OPTIMIZATION OF MERCURY REMOVAL USING PALM OIL FUEL ASH

NOR AKMALINA BINTI MUSTAZAR

BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG

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NOR AKMALINA BINTI MUSTAZAR

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Dedicated to my family, and my friends.

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ABSTRACT

The palm oil fuel ashes (POFA) were used as biosorbent for the removal of heavy metals ions from wastewater. From the preliminary experimental results, it shows that the POFA had good adsorption capability for Hg (II) ions. This study aims to employ low-cost biosorbent such as activated palm oil fuel ash to remove mercury (II) from wastewater. Initially, 5factors were screened using 2^{5-1} factorial analysis. Factors that gave the significant effect which are contact time and agitation speed had a maximum point which is likely to be the optimum point and possible for the optimization process. The effect of two biosorption variables (contact time and agitation speed) were investigated using central composite design (CCD) which is a subset of response surface methodology (RSM). Quadratic model was developed for Hg (II) percentage removals. A 22 factorial central composite design was used to get the mutual interaction between variables. The optimum adsorption conditions were obtained at contact time of 5 hr and agitation speed of 150 rpm with desirability of 0.95. At these optimum points, the mercury removal efficiency was calculated as 98.93 % in batch mode. Based on the predicted and experimental results presented, the experimental values were in good agreement with the predicted values proposed by the model with an error less than 10 % and proved to be an adequate model. The results indicated that POFA has the potential to be used as an adsorbent for the removal of Hg (II) from aqueous environments due to its significant adsorption capacity and naturally abundance at low cost value.

ABSTRAK

Abu bahan api kelapa sawit (POFA) telah digunakan sebagai penyerap untuk penyingkiran logam ion berat dari air sisa. Daripada keputusan eksperimen sebelum ini, ia menunjukkan bahawa POFA mempunyai keupayaan penyerapan yang baik untuk ion merkuri. Kajian ini bertujuan untuk menggunakan material penyerap yang berkos rendah seperti abu bahan api minyak kelapa sawit untuk membuang merkuri (II) daripada air sisa. Pada awal kajian, 5faktor telah disaring dengan menggunakan 2^{5-1} faktor analysis. Faktor-faktor yang memberi kesan yang ketara ialah masa tindakbalasdan kelajuan yang mempunyai nilai yang paling tinggi. Keadaan ini menjadi faktor optimum dalam proses pengoptimuman kadar penyingkiran merkuri daripada air sisa. Kesan dua pembolehubah bagi penyerapan merkuri (masa tindakbalas dan kelajuan) telah diuji dengan menggunakan reka bentuk eksperimen gabungan berpusat (CCD) yang merupakan subset kaedah gerak balas permukaan .Model kuadratik bagi peratusan penyingkiran merkuri (II) telah dihasilkan . Sebanyak 22 reka bentuk komposit pusat faktorial telahpun digunakan untuk mendapatkan interaksi antara pembolehubah. Syarat-syarat penyerapan optimum yang diperolehi ialah 5 jam bagi masa bertindakbalas dan 150 rpm bagi nilai kelajuan dengan galakan sebanyak 0.95. Pada bahagian optimum pula, penyingkiran merkuri telah berjaya mencapai 98.93% dalam penyingkiran merkuri yang telah dilaksanakan di dalam skala kecil. Berdasarkan ramalan dan keputusan eksperimen diperolehi, nilai eksperimen berada dalam nilai yang telah diramalkan oleh model dengan menghasilkan nilai ralat yang kurang daripada 10% dan terbukti menjadi model yang sesuai untuk digunakan. Hasil kajian mendapati bahawa POFA mempunyai potensi untuk digunakan sebagai penyerap bagi menyingkirkan merkuri(II) dari air sisa daripada industri kerana kapasiti penyerapannya yang besar dan boleh diperolehi dalam secara semula jadi dalam kuantiti yang banyak dan berkos rendah.

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LIST OF SYMBOLS

%	percent
°C	degree celcius
rpm	revolutions per minute
mg/L	milligram per litre
ppm	part per million
ppb	part per billion

LIST OF ABBREVIATIONS

AC	Activated carbon
Ag	Silver
As	Arsenic
Au	Gold
ANOVA	Analysis of Variance
Ba	Barium
BOD	Biological Oxygen Demand
CCD	Central Composite Design
DF	Degree of freedom
Cd	Cadmium
Co	Carbonous oxide
COD	Chemical Oxygen Demand
CTA	Cellulose Triacetate
Cu	Copper
Fe	Iron
HCl	Hydrochloric Acid
Hg	Mercury
$Hg1^+$	Mercurous Mercury
$Hg2^+$	Metallic Mercury
HMS	Hexagonal Mesoporous Sillica
MS	Mean Square
NaOH	Sodium Hydroxide
Ni	Nickel
NIC	Newly Industrial Country

Pb	Lead
POFA	Palm Oil Fuel Ash
RSM	Response Surface Materials
Se	Selenium
SS	Sum of Square
TFC	Thin Film Composite
TOC	Total Organic Carbon
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1   Background of the Study

Water is the most important source that is essential for all living beings, and a crucial portion of any industrial, agricultural, or other development. It is expected to be the main issue in the 21st century where the water source would increasingly polluted (Burke et al., 2009). Moreover, Malaysia is categorized as fast industrial country and a member of Newly Industrialized Country (NIC) (Norzatulakma, 2010). Thus, it has the huge number of industrial area all over the country. The major industries include petrochemical, chemical, food, manufacturing and other multifarious industries. Due to this, some of water resources of the area are being polluted caused by the discharge of industrial effluents and wastewater generated from those industries (Hossain, 2014).

Mercury (Hg) is the one of the heavy metals that has been trace as a hazardous element in the effluent from the industrial wastewater. It could lead to the negative effects to the humans, animals, and the environment. Mercury is a toxin that has been shown to bioaccumulate which can enter the environment from anthropogenic sources such as chlor-alkali wastewater (Shafeeq et al., 2012). According to Hossain (2014), the average range of mercury was from 0.01 mg/L to 0.074 mg/L. The treatment of mercury-contaminated water remains a challenge, particularly due to the very low regulatory concentrations. Thus, mercury pollution has received many attentions from environmental researchers due to its volatility. Technology such as sorbent injection by using activated carbon has proven as an effective ways to reduce the mercury concentration in industrial wastewater (Gu & Zhang, 2015). The activated carbons that are capable of adsorbing the metal include Cr(III,VI), Cd(II), Hg(II), Cu(II), Fe(II,III), Zn(II), Ni(II), V(IV,V), Au(I), and Ag(I) (Santhy & Selvapathy, 2016).

More than 90% removal efficiency of mercury removal in biosorption was recorded in lab and commercial scale when activated carbon was used (Shafeeq et al., 2012). Currently, halogenated activated carbon is the most effective commercially available mercury sorbents. Unfortunately, due the high cost of the sorbent cause a big challenges to apply it for large scale operation (Hwang et al., 2002a). Due to this issue, researchers had been considered the agricultural lignocellulosic by-products as cheaper, eco-friendly and more effective adsorbents. Malaysia is the world's second largest producer and exporter of palm oil and 47 % of the world's supply of palm oil is produced by this country. In addition, it is recorded and it is recorded about 8 million tons/year of palm oil fuel ash (POFA) has been produced as waste from boiler (Sahid et al., n.d.). Previous study shows that POFA was already been used for technology to remove the Cu (II) from aqueous solutions as it is natural low-cost adsorbent for removing the mercury (Aziz et al., 2014). However, the surface of the POFA itself as the activated carbon cause it to be further research on the effectiveness of the POFA to remove heavy metals such as mercury.

1.2 Motivation

Minamata in Japan is well known as the first disaster that inducing by mercury toxicity. Large amounts of methylmercury that was discharged from chemical factory to Minamata Bay during 1950s. Irritability, paralysis insanity, loss weight and other symptom of neurological damage was reported as the main toxicological effects of mercury. The disease was believed existed in local people who consumed the aquatic products (Attari, 2015). Thus, water that has been contaminated must be treated. Treatment of mercury can be done in few alternatives such as biosorption, coagulation, filtration, bio films, reverse osmosis, and chemical precipitation (Shafeeq et al., 2012).

However, biosorption has been focused since biosorption offers an economically feasible technology for efficient removal and recovery of metal(s) from aqueous solution (Bobade & Eshtiagi, 2016). Biosorbent usually can be obtained easily from a by-product from the industry where it can save the cost. Meanwhile, mercury removal by activated carbon (AC) is the technology most widely used to control mercury emissions (Tang et al., 2016). However, most of the ACs was prepared from nonrenewable sources such as coal, that resulting in high costs for the AC preparation.

AC is used as an inert porous carrier material for distributing chemicals on the large internal surface, thus making them accessible to reactants (Shafeeq et al., 2012). Agro-industrial by-products such as coconut shells, almond shells, hazelnut shells, cherry stones, eucalyptus, apricot stones, nuts, grape seeds, olive and peach stones, sugar cane bagasse and palm oil waste are inexpensive materials that abundantly available for which the effective utilization has been desired (Avenue, 1998; Horikawa et al., 2002). Furthermore, palm oil mill is the most important agro-industry in Malaysia (Shahrul, 2010). Hence, Malaysia would face problem in order to manage the agriculture wastes from palm fruits processing wastes. Converting it into valuable product such as activated carbon might significantly reduce the waste (Zarina et al., 2013).

1.3   Problem Statement

Due to rapid industrialization has led to increased disposal of wastewater that contains heavy metals into the environment. The tremendous increase in the use of the heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. From the eco-toxicological point of view, the most dangerous metals are mercury, lead, cadmium and chromium (VI). Mine tailing and effluents from non-ferrous metals in industry are the major sources of these heavy metals in the environment (Baysal et al, 2013). Mercury is one of the most dangerous metals. Exposures to high concentration of mercury can cause death (Akpor et al., 2014).

Other than that, the increasing of wastage palm oil from palm oil industry has become a bigger problem because the wastages are not reused and recycled (Shahrul, 2010). The activated carbon addition has proved to be efficient in lower down mercury emission. However, manufacturing the activated carbon consume high cost due to the additional of other chemicals in most of the process. Hence, many researchers has been done to overcome this problem by replacing the more cheaper, eco-friendly and effective activated carbon by using palm oil boiler mill fuel ash (Hwang et al., 2002). In addition, the huge quantities of biomass generated from the palm oil fuel ash in Malaysia also lead for further study on POFA where it will cause some of the environmental problem if it is not properly managed and dispose to landfill.

1.4   Objectives

The following is the objective of this research:

1) To optimize the mercury removal using Palm Oil Fuel Ash (POFA).

1.5   Scopes of Study

The following are the scopes of this research:

1) Optimization of mercury removal factors

The optimum condition for factors for fuel ash in removing the mercury was determined by using central composite design. Two parameters were optimized which are agitation speed (100-200 rpm) and contact time (4-6 h).

2) Validation of optimized parameters for mercury removal

Validation of the optimized parameters was done with an error below 10%.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

Biosorption method is reliable process to remove the heavy metals with low cost consumption even there are some methods that used for the removal of heavy metal ions. Some of the other treatments that can be used are precipitation, ion exchange, reverse osmosis and adsorption. The palm oil fuel ash (POFA) also shows some advantages that are considerable to replace the activated carbon was describe through this chapter. The performance of POFA in mercury removal in biosorption process was analyzed and optimized.

2.2   Industrial Wastewater

Industrial sector is the one of the main source of wastewater apart of municipal, industrial and agricultural wastewater. Industrial wastewater is liquid from industrial establishments such as factories, production units and so on. The nature of wastewater might have high contents of harmful organic compounds, heavy metals and hazardous biological materials. Thus, the criteria of industrial wastewater are being discussed:

2.2.1   Characteristic of Industrial Wastewater

2.2.1.1 Colour

Colour is a characteristic that can be used to rate the general condition of wastewater. Characteristics below shows some of the colour of the wastewater.

- Light brown colour is which about 6 h old.
- Light-to medium grey colour is wastewaters that have undergone some degree of decomposition or that have been in the collection system for some time.
- Dark grey or black, the wastewater is typically septic, having undergone extensive bacterial decomposition under anaerobic conditions. This is because of the formation of various sulphides and particularly, ferrous sulphide.

2.2.1.2 Temperature

The temperature of wastewater is usually quite higher than the water supply. The measurement of temperature is important because most wastewater treatment schemes are temperature dependent. Different season and geographic location may cause wastewater uneven reading of the temperature. In cold regions, the temperature will range from about 7 to 18 ℃, while in warmer regions the temperatures vary from 13 to 24 ℃.

2.2.1.3 Odour

Heavy metal is defined as a metallic element having relatively high density, specific gravity or atomic weight. Industrial waste water can contain heavy metals such as Lead, Cadmium, Mercury, Cobalt and etc (Bobade & Eshtiagi, 2016). Furthermore, heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se and Zn are commonly used in industry and generically toxic to animals and aerobic also anaerobic processes. However, the most commonly encountered toxic heavy metals in wastewater. Different heavy metals could found in different major industries as mentioned in Table 2.1. Heavy metals found in major industries such as pulp and paper, fertilizers, steelworks, aircraft plating, textile mills and many more. Several industries discharge heavy metals. Heavy metals mainly come from natural source, mining activity, smelting,

agrochemicals and sewage sludge applications. Most heavy metals are essential trace elements for humans, animals and plants in small amounts. While, in larger amounts of heavy metal cause acute and chronic toxicity (Metals & Wastewater, 2013).

2.2.2 Heavy metal discharges

Table 2.1: List of Heavy Metals and Its Description

No.	Heavy Metal	Source	Impact
1	Mercury (Hg)	Through the leaching of soil due to acid rain, coal burning, or industrial, household, and mining wastes.	Causes damage to nervous system, kidneys, and vision.
2	Lead (Pb)	Paint, mining wastes and automobile exhaust.	Causes damage to kidneys, nervous system, learning ability, ability to synthesize protein, and nerve and red blood cells.
3	Cadmium (Cd)	Sources include electroplating, mining, and plastic industries, as well as sewage.	Causes kidney disease.
4	Arsenic (As)	Enters the environment through herbicides, wood preservatives, and mining industry.	Causes damage to skin, eyes, and liver. May also cause cancer.
5	Chromium (Cr)	Source includes cement industry, effluents from chemical plants, tobacco smoke and contaminated land fill.	Cause pulmonary fibrosis,lung cancer.

Generally, chromium is a major heavy metal that contains in almost major industries. However, chromium is not the metal that is most dangerous to living organisms. There are much more toxic metals such as cadmium, lead and mercury. In this study, mercury is has been focused due to its toxicity that could give extremely negative impacts to the human and animals.

According to Sobahan et al. (2015), rapid development of industries has increased the pollution level of water in its surrounding area. This is because most of the wastewater released from the industries contains contaminants and dumped into the surface water. Gebeng is the best example that can be referred since it is one of the rapid growing of industrial areas in Malaysia. Different sampling sites were taken to determine and analyze the concentration of heavy metals of water collected in different sites. The different sites are stated as in Table 2.2.

Table 2.2: Description of the Sampling Site (Sobahan et al., 2015).

Sites	Location	Descriptions
S1	03°59'37"N 103°24'46"E	Hope Mining (Coal Mining), Yanox (M), Sdn. Bhd. (Wood Processing), Southern Steel Mesh. Sdn. Bhd.
S2	03°59'16"N 103°23'18"E	Opposite of East chemicals & Eco tower (Lynax) Sdn. Bhd. Gebeng Industrial area.
S3	03° 59'1"N 103°22'40"E	Opposite of Kaneka and adjacent to Flexysl, Gebeng Industrial area
S4	03°58'34"N 103°23'17"E	Near MTBE, BP chemicals
S5	03° 58'33"N 103°23'24"E	Near Asturi Metal Builders, Mieco Chips board Berhad, KNM process Systems Sdn. Bhd. Borsig, Boiler System.
S6	03°57'40"N 103°23'15"E	Cargil palm production, Chicken food, KNM process Systems Sdn. Bhd. Gas Malaysia Berhard

Table 2.3: Data of Contamination Intensity in Water Collected in Gebeng (Sobahan et al., 2015).

Parameter	Standard	Contamination Intensity					
		S1	S2	S3	S4	S5	S6
As	0.05	0.97	0.98	0.63	0.92	1.02	0.45
Ba	1.0	0.04	0.03	0.05	0.04	0.06	0.04
Cd	0.01	6.26	6.41	0.68	6.19	9.77	5.33
Co	0.11	0.86	6.31	0.43	0.89	0.50	0.60
Cr	0.05	1.43	1.15	1.29	1.29	1.24	1.13
Cu	0.05	1.86	1.63	1.52	1.46	1.77	1.28
Hg	0.001	75.20	62.70	37.10	56.30	62.90	41.30
Ni	0.05	0.51	0.50	0.54	0.78	1.14	0.72
Pb	0.05	1.04	1.09	0.91	0.87	1.44	1.30
Zn	5.0	0.02	0.01	0.01	0.01	0.02	0.02

2.3   Mercury Contamination

Mercury is one of the most hazardous trace elements that produced by coal-fired power plants. It is silvery white shimmer was entrancing. Mercury is very dense element which they can be expanded and contracts evenly when the temperature is changed, and it has high electrical conductivity. It has been used in many of industrial, agricultural, medical, and household applications. Major uses of mercury include dental amalgams, tilt switches, thermometers, lamps, pigments, batteries, reagents, and barometers (Blaszczak, 2014).
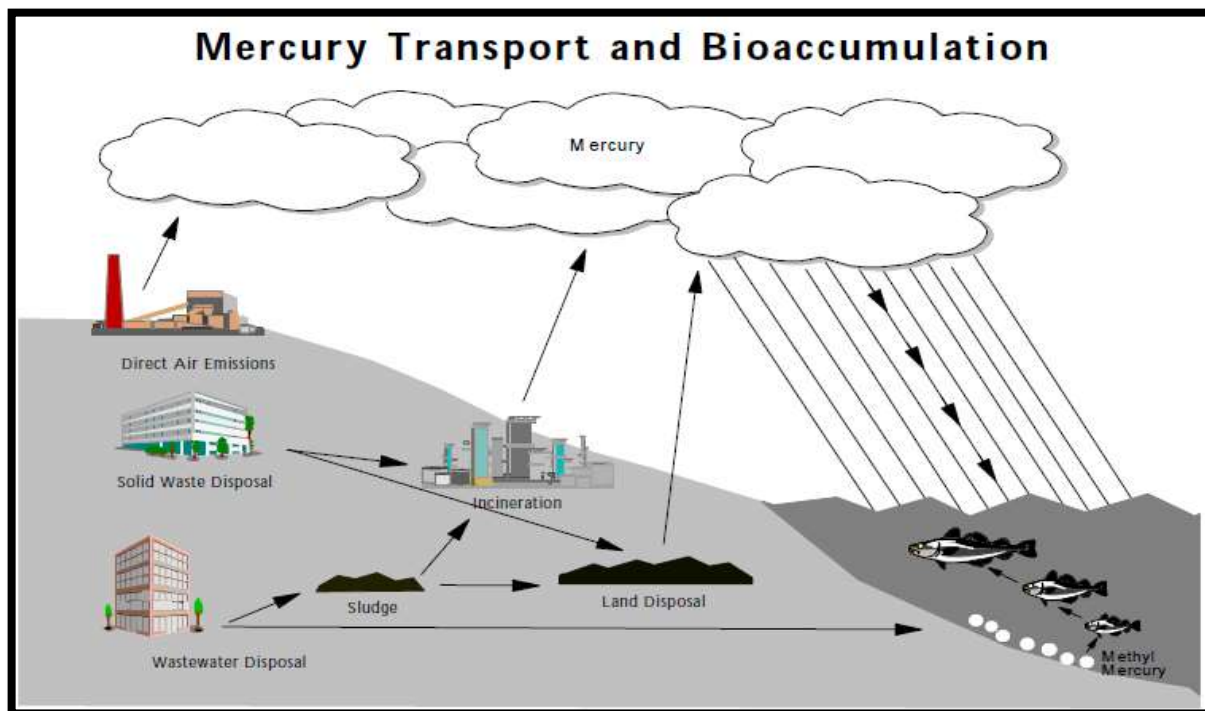
Figure 2.1: Illustration on how Hg entering the environment (Shafeeq et al., 2012).

By referring Figure 2.1, mercury can contaminate the environment from a number of paths such as direct air emissions, solid waste disposal and wastewater disposal. Mercury is the one of elements that can vaporize easily (Bayitse & Hodgson, 2016). As the garbage dispose into the land disposal, the possibility of the mercury to enter to the atmosphere is high. The worse scenario when the bacteria converting some of the mercury into an organic called methylmercury due to the disposal of mercury into wastewater system.

Mercury could cause chronic as well as acute poisoning. River and lake water in the nearby industries may contain mercuric discharges which are fatal for the aquatic as well as human life. These discharges could accumulate in the stomach and remain non digestible resulting in the formation of cancerous diseases. While, long time exposure to mercury could cause serious damage to nerve, brain, kidney, lung irritation, eye irritation, skin rashes, vomiting and diarrhea (Shafeeq et al., 2012).

2.3.1   Impact of Mercury to Health

2.3.1.1 Organic mercury exposure

Methylmercury is one of the example of organic mercury compounds. It is particularly dangerous because it bioaccumulates in the environment. It interferes with the nervous system of the human body which can reduce the ability to walk, talk, see, and hear. In extreme examples, high levels of methylmercury consumption can cause coma or death (Oehmen, 2014). It can disturb an animal's reproduction system, and lead to weight loss, or early death. In human side, it give could be inhaled and absorbed through the body skin.

2.3.1.2 Inorganic mercury exposure

The mercury could be toxic in the form of organic compounds as well as inorganic compounds. Inorganic mercury toxicity occurs in several forms: metallic mercury (Hg), mercurous mercury (Hg^{1+}), or mercuric mercury (Hg^{2+}).Inorganic highly toxic and corrosive. It gains access to the body orally or dermally and is absorbed at a rate of 10% of that ingested. It has a non-uniform mode of distribution secondary to poor lipid solubility and accumulates mostly in the kidney (Olson, 2015). Thus, existing in high or even in low concentrations, it must be effectively removed from the wastewaters (Walterick & Smith, 2012).

2.4   Technologies of Mercury Treatment In Wastewater

Due to increasing awareness about the environment and stringent environmental regulations, wastewater treatment has always been a key aspect of research. In recent years, some of new treatment such as biosorption, bio films, reverse osmosis, chemical precipitation, membrane filtration, coagulations, adsorption and sedimentation (Foo and Hameed, 2009; Naiya et al., 2009; Wang et al., 1963; Abdel et al., 2011). From the survey previously, it showed that new adsorbents and membrane filtration are the most frequently studied and widely applied to treat metal contaminated wastewater. Their advantages and limitations in application are listed in Table 2.4 (Barakat, 2011).

However, most of these methods such as reverse osmosis, chemical precipitation, and ion exchange consume high cost (Barakat, 2011). Adsorption method that usually used plant wastes as the sorbent. Plant wastes are inexpensive since there is low or no economic value. Unfortunately, the application of untreated plant wastes may cause low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compound that contained in the plant materials. Thus, biosorption method is more convenient in order to remove mercury contaminants in the wastewater.

Biosorption is a surface phenomenon where the atoms or molecules bind to the solid surface of as substrate, called the adsorbent and forms attachment via physical and chemical bonds (Foo and Hameed, 2009). Biosorption technique is a able to remove diverse contaminants and very recommended in removing heavy metal from wastewater either high solute or in dilute concentration (Popuri et al. 2009; Wang et al. 2010). , Biomaterials from inactive dead biomass have unique chemical compositions that are capable to separate metals ions and complexes from solution which able to remove the necessity to maintain growth supporting conditions (Baysal, 2013). Although various different adsorbents can be employed for the treatment of wastewater that contains heavy metals, it is important to make sure that the most suitable adsorbent is selected (Santhy & Selvapathy, 2016)

Table 2.4: Summary of treatment technologies

Technologies	Process Explanation	Advantages	Disadvantages
Biosorption	Property of certain types of dead, microbial biomass to bind and concentrate the heavy metals from dilute aqueous solutions.	- Low cost - High efficiency - No additional nutrient requirement. - Minimization of chemical and biological sludge (Tornadoo, 2011).	-Early saturation
Precipitation	This technique is preferred when the sodium sulfate is not desirable in the end product. The process is more efficient at neutral pH. The process efficiency starts to decrease as pH goes above 9.	-Simplicity of the process. -Efficient for large scale. (Shafeeq et al., 2012)	-Ineffective in removing small amount of heavy metals. -Requires other addition of chemical.
Ion Exchange	Water treatment method where one or more undesirable contaminants are removed from water by exchange with another non-objectionable, or less objectionable substance (Ion, 2009)	-Able to handle in large volume.	-Cannot handle concentrated metal solution where it is easily fouled by organics from wastewater. -Very sensitive to pH in the solution.

Reverse Osmosis	Thin Film Composite (TFC) and Cellulose Triacetate (CTA) is used this method. TFC membranes are relatively more efficient compared to CTA membrane. Both have a very high rejection rate for mercury types as well as its different contaminants.	-High regeneration of material	-High cost -Process complexity -Low removal efficiency
Adsorption	Molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces. Solid surfaces are characterized by active, energy-rich sites that are able to interact with solutes in the aqueous phase due to their specific electronic and spatial properties.	- Use low cost absorbent - Effective in removing heavy metal from aqueous solution (Baysal, 2013).	-Low capability -Narrow of metal operating temperature (Tang et al., 2016).

2.5   Activated Carbon in Biosorption Technology

Activated carbon is a solid substance produced by carbonizing and heating a carbonaceous material such as sawdust or peat to a high temperature in the presence of a gas or chemicals. Activated carbon is generally used to purify, decolorize, deodorize, dechlorinate, separate, and concentrate in order to allow recovery and to remove the harmful constituents from gases and liquid solution (Setyawan, 2011). Their adsorptive properties are due to their high degree of surface area, microporous structure, and high degree of surface reactivity. Fine powder of activated carbon is commonly used for aqueous phase, while for gas phase usually it is compressed into larger particles or granules. It is generally uses for removal of colour from raw sugar and other chemicals in aqueous solution for removal of impurities from wastewater, drinking water, air and other gases such as gas respirators for recovery of solvents in printing and other industries (Cash, 2007). According to a review by Huang, the activated carbons that are capable of adsorbing the metal include Cr(III,VI), Cd(II), Hg(II), Cu(II), Fe(II,III), Zn(II), Ni(II), V(IV,V), Au(I), and Ag(I) (Santhy & Selvapathy, 2016).

Commercialize activated carbon is commonly use in biosorption process due to their high surface area and biosorption capacity. However, application of the activated carbon is costly. Thus, a large number of agricultural lignolcellulosic by-products have been recognized in order to create more cheaper and eco-friendly nature (Modeling & Adsorbent, 2014). Agricultural lignocellulosic such as coconut shells, almond shells, hazelnut shells, cherry stones, eucalyptus, apricot stones, nuts, grape seeds, olive and peach stones, sugar cane bagasse and oil palm trunks. However in this study, POFA is chosen since it is abundantly available and eco-friendly.

2.6   Palm Oil Fuel Ash as Activated Carbon

According to Setyawan (2011), palm shell is the best raw materials for manufacturing activated carbon because of its hardness. In Malaysia, palm oil with capacity of 30 tons of fresh fruit bunches per hour and it will produce about 1.95 tonnes of palm shells per hour. In other word, it creates abundant number of waste for activated carbon production.

Preparation of activated carbon mainly has two steps which are the carbonization of carboneous raw material at temperature below 800ºC and the activated carbonized product. Thus, all the carboneous materials can be converted into activated carbon. During the carbonization process, most of the noncarbon elements such as oxygen, hydrogen, and nitrogen are eliminated as volatile gaseous species by the pyrolytic decomposition of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross linked in a random manner. Aromatics sheets are irregularly arranged which had leaves free interstices. These interstices increase the pores and make activated carbon as good absorbents (Setyawan, 2011).

2.6.1   Origin and Characteristics of POFA

Palm oil fuel ash is a by-product produced in palm oil mill. After palm oil is extracted from the palm oil fruit, both palm oil husk and palm oil shell are burned as fuel in the boiler of palm oil mill. Generally, after combustion about 5% palm oil fuel ash by weight of solid wastes is produced (Sata et al., 2004).

The ash produced in whitish grey color to darker shade based on its carbon content. In other words, the physical characteristic of POFA is very much influenced by the operating system in palm oil factory. Fuel ash has spherical particles and very high fineness. POFA has been found to contain high amounts of alumina, calcium, potassium and silica that could be utilized to synthesize active compounds that are responsible for pollutant gas sorption (Balakrishnan & Awal, 2014). POFA also has a spongy and porous structure that has large surface area and pore volume as shown in Figure 2.3. So,

by its characteristics of POFA, it is possible to assume that these similar compounds could also be used for biosorption in aqueous solution (Modeling & Adsorbent, 2014)

Figure 2.2: Fine powder of POFA applied for aqueous solution.

Figure 2.3: Structure of POFA (Aziz et. al, 2014).
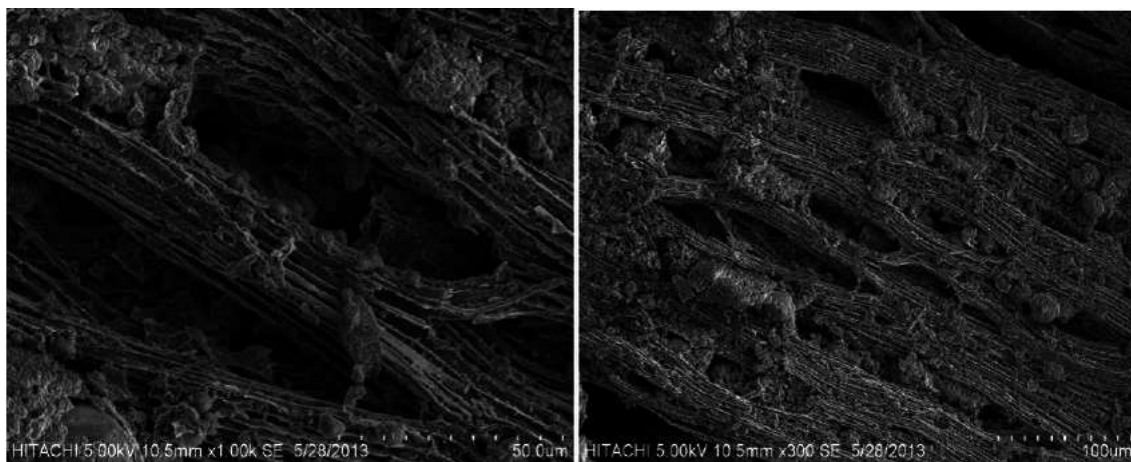
2.7   Design of Experiment

Designing experiments to study response surfaces is important for several reasons, such as the response function is characterized in a region of interest to the experimenter, statistical inferences that can be made on the sensitivity of the response to the factors of interest, factor levels can be determined for which the response variable is

optimum where the maximum or minimum can be identified. Also, factor levels can be determined that simultaneously optimize several responses.

2.7.1 Factorial Design

The factorial analysis involve in this experiment where it is use to reduce the number of resources and screen out factors that Response Surface Methods (RSM) is applied to optimize mercury removal. Factorial design have increased precision over the types of design because it built-in internal replication. Basically, effect of each factor will be investigated in the factorial design. Past study has shown the use of fractional factorial in identifying effect of critical factor such as pH, contact time, initial mercury ion concentration, biosorbent dosage, and agitation speed (Verma & Tripathi, 2014).

A screening experiment usually involves only two levels of each factor and can also be called characterization testing or sensitivity analysis (Telford, 2007). Factorial experimentation is a method in which the effects due to each factor and to combinations of factors are estimated. Factorial designs are geometrically constructed and vary all the factors simultaneously and orthogonally (Lazić, 2004). Fractional factorial experiments are important alternatives to complete factorial experiments when budgetary, time, or experimental constraints preclude the execution of complete factorial experiments.

2.7.2 Optimization

Optimization designs attempt to fit a response surface using several different types of design. Data analysis methods will be used in order to analyze the differences among group means and their associated procedures such as variation among and between groups. Optimization can improve the performance of a system of a system, or product. Two-level factorial experiments are often conducted to fit response surfaces using a standard RSM design called a central composite design (CCD). It is well suited for fitting a quadratic surface, which usually works well for process optimization. From previous research, it shows that the contact time and agitation speed has high positive response in order to remove the mercury.

CHAPTER 3

METHODOLOGY

3.1   Introduction

This chapter is about material and methodology to remove mercury from industrial wastewater. In this research, the efficient method is preferable to reduce amount of heavy metal concentration in the contaminated wastewater. Biosorption method is refer to the removal of heavy metals by passive binding to the nonliving microorganism such as bacteria, fungi and other biomass using physicochemical pathways. POFA was used as biosorbents to conduct the experimental batch scale to remove mercury in the effluents. The material used in this research is Palm Oil Flue Ash (POFA). POFA was taken from Kilang Sawit Lepar Hilir, Pahang, Malaysia. From previous study, the factors that affect the mercury removal were pH, initial Hg concentration, dosage amount, contact time and agitation speed.

3.2   Chemicals

The research was required to prepare 5 ppm from 1000 ppm of stock solutions for sample preparation. The initial pH of sample was adjusted using 0.1 M of sodium hydroxide by diluting 2 g of NaOH with distilled water. While, 0.001 % L-Cysteine was used for dilution purpose of sample to 1 ppb for further analysis. Dilution of 0.001 % L-Cysteine by weighed 10mg of L-cysteine and diluted with ultrapure water. The reagents of 50 % Sulphuric acid (H_2SO_4) and 10 % Tin (II) chloride were prepared for mercury analysis. The reagent of 50 % Sulphuric acid (H_2SO_4) was prepared by mixing 25 mL of 90 % of sulphuric acid and 25 mL of distilled water. While, the reagent of 10 % Tin (II) chloride was prepared by diluting 5 g Tin (II) chloride with 2 mL of 90 % sulphuric acid and filled up the solution with distilled water up to 50 ml of solution. Meanwhile, the

0.001 % L-Cysteine and 1 ppb of mercury stock solution with 50 µl, 100 µl, 150 µl and 200 µl was diluted as calibration standard.

3.3   Experimental Analysis

The analysis apparatus was used to determine the condition of the compound or substrate as well as to identify operating parameters of processes. In this experiment, analytical balance (Mettler Teledo), mercury analyser (RA-3000 Mercury, NIC) and incubator shaker will be used.

3.4   Experiment Methodology

3.4.1   Experiment of Biosorption

The experimental procedures of biosorption are started by preparing the aqueous solution, 1000 mg/L of mercury stock solution. The required amount of Hg (II) solution is dissolved in the ultrapure water. Next, 0.1 M HCI and 0.1 M NaOH solutions was used to adjust the initial pH of the solution. Biosorption measurement is determined by batch experiment of a known amount of the sample with 50 mL of aqueous Hg (II) solution and placed into 250 ml of the conical flask. Initial pH of the aqueous solution was adjusted to use. The mixture of the sample is shaken by using incubator shaker at the constant room temperature of 25 ℃ and biosorbent dosage is 0.25 g. The incubator shake was shaken for 4-6 h and rpm ranges from 100-200 rpm. The suspension will be filtered using a vacuum pump and the filtrates are analyzed using the direct mercury analyzer. The sample was filtered by using vacuum pump to obtain the filtrate. Next, the sample obtained was used for further analysis to perform mercury removal analysis.

3.4.2   Optimization of Contact Time and Agitation Speed

Experimental designs were performed by using Design Expert version 7.0.0. Analysis of variance, often abbreviated to ANOVA, is a broad group of techniques for identifying and measuring different sources of variation within the data (Grd et al., 2012). Optimization involved few stages before the factor can be optimized. The stages involved are screening and validation. Fractional designs were applied from the previous study to screen out the factor influence in mercury removal experiment. These factors are contact time, biosorbent doses, agitation speed, pH and initial Hg ion concentration. The optimization of the factors was taken about 13 run of the experiment.

3.4.3   Validation of Experiments

Following the design and analysis of the optimization experiment, the best and optimized condition was proposed by the using fitted model to parameters that affect the most in removing the mercury. Experiments were conducted according to the suggested experimental conditions and results of the experiment will compare with the suggested results to verify the significance of the factorial model. The chosen parameter was confirmed by running about 3 experimental works. An error below 10 % was desired between the predicted and experimental work. Then, error of the removal of mercury will be calculated using the following equation:

$$Error(\%) = \frac{|predicted\ value - experimental\ value|}{experiment\ value} \times 100\%$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Introduction

In this research, palm oil fuel ash (POFA) was used for removal of mercury ions from the industrial wastewater. Two parameters (contact time and agitation speed) were employed in the optimization study and validation using response surface methodology. Response surface methodology with central composite design was used to analyze the optimum condition of higher biosorption efficiency for the selected variables. A central composite design (CCD) consisting two variables was used in this study. The two variables and their levels were contact time (A, 4-6hr) and agitation speed (B, 100-200rpm). CCD with total of 13 run of designed experimental and optimized condition chosen by Design Expert 7.7.0 software was verified and approved to have error below than 10%.

4.2   Optimization on Mercury Removal Efficiency

CCD experiments for optimization the significant parameters of contact time (h) and agitation speed (rpm) of the POFA with 5ppm of Hg stock solution were performed to locate the maximum removal of Hg ion by Design Expert 7.0.0. The criteria of the contact time and agitation speed were set on target value whereas the mercury removal was set on maximum. The low and high level of the parameters are the determined from the previous study (Syafiqah et al., 2017). Table 4.1 shows the low level and high level of each parameter.

Table 4.1: Low Level And High Level Of Parameters.

Parameters	Low level	High level
Contact time (hr)	4	6
Agitation Speed(rpm)	100	200

Table 4.2: Experimental Design and Response For Optimization.

Std.	Factor 1: Contact Time (h)	Factor 2: Agitation Speed (rpm)	Final Hg ion concentration (mg/L)	Percentage Removal (%)
1	4.5	125	0.87	84.67
2	5.5	125	0.85	85.07
3	4.5	175	1.13	79.33
4	5.5	175	1.01	81.80
5	4	150	1.52	71.53
6	6	150	0.96	82.87
7	5	100	1.47	72.67
8	5	200	1.66	68.80
9	5	150	0.44	93.20
10	5	150	0.35	95.07
11	5	150	0.59	90.20
12	5	150	0.13	98.93
13	5	150	0.22	98.40

From Table 4.2, the parameters on Standard 12 were 5 hr of contact time and 150 rpm of agitation speed shows the highest percentage for mercury removal with the value of 98.93 %. The parameters for Standard 5 were 4 hr of contact time and 150 rpm of agitation speed shows the lowest value of mercury removal which is 71.53 %.

4.2.1 Model Fitting

Fit summary is used to identify which model to choose for in depth study (Anderson et al., 2009). The statistical tables are sequential model sum of squares in Table 4.3 and lack of fit test in Table 4.4. Then, highest order model with significant is commonly would be chosen through p-value that calculated for each type of model. The probability is less than 0.05 the terms are significant and their inclusion improves the model (Simon, 2003). Thus, the model with p-value less than 0.05 in Table 4.4 can be considered to be chosen to fit the response. From Table 4.3, quadratic model fits the criteria to be chosen to fit the response.

Table 4.3: Sequential model sum of squares

Source	Sum of squares	df	Mean Square	F-value	p-value
Mean vs Total	93507.27	1	93507.27		
Linear vs Mean	76.68	2	38.34	0.34	0.7212
2F1 vs Linear	1.07	1	1.07	8.502E-003	0.9286
Quadratic vs 2F1	1055.76	2	527.88	47.21	<0.0001
Cubic vs Quadratic	15.70	2	7.85	0.63	0.5713
Residual	62.56	5	12.51		
Total	94719.04	13	7286.08		

The lack of fit test was performed and ANOVA has been used to compare between the residual error and the pure error from experimental data. If residual error significantly exceeds pure error, the model will show significant lack of fit, and another model may be more appropriate. The desired result in a lack of fit test is that the model selected is insignificant in lack of fit (p-value > 0.05) means the model fits well (Anderson et al., 2009; Simon, 2003). The lack of fit test in Table 4.3 shows both quadratic and cubic model is insignificant in lack of fit.

Table 4.4: Lack of fit

Source	Sum of squares	df	Mean Square	F-value	p-value
Linear	1081.93	6	180.32		
2F1	1080.86	5	216.17	13.57	0.0124
Quadratic	25.10	3	8.37	16.27	0.0092
Cubic	9.40	1	9.40	0.63	0.6332
Pure Error	53.16	4	13.29	0.71	0.4476

4.2.2 ANOVA

As Table 4.5 shows the analysis of variance (ANOVA) of mercury removal indicated that experimental data had a determination coefficient (R^2) of 0.935 with the calculated model with no significant lack of fit at $P > 0.05$. That means that the calculated model was able to explain 93.5% of the results. The results indicated that the model used to fit response variables was significant ($P < 0.0001$) and adequate to represent the relationship between the response and the independent variables. Adjusted R^2 value is the correlation measure for testing the goodness-of-fit of the regression equation. The adjusted R^2 value of this model is 0.8893, which indicated only 11.1% of the total variations were not explained by the model where it is a reasonable value since the value of predicted R^2 is 0.7511. The high R^2 value specifies that the model obtained will be able to give a convincingly good estimate of response of the system within the range studied. The lack of fit test, which was not significant for the model, shows that the model satisfactorily fits the data. All of these statistical tests showed that the developed model was suitable for representing the data and able to provide a good description of the relationship between the process variables and response. Meanwhile, a relatively lower value of coefficient of variation ($CV = 3.94$) showed a better precision and reliability of the experiments carried out.

Table 4.5: ANOVA analysis for the optimization model

Source	SS	DF	MS	F-value	Prob > F	
Model	1133.51	5	226.70	20.28	0.0005	Significant
A-Contact time	54.40	1	54.40	4.87	0.0632	
B-Agitation speed	22.28	1	22.28	1.99	0.2010	
AB	1.07	1	1.07	0.096	0.7659	
A^2	468.51	1	468.51	41.90	0.0003	
B^2	863.29	1	863.29	77.21	<0.0001	
Residual	78.27	7	11.18			
Lack of fit	25.10	3	8.37	0.63	0.632	Not significant
Pure error	53.16	4	13.29			
Cor Total	1211.77	12				
C.V = 3.94% ; R^2=0.935; Adjusted R^2=0.889; Adeq. Precision=12.008						
SS=sum of squares; DF=degree of freedom; MS=mean square.						

It can be seen in Table 4.5 that all the interaction quadratic parameters were insignificant ($P > 0.1$ while for the adsorption of Hg the values of R-Squared and Adj R-Squared are 0.935 and 0.889, respectively. Both values shows quite close to each other, hence, indicating high significance and efficiency of the model (Mubarak et al., 2016). The model equation for removal of Hg of quadratic model fitting of experimental results was presented in Eq. 1.

Mercury removal = 94.65+2.13A-1.36B+ 0.52AB-4.52A^2-6.14B^2 (Eq. 1)

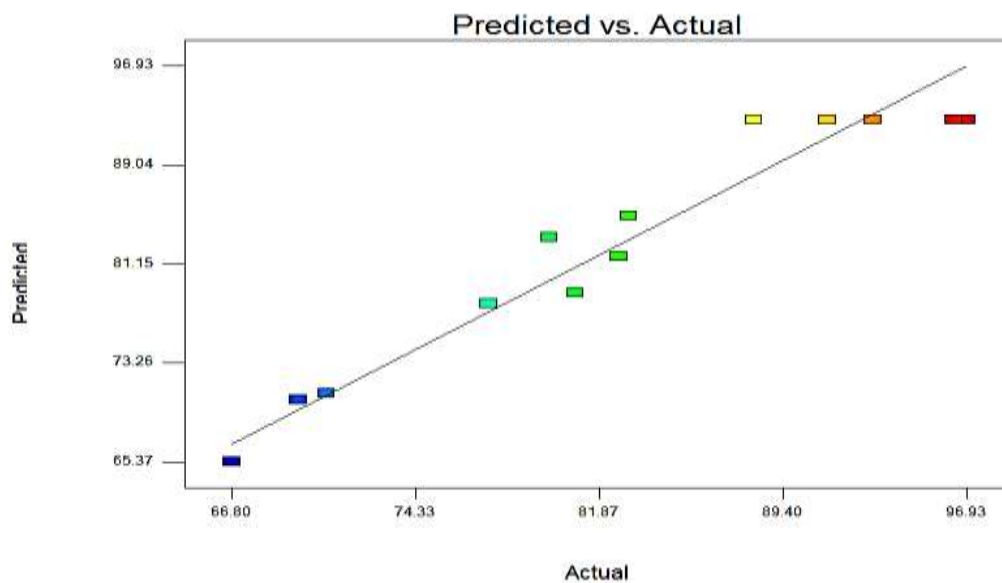Where *A* is contact time (h), and B is agitation speed (rpm).

Figure 4.1: Predicted vs. actual mercury removal factor colored by standard order

A plot in Figure 4.1 showing observed removal of Hg versus that obtained from Eq. 1. The figure indicates that the predicted response from the empirical model is in well agreement with the observed data (Uzun & Tekin, 2017).

4.2.3 Effect of Conditions on Mercury Removal Factor

Optimization has been performed by using numerical and graphical approaches. Generally, graphical optimization is limited to cases in which there are only a few responses. Numerical optimization was performed with the goal to maximize the response and gave the following best conditions as shown in Table 4.5 with predicted response at 94.651% for mercury removal at desirability of 0.950.

The effects of the two conditions for mercury removal (contact time, and agitation speed) were analyzed using RSM. Three-dimensional response surface and contour plots were generated to investigate the interaction of any two variables on the response by evaluating two variables at a time while holding the other one constant at central level. A three-dimensional plot can give a clearer geometrical representation of the nature and extent of the interaction between the variables and response within the experimental range studied.
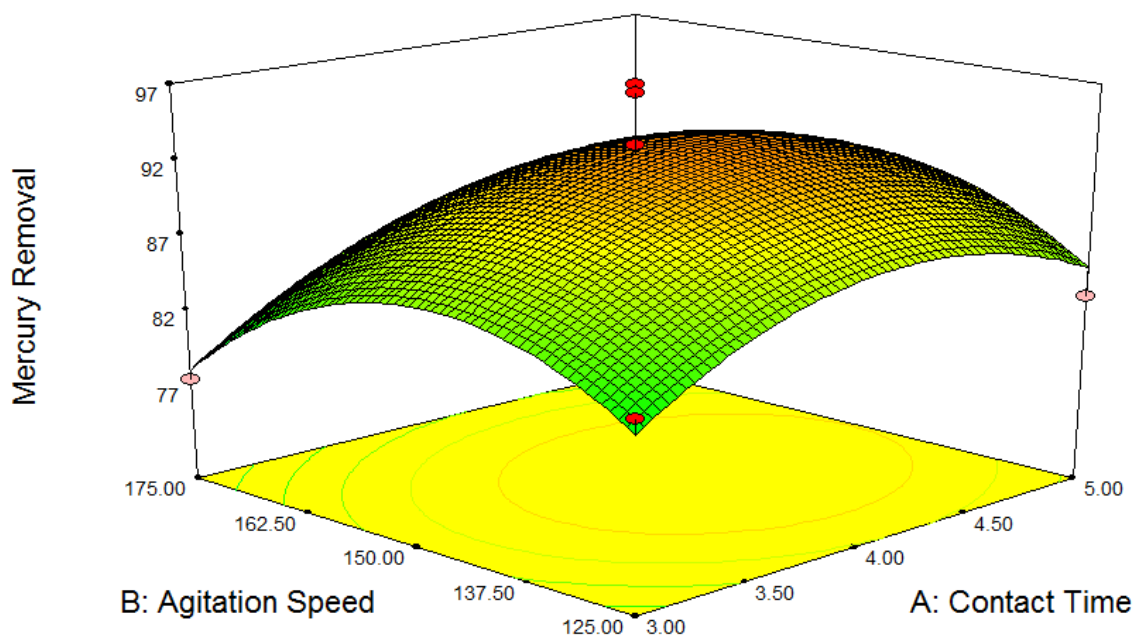
Figure 4.2: Response surface plot of mercury removal for contact time and agitation speed
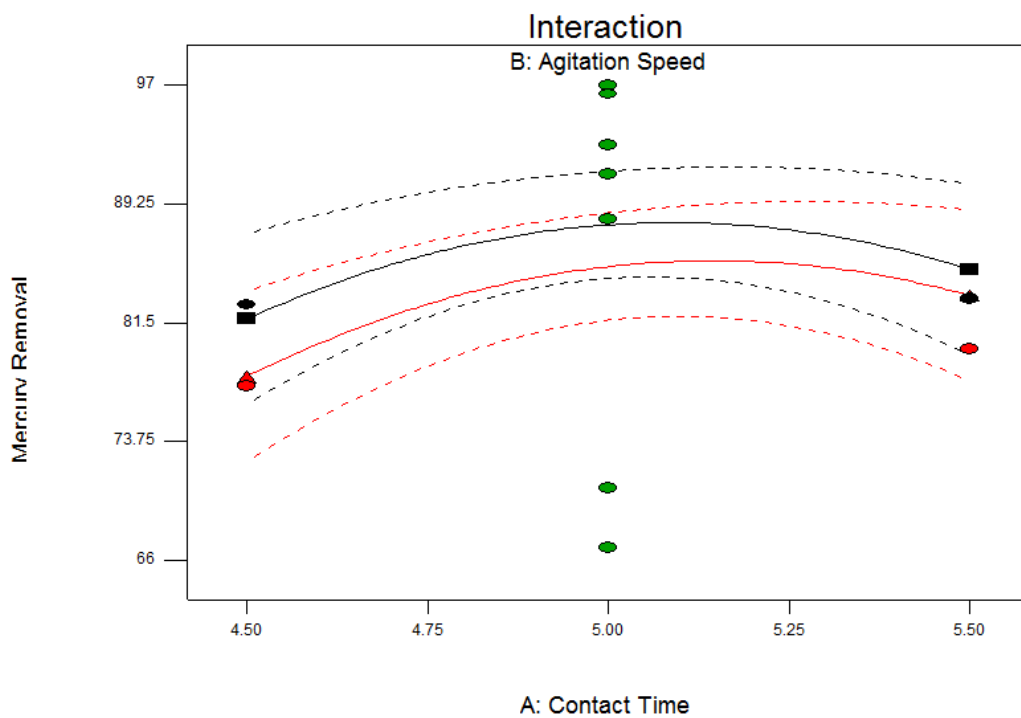

Figure 4.3 : Interaction graph for the effects of contact time and agitation speed.

4.2.3.1 Effect of Contact Time

The influence of contact time on Hg ions biosorption onto POFA, at constant room temperature (25 °C), constant biosorbent dose (0.25 g) and an initial solution pH 2. While, the initial concentrations of Hg ions were 5ppm,respectively (Bulgariu & Nemeş, 2016). The experimental data from Fig. 4.2 indicates that the biosorption efficiency of the considered heavy metal ions onto POFA increases with contact time, and reaches a maximum at 5hr. In fact, more time contact on surface of POFA and Hg ion in sample, will increase the rate of absorption because there have greater availability of hydroxyl functional group on the surface of POFA, which is required for interaction, significantly improved the binding capacity and the process proceeded rapidly (Ekebafe, Ekebafe, Erhuaga, & Oboigba, 2012). Other than that, according to the previous research, using powdered of activated carbon in mercury removal resulted the increased of contact time beyond 60 minutes that has no significant effect on biosorption efficiency. The mercury sorption was relatively fast, this probably happen due to the availability of so many sorption sites at the beginning of the experiments.

4.2.3.2 Effect of Agitation Speed on Mercury Removal

The effect of agitation speed on removal efficiency was examined under constant some of the parameters dose of adsorbents, and pH. The results in Table 4.6 show that the best value for agitation speed is 150 rpm. It is because, rate in the range of 150-180 rpm sufficiently ensure that all the binding sites are made readily available for Hg uptake (Olisedeme & Okpu, 2014). The effect of external film diffusion on adsorption rate can also be assumed but not significant. The increase in shaking speed resulting to increase in metal ions percentage removal, was due to the fact that, increase in stirring rate enhanced the metal ions diffusion to the surface of the adsorbent; and also caused reduction in the film boundary layer around the adsorbent. However, from the previous study on another heavy metal such as Pb (II) that still able to attain maximum removal of 100% at a lower shaking speed of 150 rpm (Bernard et al., 2013). The result can be associated to the fact that the increase of the agitation speed, improves the diffusion of metal ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 100-200 rpm is sufficient to ensure that all the surface binding sites are made readily available for metal uptake (Ekebafe et al., 2012).

4.3   Determination of Optimum Condition for Mercury Removal

The optimum points of the most important parameter to maximize the adsorption of Hg were evaluated as mentioned in Table 4.2. The experiments were performed according to the suggested best condition in Table 4.6. While, based on the predicted and experimental results presented, the experimental values needed shows good agreement with the predicted values proposed by the model with an error less than 10 %.

Table 4.6: The best conditions were analyzed by Design Expert 7.0.0 software.

Factors	Best condition
A-Contact time	5h
B-Agitation Speed	150 rpm

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4.4   Validation of Model

The validation experiments were conducted based on one suggested best condition in from Design Expert 7.0.0. The experiments were performed according to the suggested best condition in Table 4.6 and the result is presented in Table 4.7. The validation experiments were conducted at the suggested best conditions and the error from these runs were 2.5 %, 4.3 %, and 5.7 %. Based on the predicted and experimental results presented, the experimental values were in good agreement with the predicted values proposed by the model with an error less than 10 % and proved to be an adequate model.

Table 4.7: Result for validation of model

Description	Mercury removal		
	Run 1	**Run 2**	**Run 3**
Predicted value	94.65	94.65	94.651
Experimental Value	97.03	90.73	89.56
Error (%)	2.5	4.3	5.7

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, it is can be summarized that activated carbon which is palm oil fuel ash is identified and proved to be able to absorb Hg ion in industrial wastewater as the result obtained from this experiment is 98.93% which was close to the predicted value. Moreover, replacement of POFA as activated carbon can lower the cost of treating the industrial wastewater since the manufacturing of activated carbon consumed high cost due to its process that needed to be use a lot of energy. Also, it can be as alternative on reducing the waste of biomass generated from the oil palm mill.

Influential factors of biosorption conditions for mercury removal are contact time and agitation speed. A quadratic model obtained from CCD matched the experiment data. Based on the quadratic model, the optimized values of these factors are determined as 5h and 150 rpm for contact time and agitation speed respectively. Under these optimum conditions, the model has R^2 of 0.935, implying a high correlation between the experimental and predicted values, as shown in Table 4.7. The model obtained from CCD was significant with low p-value (0.0005) and non-significant lack of fit. Thus, it is concluded that palm oil fuel ash can highly potential to be used for mercury removal.

5.2   Recommendation

There are several recommendations that could be implemented or improved in this study in order to increase the efficiency of mercury removal. Firstly, the optimized conditions may be further improve of application from batch scale to pilot scale in order to apply in waste water system in industry. In order to improve the absorption efficiency, the surface area of ash could be modified by adding some chemical through some procedure. For example, by using a hexagonal mesoporous silica (HMS) that recorded has higher adsorption capacity compared with the natural biomass. Lastly, it is recommended for POFA can be tested in another type of heavy metals such as Chromium and Lead which also contain in the industrial wastewater since the POFA can be obtained abundantly, eco-friendly and cheaper compared to the other manufactured-activated-carbon.

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APPENDIX

1) **Calculation of sample from stock solution (1000ppm)**

$M_1V_1 = M_2V_2$

<u>200 ppm</u>

$(1000 \text{ ppm})(V_1) = (200 \text{ ppm})(1000\text{mL})$

$V_1 = 200$ ml from 1000ppm

<u>150 ppm</u>

$(200 \text{ ppm})(V_1) = (150 \text{ ppm})(1000\text{mL})$

$V_1 = 750$ ml from 200ppm

<u>100ppm</u>

$(150 \text{ ppm})(V_1) = (100 \text{ ppm})(1000 \text{ mL})$

$V_1 = 667$ ml from 150ppm

<u>50 ppm</u>

$(100 \text{ ppm})(V_1) = (50 \text{ ppm})(1000 \text{ mL})$

$V_1 = 500$ ml from 100ppm

<u>10 ppm</u>

$(150 \text{ ppm})(V_1) = (10 \text{ ppm})(1000 \text{ mL})$

$V_1 = 200$ ml from 50ppm

<u>5 ppm</u>

$(10 \text{ ppm})(V_1) = (5 \text{ ppm})(1000 \text{ mL})$

$V_1 = 500$ ml from 10ppm

<u>**Preparation Of Reagents For Mercury Standard And Mercury Analysis.**</u>

50% sulphuric acid

Dilute 25 ml of sulfuric acid by gradually adding it to 25 ml of distilled/pure water in a bottle while cooling the bottle. The bottle is sufficiently cooled with water before use Sulfuric acid generates heat when diluted.

10% Tin (II) chloride/stannous chloride solution

Dilute 5 g of Tin (II) chloride with 2.8 ml sulfuric acid to make a total volume of 50 ml by adding distilled/pure water. 10% Tin (II) chloride solution oxidizes a (1) day after being prepared, leading to a reduction in its reducing ability. Therefore, only prepare the amount necessary for a day's analysis

<u>Calibration Procedure</u>

1) 5 sample tubes were get ready and about 5ml of DI water were transfered into one of sample tubes.

2) The 50% of H_2SO_4 was transferred into sample tubes and followed by 250ul of the 10% $SnCl_2$.

3) The Impinger Cap was closed and click on the "Measurement Start" in the "Run" menu or click START button.

4) The sound of the buzzer signals the end of the analysis.

5) Remove the impinger cap and rinse thoroughly the bubbler with DIwater.

6) Repeat above step by adding 50ul, 100ul, 150ul and 200ul of 1ppb mercury standard into other sample tubes before adding H_2SO_4 and $SnCl_2$.

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<u>Running Mercury Analyser</u>

1. The SMP tab on the Table Window is clicked

2. The sample name, sample volume, specified volume and dispensed volume of each sample to be analyzed is keyed in.

3. The MES column is ticked to select the sample to be run.

4. Initially, 5ml of the pre-digested samples are transferred into the sample test tubes.

5. Then, manually introduced 250ul of 50% H_2SO_4 into the sample test tube followed by 250µl of 10% Tin (II) Chloride

6. The impinger cap to the sample test tube is closed

7. After that, "Measurement Start" in the "Run" menu or START button is clicked

8. The sound of the buzzer signals the end of the analysis.

9. Finally, the impinger cap is removed and rinsed thoroughly the bubbler with DI water.

10. Steps 4-9 are repeated for other samples.