UNIVERSITI
TEKNOLOGI
PETRONAS

Manganese (Mn) removal by adsorption using Palm Oil Fuel Ash (POFA)

by

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10707

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

SEPTEMBER 2011

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

....
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SEPTEMBER 2011

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 acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

....

(Mohamad Akmal bin Mohd Mokhtar)

ABSTRACT

Several studies have been conducted on the potential of POFA as an adsorbent to remove heavy metals such as lead and zinc. However, there is limited literature on the removal of manganese using POFA. The main objective of this research is to use POFA to adsorb manganese in aqueous solution. This study focuses on manganese removal by adsorption using POFA without pre-treatment or activation and varying the operating parameters related to adsorption process such as the amount of adsorbent, agitation time, and initial metal concentration. The results show that POFA is a good adsorbent for manganese removal with removal of manganese over 98%. The optimum contact time, adsorbent dosage and initial manganese concentration is 15 minutes, 0.5g, and 10ppm respectively. Characterization of POFA was done before the adsorption where the BET surface area is 10.72 m^2/g, the particle size is 21.125μm and the carbon content is 52.26%. FTIR analysis showed the hydroxyl, carboyl, alcohol, ethers and esters. The adsorption process followed the Freundlich isotherm with $R^2 = 0.9668$ and Pseudo Second Order with $R^2= 0.9999$.

ACKNOWLEDGEMENT

First and foremost, I would like to express my gratitude to Prof. Dr. Khairun Azizi bt Azizli, my supervisor for Final Year Project. She had been very supportive during the entire period of the project. She spent much time and energy to guide us throughout the 14 weeks despite his other commitments and packed schedule as lecturer in UTP. Under his constant supervision, we managed to start our project with a proper planning and proceed until completion according to the timeframe scheduled.

We would like to acknowledge the other Chemical Engineering lecturers and all Chemical Engineering lab technicians who had give some advice and give solution to the problems which students had countered. The advise and knowledge were very helpful and insightful. Once again, thanks to all lecturers from Universiti Teknologi PETRONAS who had provided invaluable input and untiring guidance throughout the project period. With this opportunity, students are able to deepen the knowledge remarkably, both in theory and practical in the basis of a research project.

Apart from these, we would like to express our sincere thanks to the FYP II Coordinators, Dr Lukman in handling all the undergraduates final year project successfully.

Lastly, my sincere thanks to my family for their support and also my friends who had given me encouragement and their lending hand.

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ABBREVIATIONS AND NOMENCLATURE

EFB	Empty fruit bunch
POFA	Palm oil fuel ash
EQR	Environmental Quality Survey
SEPA	Scottish Environmental Protection Agency
FTIR	Fourier Transform Infra Red
FESEM	Field Emission Scanning Electron Microscopy
BET	Brunauer, Emmett and Teller
XRD	X-ray Diffraction
$MnSO_4$	Manganese sulfate
NaOH	Natrium Hydroxide

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The existence of manganese in wastewater of numerous industries has contributed to a significant amount of pollution to the ground and surface water. To control the pollution, the wastewater containing manganese should be treated and this can be accomplished by using activated carbon adsorption, ion exchange, reverse osmosis, electrochemical treatment, evaporation and biological methods. The selection of the treatment method is usually based on the type of wastewater, removal rate, the waste concentration and cost of the treatment (Haghsheno et al., 2009). Thus, the search for the most cost effective and efficient methods for manganese removal is required.

Nowadays, agricultural and natural wastes are used in the adsorption process to remove manganese ion from aqueous solution and this process has become more preferable. Some agricultural and natural waste products have been effectively used as adsorbent for manganese ion from aqueous solution such as bean pod (Budinova et al., 2008) and crab shell particles (Vijayaraghavan et al., 2010). The agricultural and natural wastes are preferable because of their abundance in the environment and their compatibility for removing heavy metals. Therefore, agricultural waste is a good alternative of adsorbent compared to commercialize activated carbon which is costly (Qingbo et al., 2010). Table 1.1 shows latest researches using agricultural wastes in effectively removing heavy metals.

Table 1.1: Researches on agricultural wastes in removing heavy metals

Researchers	**Raw material used**	**Material removed**	**Variables**
Rafeah Wahi et al. (2010)	Sago wastes	Zinc	• Treatment time, Adsorbent dosage, pH, metal concentration
Jinghui Zhang et al. (2010)	Rice husk	Copper	• Preparation condition, pH, Temperature
Renugadevi et al. (2010)	Areca catechu (Pinang) shell	Hexavalent Chromium	• Contact time, Initial metal concentration
Chowdury et al. (2010)	Palm oil fuel ash	Lead	• Metal concentration, Contact time, pH

Kevin K.V. et al. (2011)	Banana, lemon & orange cortex	Copper, Cadmium & Lead	• Pre-treatment, Particle size & Metal concentration

In Malaysia, approximately 15 million tons of palm oil empty fruit bunch (EFB) waste is generated yearly and this agricultural waste is burnt in boilers to generate electricity which produces a lot of solid waste such as, palm oil fuel ash (POFA) (Foo & Hameed, 2010). This situation has encouraged researchers to study the use of palm oil waste as an adsorbent in removing heavy metals. As a result, various researches have shown that palm oil waste is effective in removing heavy metals such as lead (Chowdury et al., 2010), copper (Najua et al., 2008), zinc (Al-Madhound et al., 2005), nickel (Isa et al., 2005) and iron (Isa et al., 2004). However, there is limited study on the adsorption of manganese using POFA. This project will study the effectiveness of POFA to be used as adsorbent for the removal of manganese from aqueous stream.

1.2 Problem Statement

Based on the Malaysian Environment Quality Survey (EQR, 2009), it has been stated that manganese is one of the major pollutant in the underground water sources in Malaysia. Most of the pollution is from the metal processing facilities such as mining industry and may also occur from other industrial facilities producing or using compounds of manganese. So, it is very important to remove manganese as it can cause harm to the living organisms and the environment. Manganese can accumulate in the ecological food chain through consumption which will result in higher level of exposures further up the food chain. The symptoms of increased manganese level for an individual include psychiatric illness, mental confusion, neurological problems and others (Blaurock-Busch, n.d.). To reduce the risks, the manganese needs to be treated to a certain level. The suggested safe level of manganese in drinking water for human has been set at 0.1mg/l by the Malaysian National Guideline for Raw Drinking Water Quality (EQR, 2009) and the level of acceptable discharge in wastewater is 0.2mg/l as stated in the Environment Quality (Industrial Effluent) Regulation 2009.

There are various ways to treat manganese ions from the industrial waste water such as ion exchange, chemical precipitation and reverse osmosis but these methods are rather more expensive when compared to adsorption (Isa, et al., 2004). But the adsorption technique itself is also expensive due to the high cost of activated carbon (Shaarani & Hameed, 2010) and the need for regeneration. For an adsorption to be truly low cost, not only the adsorbent should be easily and cheaply available in abundance but it should also require minimum or no-pretreatment. According to the current source gathering and knowledge, no study has been reported on the adsorption of manganese using POFA.

Thus, there is a need to study effective method, using POFA with no pre-treatment as the adsorbent to find out its effectiveness in removing manganese.

1.3 Objectives

The objectives for this project are as follows:

i. To characterize the POFA before and after the adsorption process.
ii. To study the influence of different operating parameters such as the agitation time, amount of adsorbent, and the concentration of the metal in the solution on the manganese adsorption.
iii. To study the adsorption equilibrium and adsorption kinetics of POFA as an adsorbent in manganese adsorption from aqueous stream.

1.4 Scope of Study

The scope of study for this project basically revolves around the usage of POFA as adsorbent and its adsorption capability in removing manganese in aqueous solution. It is also essential to learn the most preferable adsorbent characteristic so that we can compare its performance. Methods in preparing the manganese solutions are also important to be acquired in this project in order to carry out the experiments. Besides that, wide knowledge of adsorption process, equilibrium and kinetics are also important to ensure the relevancy of this project and that the results gained will be justifiable.

CHAPTER 2

LITERATURE REVIEW

2.1 Manganese and its pollution

Under normal conditions, pure manganese is a silvery grey metal. It displays properties similar to iron, except that it is harder and more brittle. The natural sources of manganese can be found in rocks, soils and water (Scottish Environment Protection Agency (SEPA), 2006). Manganese is chemically reactive and breaks down when mixed with water. Manganese can also be transformed to various compounds which are important for industrial and commercial uses. More information on manganese can be summarized in Table 2.1.

Table 2.1: Manganese properties

Atomic number	25
Atomic mass	54.938 g/mol
Density	7.43 g/cm^3 at 20°C
Melting point	1247°C
Boiling point	2061°C
Discovered by	Johann Gahn in 1774

Source: Adapted from www.lenntech.com/periodic/elements/mn.htm.

Manganese is added to many alloys, because it brings important properties such as strength and magnetism. Besides that, the compounds of manganese also have a variety of uses. For example, potassium permanganate is used as antiseptic, preservative solution and chemical indicator. Manganese chloride is used in the production of dry-cell batteries. Manganese dioxide is used to make matches and fireworks. Manganese sulfate is used in the production of fertilizers (SEPA, 2006).

Manganese is also important for human health as it is an essential trace element. Low consumption of manganese will decrease the health but when high concentration in human body, it become toxic and causes health problems mainly in the respiratory tract and the neurological system. Manganese and its compounds can enter the body by either inhalation of air containing manganese and also ingestion of water or food containing manganese. Inhalation of air containing high levels of manganese can cause a lot of negative health effects such as hallucinations, changes in behaviour, weakness, headaches, tremors, stiffness, balance problems and bronchitis. Exposure to high levels of manganese over long periods of time can cause male impotence. Reported effects through ingestion have included weakness, stiff muscles and trembling hands. The International Agency for Research on Cancer has decided that manganese is not carcinogenic to human (SEPA, 2006). However, exposure to manganese and its compounds beyond the normal condition will still bring negative effect on human health.

The high amount of manganese in the environment is due to the pollution releases by human activities. The most significant releases of manganese to the environment are from metal processing facilities such as mining industry, ore-concentration factories and flotation of various nonferrous metals (Budinova et al., 2008). Releases may also occur from other industrial facilities producing or using compounds of manganese. When released to the environment, manganese has a tendency to accumulate in some organisms such as shellfish and plants such as cereal crops and nuts and this could lead to higher level of exposures further up the food chain.

The increase of manganese may become noticeable in tap water at concentration more than 0.05 mg/l by changes in the color, odor or taste of the water. However, health effects from manganese are not a concern until concentrations are approximately 10 times higher (Connecticut Department of Public Health, n.d.). In Malaysia, as the effort of maintaining the environment safety, the Department of Environment has implemented the effluent discharge standard for manganese at 0.2 mg/l as stated in the Environment Quality (Industrial Effluent) Regulation 2009. Besides that, the Ministry of Health has set the safe level of manganese in drinking water at 0.1 mg/l as stated in the National Guideline for Raw Drinking Water Quality (Environment Quality Report (EQR), 2009) to ensure protection against manganese toxicity.

Figure 2.1 shows the percentage of non-compliance to the effluent discharge limit of manganese at different places in Malaysia (EQR, 2009). So, all the industries in Malaysia must comply with the regulations and must remove manganese from their effluent discharge using appropriate method.

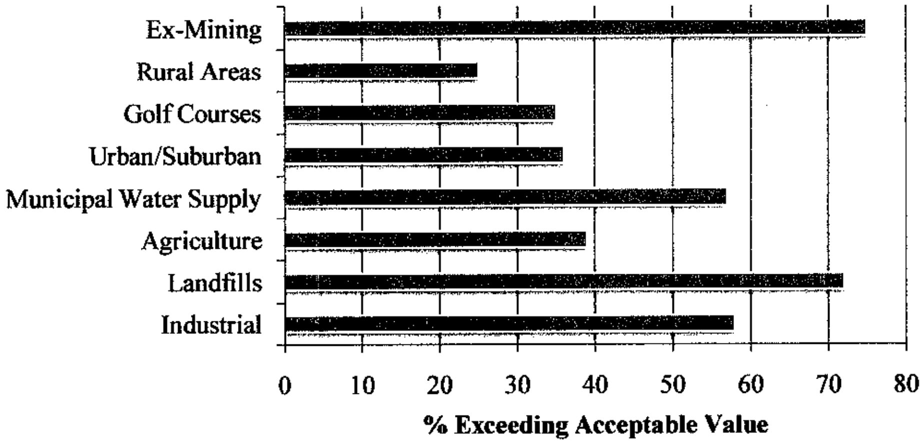

Figure 2.1: Percentage of non-compliance of manganese in Malaysia

Source: Adapted from Environment Quality Report, 2009

2.2 Adsorption Process

Several methods can be used for the removal of manganese from wastewater such as ion exchange, reverse osmosis, biological method, oxidation and filtration, but these methods are rather more expensive compared to adsorption. Nowadays, the use of solids for removing substances from either gaseous or liquid solutions has been widely used. This process, known as adsorption involves the binding of molecules or particles from the gaseous or liquid phase onto the surface of a solid substrate (Ruthven, 1984).

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation at the surface of another phase. Figure 2.2 illustrates the adsorption process where the adsorbing phase is the adsorbent and the material concentrated or adsorbed at the surface of the adsorbent is the adsorbate (Metcalf and Eddy, 2004).

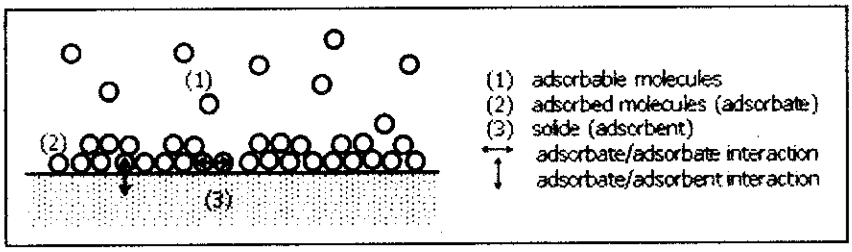

Figure 2.2: Illustration of adsorption process

Source: Adapted from http://lecarbone.com/uk/IMG/adsorption-physique.jpg

There are two principals of adsorption of molecules on surfaces which are physical adsorption and chemical adsorption. The difference between them is the nature of the bonding between the molecule and the surface. In physical adsorption, the only bonding is by the weak Van der Waals force and there is no significant redistribution of electron. In chemical adsorption, the molecule is chemically bonded and substantial rearrangement of electron density is formed between the adsorbate and substrate (Tushar, 2004).

2.2.1 Adsorption Equilibrium

Adsorption results in the removal of solutes from solution and their concentration at a surface, until the amount of solute remaining in solution is in equilibrium with that at the surface. This equilibrium is described by expressing the amount of solute absorbed per unit weight of adsorbent q, as a function of C, the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. The Langmuir and Freundlich isotherm are most frequently used to represent the data of sorption from solution. The Langmuir equation is shown in Equation 2.1:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{C_e} q_m K_L \qquad \text{(Eq. 2.1)}$$

where C_e is the concentration of the adsorbate at equilibrium (mg/l), q is the amount of adsorbate sorbed at equilibrium (mg/g), q_m is the maximum sorption capacity of the adsorption system and K_L is a constant related to the energy of adsorption (Itodo A. U. & Itodo H. U., 2010).

The Freundlich equation has the general form as shown in Equation 2.2:

$$\log q = \frac{1}{n} \log C_e + \log K_f \qquad \text{(Eq. 2.2)}$$

where K_f and 1/n are constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity (Itodo A. U. & Itodo H. U., 2010)

The adsorption isotherm is useful for representing the capacity of an adsorbent and in providing description of the functional dependence of capacity on the concentration of pollutant (W.J. Weber, Jr, 1974).

2.2.2 Adsorption Kinetics

Kinetic study can determine the adsorption kinetic rates and controlling mechanisms of adsorption such as mass transfer and chemical reaction (Vijayaraghavan et al., 2010). Pseudo second order will be used for the kinetic study and the equation can be expressed as shown in Equation 2.3:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \qquad \text{(Eq 2.3)}$$

Where $h=kq_e^2$ (mg g^{-1} min^{-1}) can be regarded as the intial adsorption rate as t approaching 0 and k is the rate constant of pseudo second order (g mg^{-1} min^{-1}).

2.2.3 Adsorption Parameters

From literature, it has been found that the adsorption of metallic ions can be optimized through the analysis of several operating parameters (Vijayaraghavan et al., 2010) such as pH value, agitation time, temperature, adsorbate initial concentration, amount of adsorbent, and desorption capability.

2.2.3.1 pH

The pH of the adsorbate is an important factor in adsorption from aqueous solution because it can change the carbon surface properties with variations of the pH. Moreover, pH value can also affect the state of the ionic species in the solution. Budinova et al. (2008) found that the adsorption of manganese using bean pod activated carbon increase drastically between pH 2 and 4 and reached the maximum value at pH 4. At pH value above that, the adsorption remains constant. Meanwhile, Vijayaraghavan et al. (2010) showed that the biosorption of manganese using crab shell particle reached the maximum value at pH 6.

2.2.3.2 Agitation Time

Isa et al. (2005) found that agitation time plays an important role in the efficient removal of heavy metals. Vijayaraghavan et al. (2010) studied the effect of time with the adsorption of manganese using crab shell and found that 90% of the metal had been adsorbed within 120 minutes and the equilibrium time was approximately 8 hours. This is because the manganese adsorption is higher in the beginning due to the large surface area available but after a certain period it will become saturated and the process will be slowed down to a halt.

2.2.3.3 Temperature

Shaarani and Hameed (2010) showed that temperature can increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles. Temperature can also change the equilibrium capacity of the adsorbent for a particular adsorbate (Almeida et al., 2009). Yuh-Shan & Augustine (2006) used the range between 26^0C and 66^0C to test the effect of temperature on the copper adsorption capacity, and the results showed increased in the adsorption capacity with higher temperature.

2.2.3.4 Adsorbate Initial Concentration

Renugadevi et al. (2010) studied the relation between the concentrations of chromium and the adsorption capacity of shells of Areca catechu where the adsorbate concentrations were varied from 0.06 to 0.12 mg/l. The results showed an increasing percentage of chromium removal when the adsorbate concentration was the lowest. When the adsorbent amount was fixed, the total available adsorption sites were limited thus causing the adsorption to decrease even when the initial adsorbate concentration has increased.

2.2.3.5 Amount of Adsorbent

Tan et al. (2010) studied the effect of adsorbent dosage on the adsorption of dye using pretreated mangrove bark. The range used was between 0.02 g and 1.00 g of adsorbent at a dye concentration of 100 mg/l. The results showed that the adsorption of dye decreased with increasing adsorbent dose. The adsorption decreases because some of the adsorption sites remain unsaturated during the adsorption process and the reduction of adsorbent surface ar

2.2.3.6 Desorption and regeneration

Desorption purpose is to recover the metal adsorbed in concentrated form and also to reuse the adsorbent for more usage thus lowering the adsorption process cost. Vijayaraghavan et al. (2010) had studied desorption of manganese using hydrochloric acid (HCl) and found out that 99.4% desorption could be managed using 0.1M, HCl.

2.3 Adsorbent

Based on the Adsorbent Selection journal by Kent S. Knaebel (n.d), the most important attributes of adsorbent for any application are capacity, selectivity, regenerability, kinetics, compatibility and cost. Adsorption capacity is the most important characteristic of an adsorbent and it can be define as the amount of adsorbate taken up by the adsorbent, per unit mass or volume of the adsorbent. The adsorbent capacity depends on the fluid-phase concentration, temperature, pH and initial condition of the adsorbent. The commercialized adsorbent widely used in the industry is the activated carbon but it is rather costly.

2.3.1 Activated Carbon as Adsorbent Material

Based on Nurul'Ain (2007), activated carbon (AC) can be define as a black, shapeless solid containing major portion of fixed carbon content and other materials such as ash, water vapor and volatile matters in small percentage. Besides that, AC also contain physical characteristic such as internal surface area and pore volume. The large surface area results in a high capacity for absorbing chemicals from gases or liquids.

Activated carbons are usually derived from non-renewable and relatively expensive raw materials such as coconut shell (Gratuito et al., 2008), bituminous coal (Sze and McKay, 2010) and wood (Yorgun et al., 2009). Therefore, researchers have tried to identify alternative resources for manufacturing affordable adsorbent to replace the commercialized activated carbon. In recent years, many researchers have focused on adsorbent from industrial or agricultural by-products and waste materials, for example, wood particleboard wastes (Girods et al., 2009), sugar beet bagasse (Demiral and Gunduzog˘lu, 2010), and palm oil waste (Chowdhury et al., 2010).

2.3.2 Palm Oil Wastes as Adsorbent Material

Malaysia is one of the major palm oil production countries in the world producing up to 17 million tons of palm oil in 2010 (Yusof Basiron, 2011.) The oil consists of only 10% of the palm yield and the other 90% will be biomass wastes (ClimateAvenue, 2010). Thus, there will be a large generation of biomass wastes from oil palm industries up to 150 million ton which consists of empty fruit bunch, fibers and palm shell kernels. This biomass is used for electricity generation using burning method which produces a lot of solid waste or usually known as palm oil fuel ash (POFA).

With such abundance of raw material, it is desirable to produce adsorbent from palm oil wastes as it provides a potentially inexpensive alternative to existing commercial activated carbon (Chowdhury et al., 2010).

Saifuddin M. N. and Kumaran (2005) have shown that it is feasible to prepare adsorbent with sufficient densities and high porosity from oil palm fruit waste. The exchange/sorption properties of palm oil waste are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have a high affinity for metal ions. Besides that, palm oil waste contains lignin which is compatible with chemical adsorption (Yuh-Shan, 2006). Nor Fatiha Zainudin et al. (2005) had determined the chemical composition and BET surface area of POFA and the result is included in Table 2.2. Table 2.3 below shows other researches that had studied the effectiveness of palm oil wastes as adsorbent.

Table 2.2: Chemical composition and BET surface area of POFA

Chemical composition	**SiO_2**	**K_2O**	**CaO**	**P_2O_5**	**MgO**	**Al_2O_3**	**C**	**Fe_2O_3**	**Others**	**Ignition loss**
Percentage (%)	40.0	12.1	10.0	8.2	6.4	6.1	5.4	2.5	2.0	7.3
BET surface area, m^2/g						10.2				

Source: Adapted from Nor Fatiha Zainudin et al (2005)

Table 2.3: Other researches using palm oil waste as adsorbent

Researchers	**Raw material used**	**Material removed**
Najua et al. (2008)	Palm oil kernel shell	Copper
Foo and Hameed (2010)	Palm oil empty fruit bunch	Methylene blue
Shaarani et al. (2010)	Palm oil empty fruit bunch	2,4-dichlorophenol
Chowdury et al. (2010)	Palm oil fuel ash	Lead
Bakhtiar et al. (2011)	Palm oil shell	4-Chloro-2-Methoxyphenol

CHAPTER 3

METHODOLOGY

3.1 Overview of the Project

Figure 3.1 shows the overall project flow chart for the experimentation and also analysis of results. More detailed explanation of the methodology is provided further in this chapter.

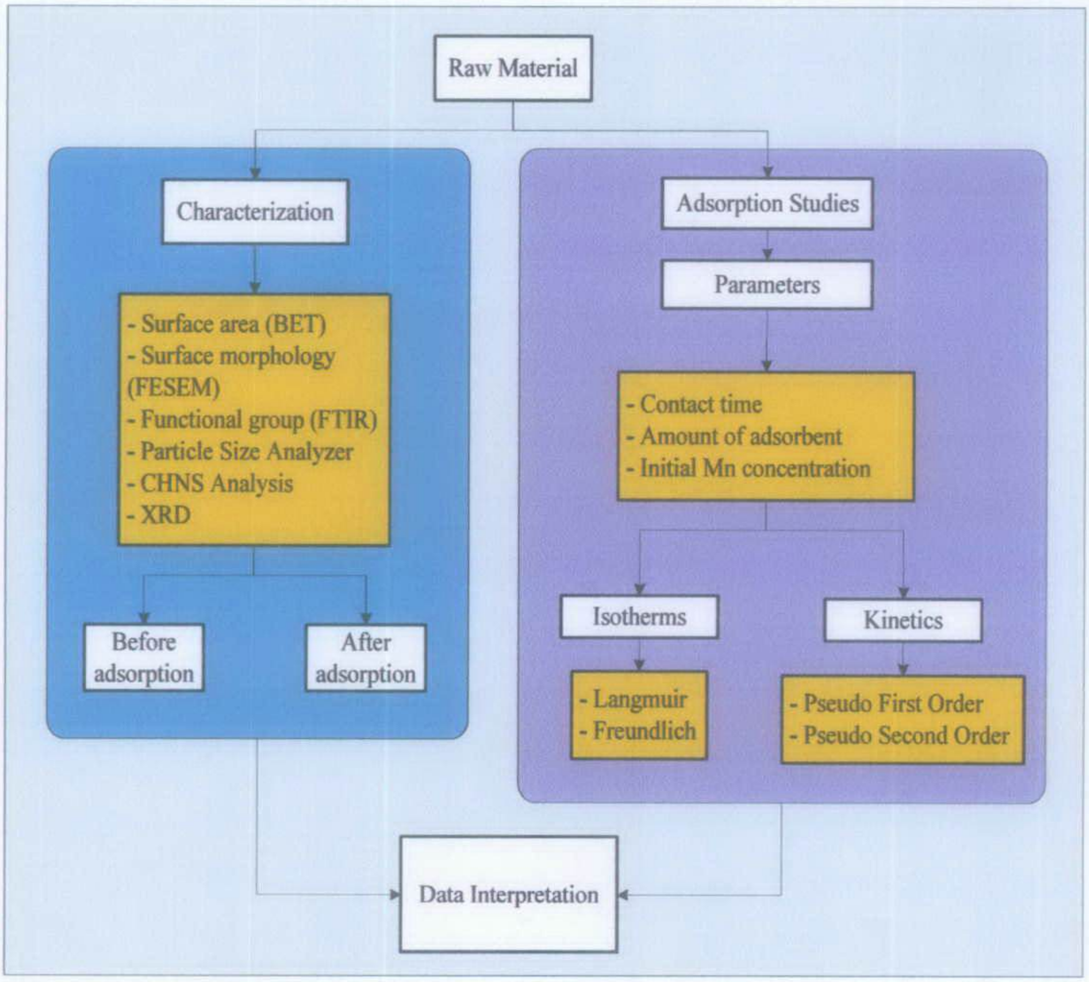

Figure 3.1: Flow chart of overall project

3.2 Equipment and chemicals required

Tables 3.1 and 3.2 list all the required equipments and chemicals that had been identified for this project. The purpose for each equipment and chemical is also provided.

Table 3.1: Equipment lists and its purposes

No	Equipment	Purpose
1	Conical flasks	To carry out the experiments.
2	Digital weighting scale	To measure the weight of adsorbent
3	Magnetic strirrer	To carry out the experiments
4	pH meter	To measure the pH of the solution.
5	Direct reading spectrophotometer	To measure the concentration of the solution.
6	Filter paper	To measure the concentration of the solution.
7	Adsorption analyzer, spectrometer and electron microscope	To analyze the adsorbent.

Table 3.2: Chemical lists and its purposes

No	Chemicals	Purpose
1	Palm oil fuel ash (POFA)	Adsorbent material
2	Manganese sulfate ($MnSO_4$)	Adsorbate material
3	Sulphuric Acid (H_2SO_4)	pH adjuster
4	Natrium Hydroxide (NaOH)	pH adjuster
5	Hydrochloric Acid (HCl)	Desorption solution
6	Deionized water	Adsorbent pretreatment

3.3 Experimental Procedures

3.3.1 Adsorbent preparation and Characterization

The palm oil fuel ash (POFA) used was collected from a local palm oil mill. 500g of the raw POFA was weighted and put into a 500ml beaker. For the pre-treatment, the POFA was first washed thoroughly with distilled water to remove foreign particles. After each washing, the POFA was filtered and then dried at 110°C for 24 hours in an oven. For storage, the 500ml beaker was labeled and covered with aluminium foil.

Fourier transform infrared (FTIR) spectroscopy was applied to determine surface functional groups of POFA from the scanning range of 4000 to 400 cm^{-1}, while elemental analysis was detected by using CHNS analyzer. POFA's particle size was determined using the Particle size analyzer (Mastersizer 2000, Malvern). POFA surface study was also done using the BET analysis.

3.3.2 Preparation of solution

For the preparation of solution, analytical grade manganese sulfate ($MnSO_4$) monohydrate was weighted and dissolved in distilled water. The amount of $MnSO_4$

needed was determined using manual calculations to get solutions with 1000ppm, 30ppm, 20ppm and 10ppm of manganese. Volumetric flasks 1L and 500ml were used in the preparation of the solution with different concentrations. The pH of the solution was measured and observed as 6.5 ± 0.5 and no chemicals were added to change the pH value.

Figure 3.2: Manganese sulfate solutions

3.3.3 Contact Time Experiment

Eight 100ml beakers were each filled with 50ml of manganese sulfate solution, 10ppm. 0.5g of POFA was weighted and added to the beakers. The eight beakers were then agitated at 360 rpm using a mechanical stirrer for a predetermined time. For beaker 1, it will be agitated for 15 minutes and for beaker 2, it will be agitated for 30 minutes and the trends goes on with the increment of 15 minutes until beaker 8 which will be agitated for 2 hours. The samples were then filtered and stored in test tubes and the final Mn concentrations were measured.

Figure 3.3: Batch experiment conducted on a magnetic stirrer

3.3.4 Adsorbent Dosage Experiment

Four 100ml beakers were each filled with 50ml of manganese sulfate solution, 10ppm. 0.05g, 0.5g, 1.0g, and 1.5g of POFA was weighted and added to each of the beaker. The beakers were then agitated at 360 rpm using a mechanical stirrer for 15 minutes. The samples were then filtered and stored in test tubes and the final Mn concentrations were measured.

3.3.5 Initial Concentration Experiment

Three 100ml beakers were each filled with 50ml of manganese sulfate solution with different concentration of 10ppm, 20ppm and 30ppm. 0.5g of POFA was weighted and added to the beakers. The three beakers were then agitated at 360 rpm using a mechanical stirrer for 15 minutes. The samples were then filtered and stored in test tubes and the final Mn concentrations were measured.

3.3.6 Analytical Techniques

Manganese concentrations of the samples were measured using an Atomic Adsorption Spectrophotometer (DR4000 UV-Vis Spectrophotometer) after filtration with filter papers.

CHAPTER 4
RESULT AND DISCUSSION

This chapter presents the results and discussions for the main aspects of the research which is the adsorbent characterizations and the adsorption performance of the palm oil fuel ash (POFA) towards manganese ions at different conditions. Figure 4.1 shows the pre-treated POFA before being used in the experiments.

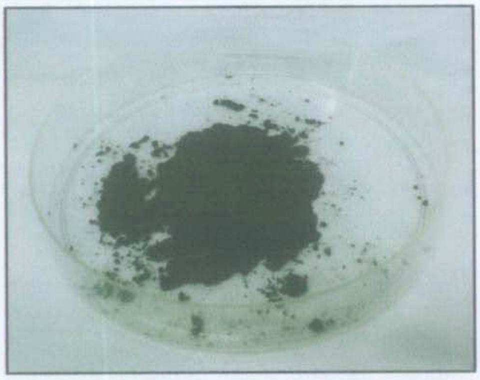

Figure 4.1: Picture of pre-treated POFA

4.1 Characterization of POFA

Characterization of the POFA is very important in order to classify the adsorbent for specific uses. Besides that, with characterization we can further understand the adsorbent material being used and relates it with the adsorptions results to further support our findings. Adsorbent material is normally characterized according to their physical and chemical properties. The characteristics of adsorbent depend on the physical and chemical properties of the raw materials as well as the activation method used. In this project, the characterization of POFA will be done using various methods and techniques such as FTIR, PSA, CHNS, and BET, which will be explained later in this chapter

4.1.1 Fourier Transform Infra Red (FTIR)

FTIR technique is an analytical method used to identify the chemical structure of many inorganic chemical and also organics materials or compound. Infrared can also identify the presence of certain functional groups within a molecule. Figure 4.2 show the result of FTIR obtained for the pre-treated POFA

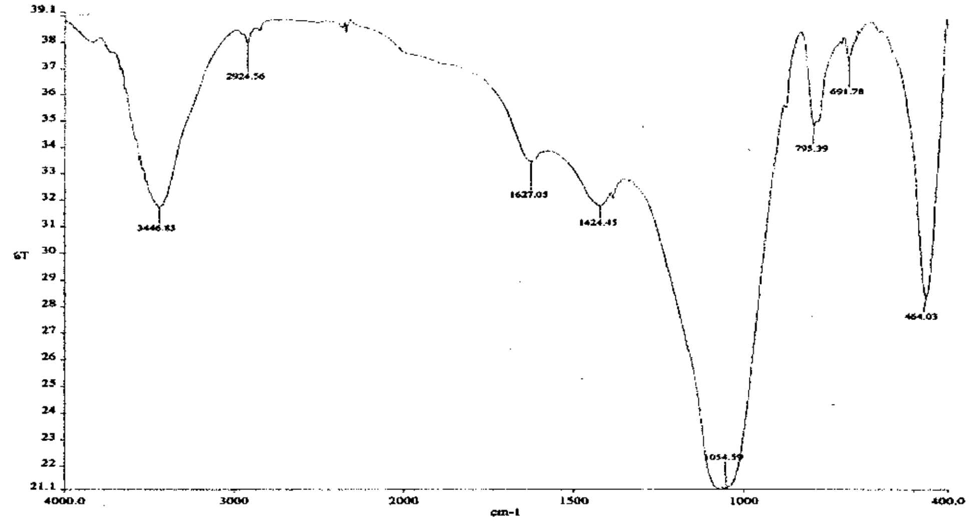

Figure 4.2: Infrared Spectra of POFA

The broad band at 3200 – 3700 cm^{-1} corresponds to the stretching vibration of the –OH group. The peak at 2924.56 cm^{-1}, 795.39 cm^{-1} and 691.78 cm^{-1} corresponds to the C-H stretch of alkanes groups, C=C of alkenes group and C≡C of alkynes group respectively. The peak at 1054.59 corresponds to the C-O stretch of alcohol, esters or ethers functional groups. The stretching of Si-O groups alternating bound to the Al-O bonds detects a signal at 1050cm^{-1} and band around 800cm^{-1} is an indicative of the Al-O or Si-O-Al groups (Chun et al., 2008). As shown in Figure 4.3, it can be concluded that FTIR analysis of pre-treated POFA is similar to the FTIR spectra shown by oil palm ash studied by Foo & Hameed (2009).

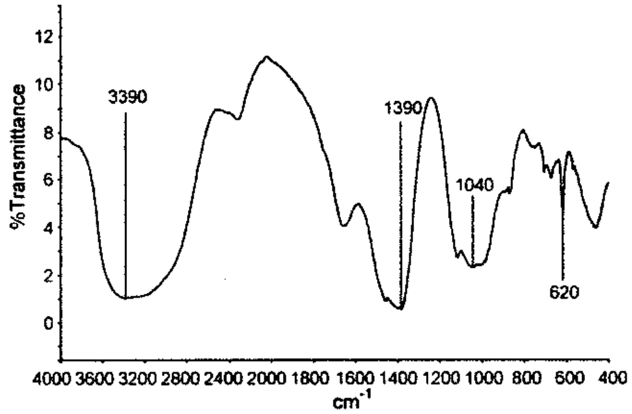

Figure 4.3: FTIR transmission image of oil palm ash

Source: Adapted from Foo & Hameed (2009).

4.1.2 Particle Size Analyzer (PSA)

Particle Size Analyzer (PSA) is a method used to identify the particle size of a sample. The POFA obtained for this project is taken directly from the boiler and the particle size is unknown. Therefore, the particle size is needed in order to understand more about the adsorbent being used. Zainudin et al. (2005) reported that smaller adsorbent particle size will result in higher range of adsorption capacity for the adsorbent. The result as shown in Figure 4.4 shows that the mean particle size of POFA is 21.125μm.

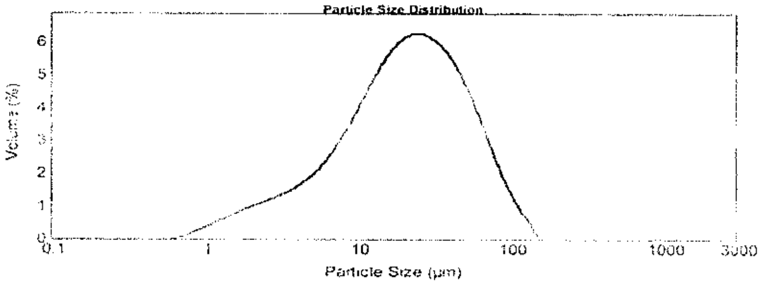

Figure 4.4 Particle size distributions for POFA

4.1.3 CHNS Analyzer (PSA)

CHNS analysis is a method to identify the elements of carbon, hydrogen, nitrogen and sulphur of a given sample. Based on Foo & Hameed (2010), with higher carbon content, we can see a higher value of surface area and pore volume. Table 4.1 shows the results of CHNS analysis of POFA

Table 4.1: CHNS analysis result of POFA

Element	POFA
Carbon	52.26
Hydrogen	4.891
Nitrogen	20.27
Sulphur	11.71

4.1.4 Brunauer, Emmett and Teller (BET)

The BET method is based on adsorption of gas on a surface. The amount of gas adsorbed at a given pressure allows the determination of the surface area. From the surface analysis, we can relate them to the adsorption capacity. The result is shown in Table 4.2.

Table 4.2: BET analysis result of POFA

Properties	**POFA**
BET surface area (m^2/g)	10.72
Langmuir surface area (m^2/g)	16.33
Average pore size (Å)	74.01
Total pore volume (cm^3/g)	0.02

4.1.5 Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscope (FESEM) creates the magnified images by using electrons. FESEM shows 3 dimensional images at much higher magnifications. The image created without light waves will be rendered black and white. It can be used to estimate the pore size of an adsorbent quantitatively and the morphology of the adsorbent. With this we can see how the pore and structure of POFA before and after the adsorption. With the generated images, we can conclude that adsorption had happened or not and what is the material being adsorbed using EDX analysis. The result of FESEM is not available due to some constrains.

4.1.6 X-Ray Fluorescence (XRF)

XRF analysis is the emission of characteristic from a material that has been excited by bombarding with high energy X-rays. This analysis can be used for elemental analysis and chemical analysis. In most cases, the chemical elements of POFA are found to be silicon dioxide, aluminium oxide, iron oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide and sulfur trioxide (Foo & Hameed, 2009). The result of the XRF for this project had been taken from the previous studies done using the same source of POFA by Chea Chandara et al. (2010) and the chemical composition is shown in Table 4.3

Table 4.3: Chemical composition of POFA

Component	Chemical composition (mass %)
SiO_2	61.85
Al_2O_3	5.65
Fe_2O_3	5.45
CaO	5.09
MgO	2.79
SO_3	0.28
Na_2O	0.10
K_2O	5.09
Ti_2O	0.32
P_2O_5	3.32
Unburned Carbon	6.01

Source: Adapted from Chea Chandara et al (2010).

4.1.7 X-Ray Diffraction (XRD)

XRD analysis is a method used to investigate crystalline material structure. The result of XRD is not available due to some constrains and only the expected result will be discussed here. Foo & Hameed (2010) have done the XRD analysis on a similar oil palm ash. The XRD of oil palm ash in the adsorption of sulfur dioxide gas, reflected the quantitative presence of crystalline minerals, endorsed by vaporization, melting, crystallization, condensation and precipitation processes during the combustion process. Sylvite was found at almost all prominent peaks. Figure 4.5 shows the result of XRD done by Foo & Hameed (2010).

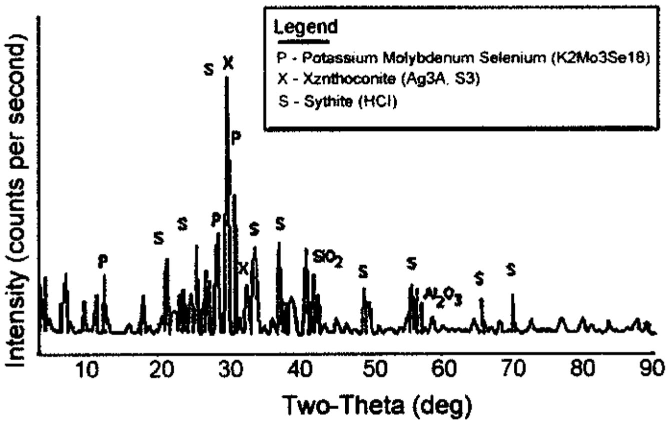

Figure 4.5: XRD spectroscopy of oil palm ash

Source: Adapted from Foo & Hameed (2010).

4.2 Effect of contact time

Adsorptions of manganese using POFA were measured at a given contact for initial manganese concentrations of 10 mg/L. Figure 4.6 shows that percentage of manganese removal increases with increasing contact time. In other words, the amount of manganese adsorbed into POFA increases with increasing contact time until equilibrium is attained within 15 minutes. The equilibrium time is taken at 15 minutes because after that time interval the percentage of manganese removal varies very little within 97 – 98%. For the optimization of later experiments, 15 minutes will be used as the time parameter. From the results, we can observe that POFA is a very good adsorbent for manganese removal because it can remove about 98% of the initial amount of manganese concentration within only 15 minutes.

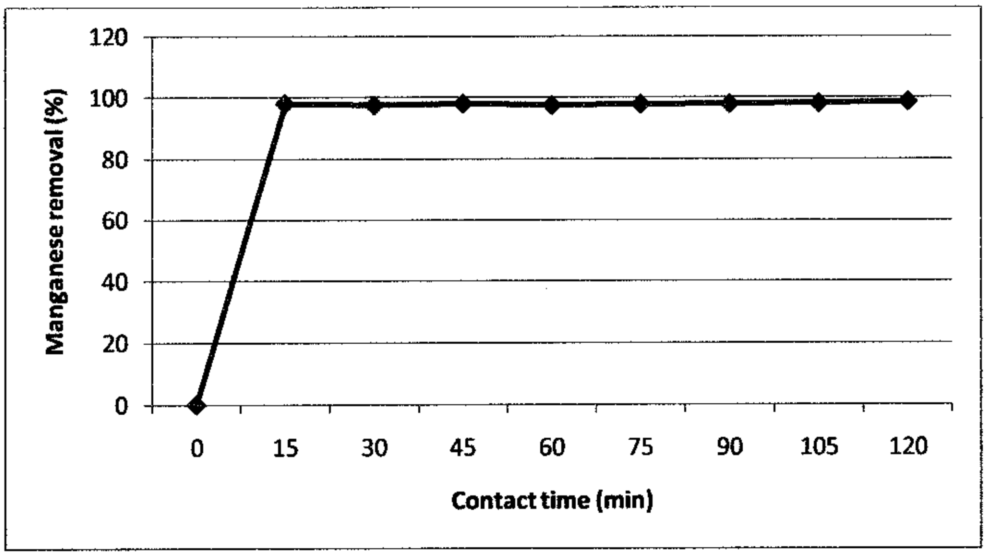

Figure 4.6: Effect of contact time for POFA

From Figure 4.6, there was a sharp increase in the amount of manganese adsorbed during the first 15 minutes of the experiment but after that, the rate and amount of manganese adsorbed fluctuate and reached a nearly constant value or had reached equilibrium. This is because the manganese adsorption is higher in the beginning due to the large surface area available but after a certain period it will become saturated and the process will be slowed down to a halt.

4.3 Effect of initial manganese concentration

A series of batch experiments were conducted for various initial manganese concentrations to establish the adsorption isotherms. This experiment is done under the specified conditions of the initial pH of 6.5, contact time of 15 minutes, adsorbent dosage of 0.5 g, and temperature of 25°C using mechanical stirrer. Figure 4.7 shows the initial adsorbate concentration versus percentage of manganese removal. From the results, we can observe that the optimum value for the initial manganese concentration is 10ppm which gives the highest manganese removal percentage of 98%.

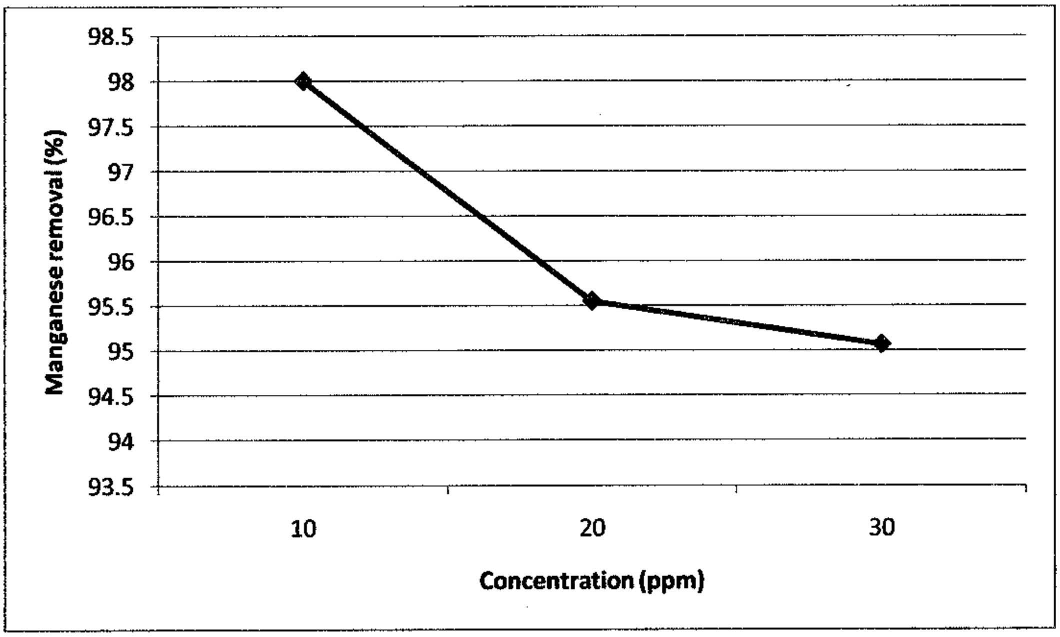

Figure 4.7: Effect of initial manganese concentration on the adsorption process

The results showed an increasing percentage of chromium removal when the adsorbate concentration was the lowest. When the adsorbent amount was fixed, the total available adsorption sites were limited thus causing the adsorption to decrease even when the initial adsorbate concentration has increased.

4.4 Effect of adsorbent dosage

A series of batch experiments were conducted for various dosage of POFA which was 0.05g, 0.5g, and 1.0g. This experiment is done under the specified conditions of the initial pH of 6.5, contact time of 15 minutes, initial manganese concentration of 10ppm, and temperature of 25°C using mechanical stirrer. Figure 4.8 shows the adsorbent dosage versus the percentage of manganese removal. From the results, we can observe that 0.5 g of adsorbent dosage give the highest manganese removal with 95%.

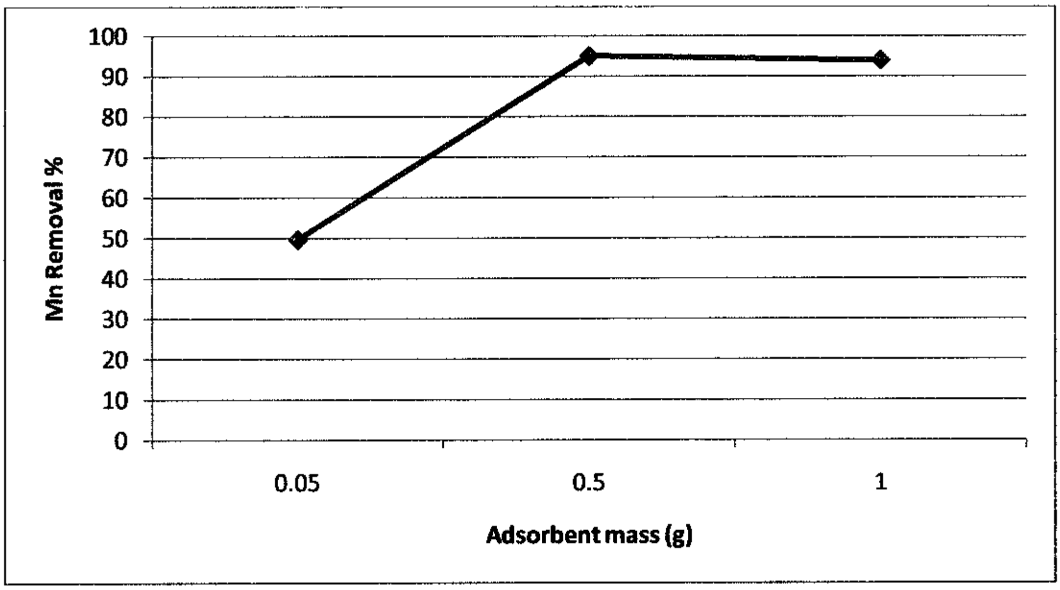

Figure 4.8: Effect of adsorbent dosage on the adsorption process

The results showed that the adsorption of manganese increase from 0.05 g of adsorbent to 0.5 g. This is because the small amount of available pore cannot adsorb the manganese ion thus limiting the adsorption capacity. From 0.5 g to 1.0 g, the manganese removal decreased with increasing adsorbent dose. The adsorption decreases because some of the adsorption sites remain unsaturated during the adsorption process and the reduction of adsorbent surface area.

4.5 Equilibrium study

Both Langmuir and Freundlich isotherms graph are plotted to see which isotherm best represent the adsorption. The Langmuir and Freundlich models were fitted to the experimental data obtained from POFA with relatively good applicability as shown in Figure 4.9 and Figure 4.10. The fitted parameters for these two models are summarized in Table 4.4 and indicate that the adsorption of manganese by POFA is assumed to be favorable.

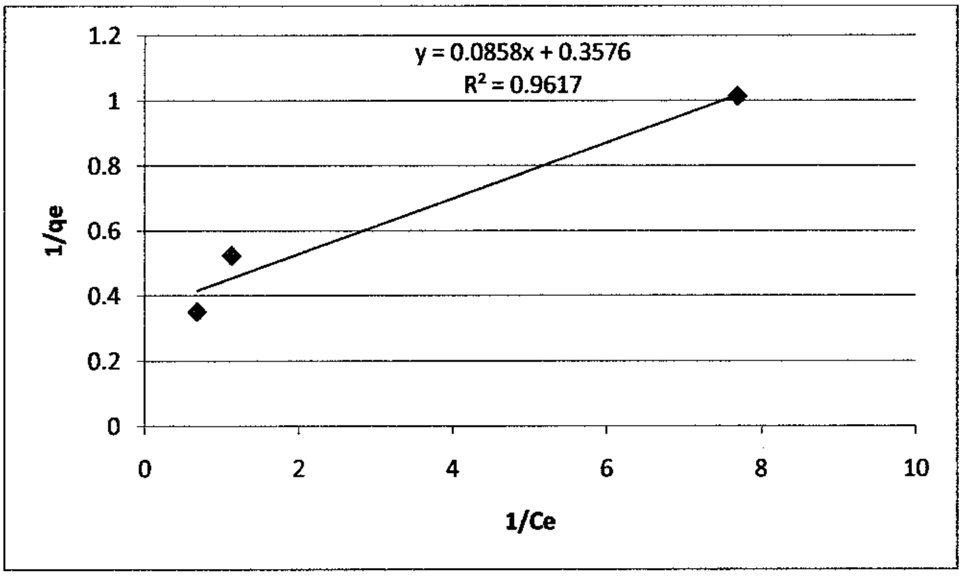

Figure 4.9: Langmuir isotherm for POFA

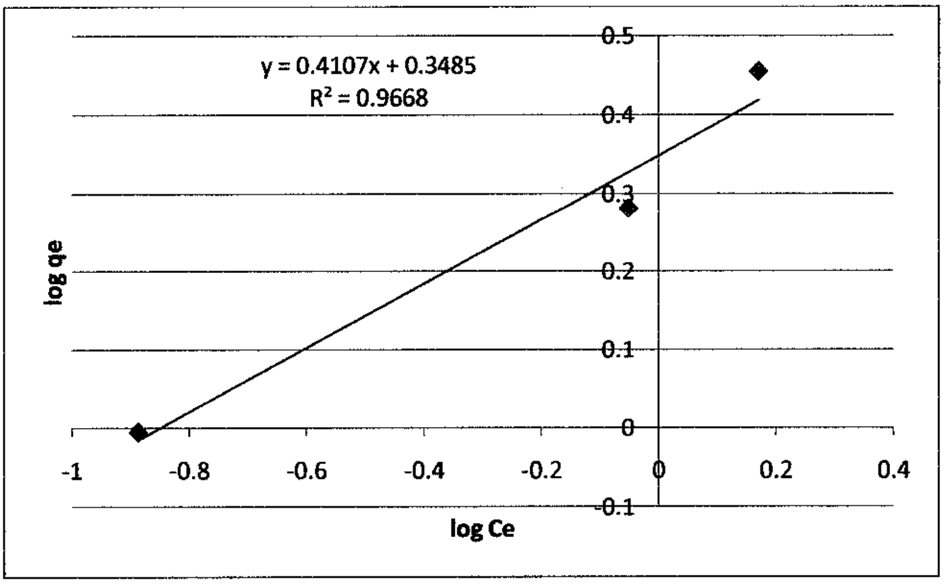

Figure 4.10: Freundlich isotherm for POFA

The adsorption using POFA is best represent by Freundlich model with R^2 of 0.9668. The best fitted isotherm is selected based on value of R2 which is goodness of fit criteria computed by linear regression (Vondrias et al., 2002).

The surface of adsorption that follows Langmuir model is assumed to be homogenous that indicates surface energy is constant over all sites. Adsorbed atoms or molecules are adsorbed at definite and localized sites where only one atom or molecule can accommodate those sites. On the other hand, Freundlich model assumed that surface of adsorption is heterogeneous in the sense that the adsorption energy is distributed. Surface topography is patchwise where sites having same adsorption energy are grouped together into one patch. Adsorption energy can be defined as the energy of interaction between adsorbate and adsorbent. However, each patch is independent from each other, that there is no interaction between patches. Freundlich further assumed that on each patch, only one adsorption site can be adsorbed by the adsorbate molecule. Thus, the Langmuir model may be applicable for the description of equillibria of each patch (Duang D. Do, 1998). Table 4.4 shows the constants from the equilibrium study.

Table 4.4: Freundlich and Langmuir constants for POFA

Freundlich Isotherm			**Langmuir Isotherm**		
K_f	n	R^2	K_L	q_m	R^2
2.231	2.435	0.9668	4.168	2.796	0.9617

4.6 Kinetic Study of Adsorption

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo second equations are applied to model the kinetics of manganese adsorption onto POFA. The t/q_t versus t is plotted to determine the constants qe, k and h. Figure 4.11 shows the plotted graph.

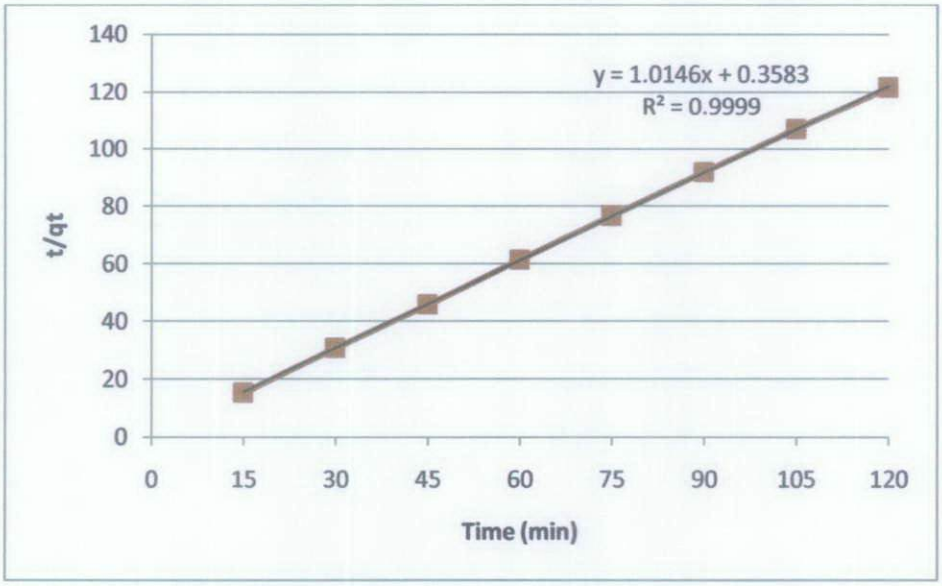

Figure 4.11: Pseudo second order kinetics graph

The plots of the pseudo second order kinetics graph give a straight line which shows that it is applicable with R^2 is 0.9999. The constant related to the model are presented in Table 4.5. The theoretical values of q_e for POFA agree very well with the experimental value. This suggests that the adsorption of manganese follows the pseudo second order kinetics model which relies on the assumption that chemisorptions may be the rate limiting step. The manganese ion will stick to the alumina surface by forming a chemical bond. Covalent bond wasusually formed where adsorbate is tends to find sites that maximize their coordination number with the surface.

Table 4.5: Pseudo second order constants for POFA

Initial Concentration(mg/L)	**k (g/mg min)**	**Q_e (mg/g)**	**h (mg g^{-1} min^{-1})**	**R^2**
10	2.711	0.985	2.7909	0.9999

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The present study showed that POFA is a good adsorbent for manganese removal due to its capability of removing over 98% of Mn from aqueous solution. The final concentration of manganese can be reduced down to lower than 0.2 mg/L which comply with the industrial effluent regulation.

Result from the FTIR studies shows POFA's functional group. POFA used in this study have a median particle size of 21.125 μm and contains carbon content of 52.26%.

The optimum contact time for manganese adsorption is 15 minutes. The optimum initial concentration for Mn adsorption is 10ppm. The optimum adsorbent dosage is 0.5 g. Both Langmuir and Freundlich models were fitted to the experimental data with relatively good applicability but the adsorption is well described by the Freundlich model with R^2 of 0.9668. The Freundlich equation for this manganese adsorption is: $q_e=2.231C_e^{0.4107}$

5.2 Recommendations

For further studies, it is recommended to study more adsorption parameters such as temperature and pH value. It is important to find out all the optimum parameters in manganese adsorption for the most effective adsorption process.

Since this study only focus on removing manganese, further studies can be done involving the real wastewater which contains more heavy metal in one solution. With this, we can get one step closer to implement POFA for removal of heavy metal.

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APPENDICES

Appendix I

Calculation for percentage of metal uptake

$$Percentage\ Uptake = \frac{Initial\ concentration - Final\ concentration}{Initial\ concentration} \times 100\%$$

Let say the initial concentration is 40 ppm and the final concentration is 20 ppm, therefore the percentage of metal uptake is:

$$\frac{40\ ppm - 20\ ppm}{40\ ppm} \times 100\% = 50\%$$

Calculation for adsorption capacity

$$\frac{Initial\ concentration - Final\ concentration}{Weight\ of\ adsorbent\ (g)} \times volume\ of\ solution\ (L)$$

Let say the initial concentration is 40 ppm and the final concentration is 20 ppm, volume of solution 0.025 L and the weight of adsorbent used is 0.1 g, therefore the adsorption capacity is

$$\frac{40\ ppm - 20\ ppm}{0.1\ g\ MnSO_4} \times 0.025\ L = 5\ mg\ Mn/MnSO_4$$

Preparation of manganese sulfate solution

i. Stock solution

MW $MnSO_4$ = 169.01 g/mol

MW Mn = 54.938 g/mol

1 g of Mn in relation to $MnSO_4$ = 169.01 / 54.938 = 3.076 g

Hence, weight out 3.076 g $MnSO_4$ and dissolve in 1 L distilled water to make a 1000 ppm Mn standard solution.

ii. Different concentration

Dilution formula: $M_1V_1 = M_2V_2$

M_1 = Concentration of stock solution

V_1 = Volume of stock solution

M_2 = Concentration of desired solution

V_2 = Volume of desired solution

Appendix 2

Experimental Data

i. Effect of contact time on different metal concentration

contact time (min)	residue conc. (ppm), Ct	initial conc. (ppm), Co	weight of adsorbent (g), m	Volume of solution (L), V	% Mn removal
0	10	10	0.5	0.05	0
15	0.2	10	0.5	0.05	98
30	0.25	10	0.5	0.05	97.5
45	0.2	10	0.5	0.05	98
60	0.25	10	0.5	0.05	97.5
75	0.22	10	0.5	0.05	97.8
90	0.21	10	0.5	0.05	97.9
105	0.19	10	0.5	0.05	98.1
120	0.13	10	0.5	0.05	98.7

contact time (min)	residue conc. (ppm), Ct	initial conc. (ppm), Co	weight of adsorbent (g), m	Volume of solution (L), V	% Mn removal
0	20	20	0.5	0.05	0
15	0.65	20	0.5	0.05	96.75
30	0.46	20	0.5	0.05	97.7
45	0.64	20	0.5	0.05	96.8
60	0.55	20	0.5	0.05	97.25
75	0.65	20	0.5	0.05	96.75
90	0.71	20	0.5	0.05	96.45
105	0.72	20	0.5	0.05	96.4
120	0.89	20	0.5	0.05	95.55

contact time (min)	residue conc. (ppm), Ct	initial conc. (ppm), Co	weight of adsorbent (g), m	Volume of solution (L), V	% Mn removal
0	30	30	0.5	0.05	0
15	0.78	30	0.5	0.05	97.4
30	1.17	30	0.5	0.05	96.1
45	1.25	30	0.5	0.05	95.83333
60	1.22	30	0.5	0.05	95.93333
75	1.24	30	0.5	0.05	95.86667
90	1.33	30	0.5	0.05	95.56667
105	1.34	30	0.5	0.05	95.53333
120	1.48	30	0.5	0.05	95.06667

ii. Effect of adsorbent dosage

volume of solution (L)	weight of adsorbent (g)	residue conc. (ppm)	intial conc. (ppm)	% Mn removal	adsorption capacity (mg/g)
0.05	0.05	10.08	20	49.6	9.92
0.05	0.5	1	20	95	1.9
0.05	1	1.2	20	94	0.94

iii. Isotherm study

volume of solution (L)	weight of adsorbent (g)	residue conc. (Ce)	intial conc. (ppm)	q (mg/g)	1/Ce	1/q	log Ce	log q
0.05	0.5	0.13	10	0.987	7.6923	1.0131712	-0.88605	-0.005682847
0.05	0.5	0.89	20	1.911	1.1235	0.5232862	-0.05060	0.281260687
0.05	0.5	1.48	30	2.852	0.6757	0.3506311	0.17026	0.455149521

iv. Kinetic study

contact time (min)	residue conc. (ppm), Ct	initial conc. (ppm), Co	weight of adsorbent (g), m	Volume of solution (L), V	qt (mg/g)	qe	(qe-qt)	log(qe-qt)	t/qt
15	0.2	10	0.5	0.05	0.98	0.987	0.007	-2.15490	15.30612
30	0.25	10	0.5	0.05	0.975	0.987	0.012	-1.92081	30.76923
45	0.2	10	0.5	0.05	0.98	0.987	0.007	-2.15490	45.91836
60	0.25	10	0.5	0.05	0.975	0.987	0.012	-1.92081	61.53846
75	0.22	10	0.5	0.05	0.978	0.987	0.009	-2.04575	76.68711
90	0.21	10	0.5	0.05	0.979	0.987	0.008	-2.09691	91.93054
105	0.19	10	0.5	0.05	0.981	0.987	0.006	-2.22184	107.0336
120	0.13	10	0.5	0.05	0.987	0.987	0	#NUM!	121.5805