4

Table 4.3.2b: Phenol sorption result in pH 10 solution

Cellulose samples	C_e **(ppm)**	q_e **(mg/g)**	**Phenol removal (%)**
Mercerized cellulose	940	3	6.0
Cellulose-EDTA (Pb-loaded)	680	16	32.0
Cellulose-fumarate (Pb-loaded)	660	17	34.0
Cellulose-malate (Pb-loaded)	880	6	12.0
Cellulose-EDTA	840	8	16.0
Cellulose-malate	820	9	18.0
Cellulose-fumarate	900	5	10.0

Comparing table 4.3.2a with 4.3.2b, cellulose-EDTA (Pb-loaded) in pH 5 solution gives the highest sorption of phenol. The amount of phenol adsorbed per unit mass of cellulose (q_e) is 39.6 mg/g, leading to sorption percentage of 79.2%.

4.3.3 Batch adsorption of 2,4-D

Table 4.3.3: 2,4-D sorption result in pH 5 solution

Cellulose samples	C_e **(ppm)**	q_e **(mg/g)**	**2,4-D removal (%)**
Mercerized cellulose	458	27.1	54.2
Cellulose-EDTA (Pb-loaded)	247	37.9	75.8
Cellulose-fumarate (Pb-loaded)	299	35.1	70.1
Cellulose-malate (Pb-loaded)	147	42.6	85.2
Cellulose-EDTA	228	38.6	77.2
Cellulose-malate	187	40.6	81.2
Cellulose-fumarate	192	40.4	80.8

Table 4.3.3b: 2,4-D sorption result in pH 10 solution

Cellulose samples	**C_e (ppm)**	**q_e (mg/g)**	**Phenol removal (%)**
Mercerized cellulose	980	1	2.0
Cellulose-EDTA (Pb-loaded)	665	16.8	33.5
Cellulose-malate (Pb-loaded)	645	17.8	35.5
Cellulose-fumarate (Pb-loaded)	815	9.3	18.5
Cellulose-EDTA	815	9.3	18.5
Cellulose-malate	760	12	24.0
Cellulose-fumarate	965	1.8	3.5

Comparing table 4.3.3a with 4.3.3b, cellulose-malate (Pb-loaded) in pH 10 solution showed the highest sorption of 2,4-D compared to other modified cellulose. The amount of 2,4-D adsorbed per unit mass of cellulose (q_e) is 42.6 mg/g, giving a sorption percentage of 85.2%. According to Srihari and Ashutosh (2009), the sorption of 2,4-D and phenol is most effective at neutral pH. The ineffectiveness of phenol sorption at other pH range may be due to the suppression of hydroxyl ions at higher pH and hydrogen ions at lower pH.

4.5 Adsorption Isotherm

Adsorption isotherm study aims to investigate the possibility of interaction between the adsorbate and adsorbent. The adsorption data of 2,4-D onto cellulose-malate (Pb-loaded) is chosen to carry out adsorption study as it gives the highest sorption %. The data is fitted into Langmuir, Freundlich and Temkin isotherms. Langmuir isotherm assumes monolayer coverage of adsorbate over adsorbent surface and all the adsorption sites are the same and limited as well. The Langmuir model is expressed as

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Where q_e (mg/g) is the equilibrium metal ion concentration onto adsorbent, C_e (mg/L) is the equilibrium metal ion concentration in solution, q_m (mg/g) is the monolayer capacity of the adsorbent and K_L (L/mg) is the Langmuir constant. The plot of C_e/q_e versus C_e is presented below:

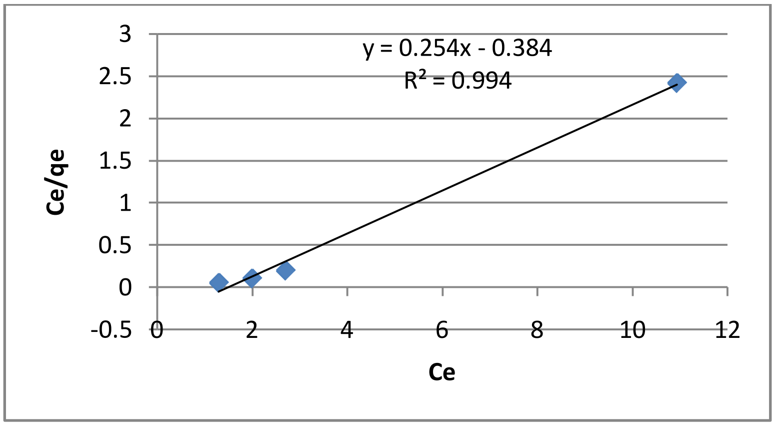


Figure 4.5.1: Plot of Langmuir isotherm

Freundlich isotherm assumes the adsorption occurs on heterogeneous adsorption surfaces, which means all the adsorption sites are not the same. The adsorption is not limited to monolayer formation as well. Freundlich isotherm, expressed as

$$q_e = K_F C_e^{1/n} \text{ or } log q_e = log K_F + \frac{1}{n} log C_e$$

Where K_F is the relative adsorption capacity of the adsorbent and n is the degree of dependence of adsorption on the equilibrium dye concentration, both are Freundlich constants. The slope of log q_e versus log C_e is used to determine the value of n. n>1 suggests that the adsorption is favourable (Sajab et al., 2013).

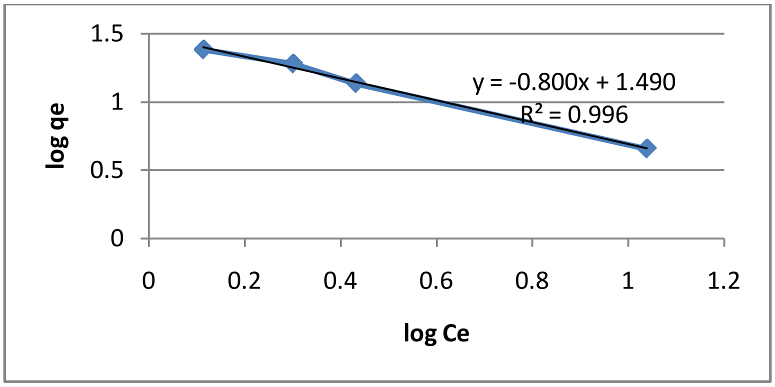


Figure 4.5.2: Plot of Freundlich isotherm

Temkin isotherm assumes that the heat of adsorption of all molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions. The bonding energies during adsorption are distributed uniformly, up to some binding energy. Temkin model is represented as

$$q_e = a + b\ logC_e$$

Where *a* and *b* are Temkin constants. The plot of q_e versus $logC_e$ is plotted below:

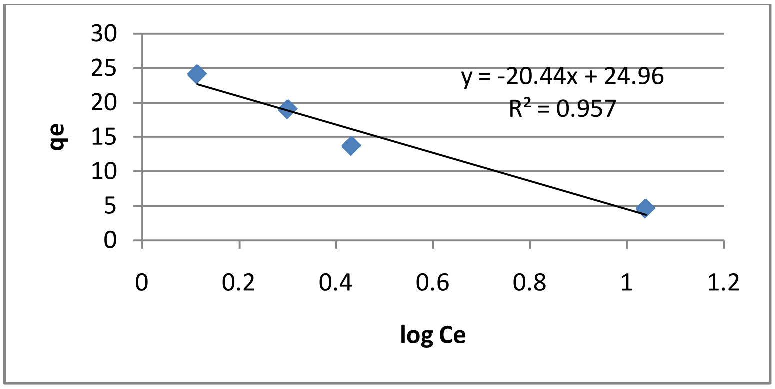


Figure 4.5.3: Plot of Temkin isotherm

The best isotherm model is decided based on the fitness of the data (R^2). The Freundlich isotherm model gives a higher $R^2 = 0.996$ compared to Langmuir ($R^2 = 0.994$) and Temkin ($R^2 = 0.957$). Hence, Freundlich isotherm model best describes the sorption of 2,4-D by cellulose. The value of n is calculated to be 1.25>1, which indicated the adsorption is favourable at high concentrations (El-Sheikh et al., 2013).

4.6 Kinetic Study

Kinetic models pseudo first order and pseudo second order are analyzed to determine the controlling mechanisms of the mass transfer during sorption. Pseudo first-order and pseudo second-order equations are applied to model the kinetics of 2,4-D adsorption onto cellulose-malate (Pb-loaded). The pseudo first-order rate equation is

$$\log(q_e - q_t) = log q_e - \frac{k_{ad}}{2.303}t$$

Where q_t is the amount adsorbed (mg/g) at time t, and k_{ad} is the rate constant of the pseudo first-order adsorption process (min^{-1}). Straight line plots of $\log(q_e - q_t)$ against time were plotted:

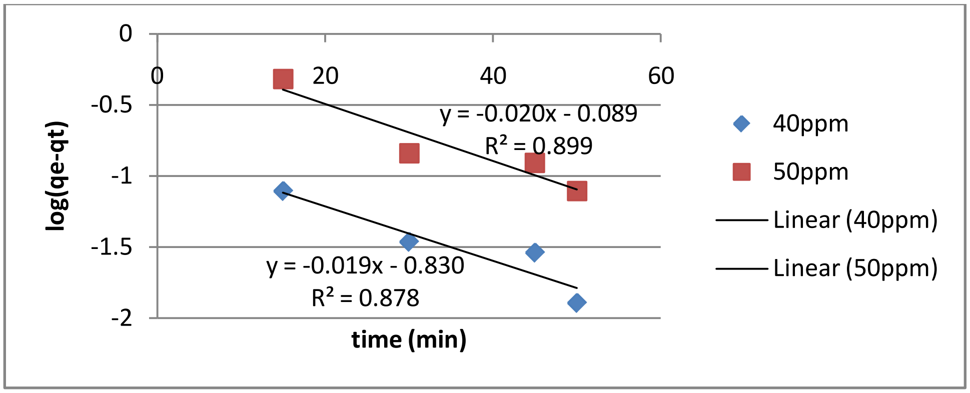


Figure 4.6.1: Plot of pseudo first-order rate reaction

The pseudo second-order equation is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t$$

Where $h = kq_e^2$ (mg g^{-1} min^{-1}) is the initial adsorption rate as t approaches zero and k is the rate constant of pseudo second-order adsorption (g mg^{-1} min^{-1}).

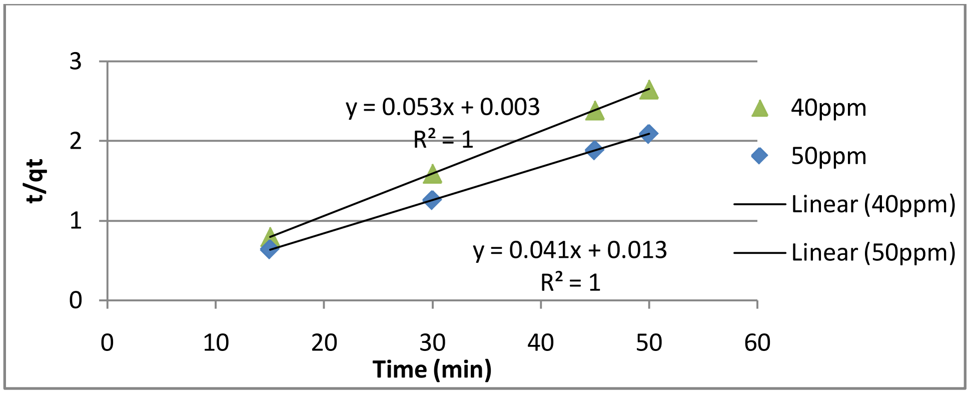


Figure 4.6.2: Plot of pseudo second-order rate reaction

The plot of pseudo second-order yields straight line ($R^2 = 1$). It has higher R^2 value compared to pseudo-first-order ($R^2 > 0.8$). Hence, pseudo second-order kinetics is more applicable to describe the 2,4-D sorption by modified cellulose. The pseudo second-order constants are in the range of 19 to 63 g mg^{-1} min^{-1}. The pseudo second-order is based on a chemical reaction mechanism whereby the adsorption rate depends on the chemical adsorption through sharing or exchange of electrons between the adsorbent and adsorbate. (Sun, Lin, Liu, & Liu, 2011)

CHAPTER 5

CONCLUSION AND FUTURE RECOMMENDATION

Surface engineering of cellulose has been studied extensively to fulfill demands for industrial use. The modification leads to changes in properties of the cellulose, further improving the positive attributes possessed by cellulose.

From this study, we have learnt that the modified cellulose has higher sorption capacity compared to the unmodified cellulose. The percentage of phenol removal for mercerized cellulose is 65% and cellulose-EDTA (lead-loaded) is 79.2%, this has a difference of 14.2%. Meanwhile, for 2,4-D removal, mercerized cellulose gives a removal percentage of 54.2% and cellulose-malate (lead-loaded) is 85.2%, which leads to a difference of 31%.

The highest adsorption capacity for lead is 62.8 mg/g. On the other hand, phenol has adsorption capacity of 39.6 mg/g, while 2,4-D is 42.6 mg/g. The adsorption process follows Freundlich adsorption isotherm and pseudo second-order, which is based on chemical adsorption mechanism. Higher initial concentration of phenol and 2,4-D yields better adsorption efficiency. On the other hand, the adsorption is more effective in acidic solution. Phenol sorption in pH 10 yields removal percentage of 6-34%, while in pH 5 is 65-75%.

To further investigate the adsorption capability of the surface engineered cellulose, sorption study can be done on wastewater samples. Another way is to carry out sorption study on solutions that contains both heavy metals and phenol derivatives to determine whether the modified cellulose could sorp both at the same time.

REFERENCES

Abdelwahab, O., Amin, N. K., & El-Ashtoukhy, E. S. Z. (2009). Electrochemical removal of phenol from oil refinery wastewater. *Journal of Hazardous Materials, 163*(2–3), 711-716. doi: http://dx.doi.org/10.1016/j.jhazmat.2008.07.016

Ahmaruzzaman, Md. (2008). Adsorption of phenolic compounds on low-cost adsorbents: A review. *Advances in Colloid and Interface Science, 143*(1–2), 48-67. doi: http://dx.doi.org/10.1016/j.cis.2008.07.002

Akma, N.M.H., Samsuri, A.W., Ainie, H.K., & Rosenani, A. B. (2009). Sorption-Desorption Study of a Herbicide 2,4-Dichlorophenoxyacetic Acid on Acidic Tropical Soils. *Malaysian Journal of Soil Science (MJSS), 13*, 119-131.

Aravindhan, Rathinam, Rao, Jonnalagadda Raghava, & Nair, Balachandran Unni. (2009). Application of a chemically modified green macro alga as a biosorbent for phenol removal. *Journal of Environmental Management, 90*(5), 1877-1883. doi: http://dx.doi.org/10.1016/j.jenvman.2008.12.005

Ariffin, H., Hassan, M.A., Umi Kalsom, M.S., & Abdullah, N. Shirai, Y. (2008). Effect of physical, chemical and thermal pretreatments on the enzymatic hydrolysis of oil palm empty fruit bunch (OPEFB). *J. Trop. Agric. Fd. Sci., 36*(2), 259-268.

Aydın, Handan, Özdemir, Nurullah, & Uzunören, Nuray. (2005). Investigation of the accumulation of 2,4-dichlorophenoxyacetic acid (2,4-D) in rat kidneys. *Forensic Science International, 153*(1), 53-57. doi: http://dx.doi.org/10.1016/j.forsciint.2005.04.018

Barlow, J., & Johnson, J. (2007). Fact Sheet on Phenols. Retrieved from Breast Cancer & The Environment Research Centers website: http://www.bcerc.org/cotcpubs.htm

Bevilaqua, J. V., Cammarota, M. C., Freire, D. M. G., & Sant'Anna Jr, G. L. (2002). Phenol removal through combined biological and enzymatic treatments. *Brazilian Journal of Chemical Engineering, 19*, 151-158.

Budavari, S. (2001). *The Merck Index* (13 ed.). Whitehouse Station, NJ: Merck and Co., Inc.

Carey, F.A. (2000). Organic chemistry: McGraw-Hill.

Council, Natural Resources Defense. (2012). What You Should Know About 2,4-D. http://www.nrdc.org/health/pesticides/2-4-d.asp

El-Sheikh, Amjad H., Newman, Alan P., Said, Adi J., Alzawahreh, Abdullah M., & Abu-Helal, Malek M. (2013). Improving the adsorption efficiency of phenolic compounds into olive wood biosorbents by pre-washing with organic solvents: Equilibrium, kinetic and thermodynamic aspects. *Journal of Environmental Management, 118*(0), 1-10. doi: http://dx.doi.org/10.1016/j.jenvman.2013.01.009

Foo, Y. N., Foong, K.K., Yusof, B., & Kalyana, S. (2011). A Renewable Future Driven With Malaysian Palm Oil-based Green Technology. *Journal of Oil Palm & The Environment (JOPE), 2*, 1-7. doi: 10.5366/jope.2011.01

Gervais, J. A., Luukinen, B., Buhl, K., & Stone, D. . (2008). 2,4-D Technical Fact Sheet. Retrieved from National Pesticide Information Center website: http://npic.orst.edu/factsheets/2,4-DTech.pdf

Gurgel, Leandro Vinícius Alves, & Gil, Laurent Frédéric. (2009). Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine. *Carbohydrate Polymers, 77*(1), 142-149. doi: http://dx.doi.org/10.1016/j.carbpol.2008.12.014

Hasanoğlu, Ayça. (2013). Removal of phenol from wastewaters using membrane contactors: Comparative experimental analysis of emulsion pertraction. *Desalination, 309*(0), 171-180. doi: http://dx.doi.org/10.1016/j.desal.2012.10.004

Honma, S., Suzuki, A., Buchanan, D. L., Katsu, Y., Watanabe, H., & Iguchi, T. (2002). Low dose effect of in utero exposure to bisphenol A and diethylstilbestrol on female mouse reproduction. *Reprod Toxicol, 16*(2), 117-122.

Jahan, M. Sarwar, Saeed, Abrar, He, Zhibin, & Ni, Yonghao. (2011). Jute as raw material for the preparation of microcrystalline cellulose. *Cellulose, 18*(2), 451-459. doi: 10.1007/s10570-010-9481-z

Ji, Fei, Li, Chaolin, Tang, Bo, Xu, Jianhui, Lu, Gang, & Liu, Peng. (2012). Preparation of cellulose acetate/zeolite composite fiber and its adsorption behavior for heavy metal ions in aqueous solution. *Chemical Engineering Journal, 209*(0), 325-333. doi: http://dx.doi.org/10.1016/j.cej.2012.08.014

Kundu, Sanghamitra, Pal, Anjali, & Dikshit, Anil K. (2005). UV induced degradation of herbicide 2,4-D: kinetics, mechanism and effect of various conditions on the degradation. *Separation and Purification Technology, 44*(2), 121-129. doi: http://dx.doi.org/10.1016/j.seppur.2004.12.008

Liu, Jun Hu, Huiren. (2012). The role of cellulose binding domains in the adsorption of cellulases onto fibers and its effect on the enzymatic beating of bleached kraft pulp. *Bioresources, 7*(1), 878-892.

Mahugo Santana, Cristina, Sosa Ferrera, Zoraida, Esther Torres Padrón, M., & Juan Santana Rodríguez, José. (2009). Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches. *Molecules, 14*(1), 298-320.

Mattson, James A., Mark Jr, Harry B., Malbin, Michael D., Weber Jr, Walter J., & Crittenden, John C. (1969). Surface chemistry of active carbon: Specific adsorption of phenols. *Journal of Colloid and Interface Science, 31*(1), 116-130. doi: http://dx.doi.org/10.1016/0021-9797(69)90089-7

Means, J.L., & Hinchee, R.E. (1994). *Emerging Technology for Bioremediation of Metals 2(4)*: Lewis Publishers.

Morgado, Daniella L., & Frollini, Elisabete. (2011). Thermal decomposition of mercerized linter cellulose and its acetates obtained from a homogeneous reaction. *Polímeros, 21*, 111-117.

Navarro, Abel E., Portales, Rosario F., Sun-Kou, María R., & Llanos, Bertha P. (2008). Effect of pH on phenol biosorption by marine seaweeds. *Journal of Hazardous Materials, 156*(1–3), 405-411. doi: http://dx.doi.org/10.1016/j.jhazmat.2007.12.039

Nazir, M.S., Wahjoedi, B.A., Yussof, A.W., & Abdullah, M.A. (2013). Eco-Friendly Extraction and Characterization of Cellulose from Oil Palm Empty Fruit Bunches. *Bioresources, 8*(2), 2162-2172.

NOES. (1983). Probable Routes of Human Exposure by Phenol. Hazardous Substances Data Bank (HSDB) Retrieved April 2013

Oh, Sang Youn, Yoo, Dong Il, Shin, Younsook, Kim, Hwan Chul, Kim, Hak Yong, Chung, Yong Sik, . . . Youk, Ji Ho. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy.

Carbohydrate Research, 340(15), 2376-2391. doi: http://dx.doi.org/10.1016/j.carres.2005.08.007

Oilgae (Producer). (2008). New Technologies in Heavy Metal Removals from Wastewater. *Oilgae*. Retrieved from http://www.oilgae.com/algae/cult/sew/new/hmr/hmr.html

OSHA. (1996a). Occupational Safety and Health Guideline for 2,4-D (Dichlorophenolxyacetic Acid). Retrieved April 2013 http://www.osha.gov/SLTC/healthguidelines/2_4d-dichlorophenoxyaceticacid/recognition.html

OSHA. (1996b). Occupational Safety and Health Guideline for Phenol. Retrieved April 2013 http://www.osha.gov/SLTC/healthguidelines/phenol/recognition.html

Park, Baker, Himmel, Parilla, & Johnson. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnology for Biofuels 2010, 3*(10). doi: 10.1186/1754-6834-3-10

Qin, W., Wei, H., & Li, S.F.Y. (2002). Determination of Acidic Herbicides in Surface Water by Solid-Phase Extraction Followed by Capillary Zone Electrophoresis. *Journal of Chromatographic Science, 40*, 387-391.

Rubín, Eugenia, Rodríguez, Pilar, Herrero, Roberto, & Sastre de Vicente, Manuel E. (2006). Biosorption of phenolic compounds by the brown alga Sargassum muticum. *Journal of Chemical Technology & Biotechnology, 81*(7), 1093-1099. doi: 10.1002/jctb.1430

Saeed, Muhammad, & Ilyas, Mohammad. (2013). Oxidative removal of phenol from water catalyzed by nickel hydroxide. *Applied Catalysis B: Environmental, 129*(0), 247-254. doi: http://dx.doi.org/10.1016/j.apcatb.2012.09.028

Sajab, Mohd Shaiful, Chia, Chin Hua, Zakaria, Sarani, & Khiew, Poi Sim. (2013). Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions. *Bioresource Technology, 128*(0), 571-577. doi: http://dx.doi.org/10.1016/j.biortech.2012.11.010

Srihari, V., & Ashutosh, Das. (2009). Adsorption of phenol from aqueous media by an agro-waste based activated carbon. *Applied Ecology and Environmental Research, 7*(1), 13-23.

Sun, Yan, Lin, Chun-Xiang, Liu, Ming-Hua, & Liu, Yi-Fan. (2011). Equilibrium Adsorption Behaviours and Kinetics Characteristics of Oxymatrine On A Spherichal Cellulose Adsorbent. *Bioresources, 6*(1), 631-640.

Tay, J.H., Tay, S.T.L., Liu, Y., Show, K.Y., & Ivanov, V. (2006). *Biogranulation Technologies for Wastewater Treatment: Microbial granules*: Elsevier Science.

Vighi, Marco, & Funari, Enzo. (1995). Pesticide Risk in Groundwater (pp. 3-40): Lewis Publishers.

Yang, Ralph. (2003). *Adsorbents - Fundamentals and Applications*: John Wiley & Sons.

Zugenmaier, Peter. (2008). Crystalline Cellulose and Cellulose Derivatives: Characterization and Structures (pp. 1-5): Springer.