EFFECT OF MERCURY CONCENTRATION AND OPERATING PARAMETERS TO MERCURY REMOVAL USING PORTABLE MERCURY REMOVAL RIG (PMRR) FOR PETROCHEMICAL WASTEWATER

ZULKIFLEE BIN SULAIMAN

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for award of the Degree of Chemical Engineering.

Signature :
Name of Supervisor : Abdul Aziz Mohd Azoddein
Position :
Date :

STUDENT'S DECLARATION

I hereby declare that that the work in this thesis is my own except for the quotations and summaries which have been duty acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name of Supervisor : Zulkiflee Bin Sulaiman
ID Number : KA09086
Date :

Special Dedicated to my beloved father, Sulaiman Bin Ali

Mother, Safiaton Binti Madon

Brothers and sisters

Lecturers and friends…

Special Thanks for all of their Care, Love, Supports, Encouragement and Best Wishes.

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EFFECT OF MERCURY CONCENTRATION AND OPERATING PARAMETERS TO MERCURY REMOVAL USING PORTABLE MERCURY REMOVAL RIG (PMRR) FOR PETROCHEMICAL WASTEWATER

ABSTRACT

Mercury is a type of heavy metal that naturally occurs on the earth crust. It can be found in soil, rocks and sea. It can be release to the environment through natural processes such as rock erosion, soil decomposition or volcanoes eruptions. It also released to the environment by human activities such as mining and industrial processes from petrochemical and chlor-alkali industries. Mercury is usually used in the thermometer, thermostat, barometer, bulbs, dental amalgams and switches. Mercury is one of the hazardous chemical elements that exist on the earth. It can attack human central nervous system, kidney, lungs and other body systems. Thus the objective of this research is to study on the mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR) for petrochemical wastewater. The mercury removal process was conducted under different inlet pressure; 5, 10 and 23 psig, different inlet concentration; 2, 4, 6 and 8 ppm, different pH and lastly using different absorbent; extruded activated carbon (EAC), granular activated carbon (GAC) and ion exchange (IE) resins. As the result, the best inlet pressure was 5 psig while the best inlet concentration is from 2-4 ppm. The best absorbent is ion exchange because of faster mercury removal mechanism while low pH is preferred for operating parameter of PMRR. As the conclusion, the mercury removal is increased as the pressure, inlet concentration and pH value are decreased.

KESAN KEPEKATAN MERKURI DAN OPERASI PARAMETER KEPADA PENYINGKIRAN MERKURI MENGGUNAKAN ALAT PENYINGKIR MERKURI MUDAH ALIH (PMRR) BAGI AIR SISA PETROKIMIA

ABSTRAK

Merkuri adalah sejenis logam berat yang secara semulajadi wujud pada kerak bumi. Ia boleh didapati di dalam tanah, batu-batu dan laut. Ia boleh dilepaskan ke persekitaran melalui proses semula jadi seperti hakisan batu, penguraian tanah atau letusan gunung berapi. Ia juga dilepaskan kepada alam sekitar oleh aktiviti manusia seperti perlombongan dan proses perindustrian daripada petrokimia dan industri klor-alkali. Merkuri biasanya digunakan dalam termometer, termostat, barometer, mentol, amalgams gigi dan suis. Merkuri adalah salah satu daripada unsur-unsur kimia berbahaya yang wujud di muka bumi. Ia boleh menyerang pusat sistem saraf manusia, buah pinggang, paru-paru dan sistem badan yang lain. Oleh itu, objektif kajian ini adalah untuk mengkaji kandungan merkuri dan parameter operasi untuk membuang merkuri menggunakan Alat Penyingkir Merkuri Mudah Alih (PMRR) untuk air sisa petrokimia. Proses penyingkiran merkuri telah dijalankan di bawah tekanan masuk yang berbeza; 5, 10 dan 23 psig, kandungan merkuri pada aliran masuk yang berbeza, 2, 4, 6 dan 8 ppm, pH yang berbeza dan akhir sekali menggunakan penyerap berbeza; karbon aktif mampat, karbon aktif berbutir dan resin pertukaran ion. Hasilnya, tekanan masuk terbaik adalah 5 psig manakala kepekatan aliran masuk yang terbaik adalah 2-4 ppm. Penyerap terbaik adalah pertukaran ion kerana kepantasan mekanisma pembuangan merkuri manakala pH rendah lebih sesuai untuk parameter operasi PMRR. Sebagai kesimpulan, penyingkiran merkuri meningkat kerana tekanan, kepekatan masuk dan nilai pH menurun.

TABLE OF CONTENTS

LIST OF FIGURES

PAGE

LIST OF TABLES

LIST OF SYMBOLS

Hg	Mercury
Xe	Xenon
˚C	Degree Celsius
µg/L	Microgram per litre
mg/L	Milligram per litre
µg/kg	Microgram per kilogram
ppm	Parts per million
mL	Millilitre
g	Gram
%	Percent
L	Litre
psig	Pounds per square inch gauge
psi	Pounds per square inch

LIST OF ABBREVIATIONS

DOE	Department of Environment
PMRR	Portable Mercury Removal Rig
FAO	Food and Agriculture Organization
PTWI	Provisional Tolerated Weekly Intake
COD	Chemical Oxygen Demand
EAC	Extruded activated carbon
GAC	Granular activated carbon
IE	Ion exchange
BOD	Biochemical Oxygen Demand

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Mercury is one of a very hazardous chemical element that exists on the earth. It is a naturally occurring element and can be found in soil, rock and ocean. It can be released to the environment by volcanoes eruption, rocks erosions and soil decomposition. With chemical symbol of Hg, mercury is located in group 12 and period 6 in the periodic table. It is also located under d-block in the periodic table with electron configuration of [Xe] $4f^{14}5d^{10}$ $6s^2$. Having an atomic number of 80, it is a transition metal that is silver in colour and also called quicksilver or hydrargyrum. Mercury is the only metal that exists in liquid form under standard room temperature. It has melting point of -38.87°C and boiling point of 356.72°C (Risher, 2003). It does not react with most acid but dissolve in many metals such as gold, aluminium and zinc to form amalgams. Examples of metal that do not dissolve mercury include iron, platinum, tungsten and tantalum.

Mercury has been widely used thoroughly in the industries. It is used in the thermometer to measure the temperature. Besides, it is also used in the manometer and barometer, devices that are used in order to measure the pressure. Mercury amalgams are widely in dentistry by applying it on the teeth. Amalgams become dental restorative material choice because of it low in cost, easy for application, high strength and durable. Mercury is also used in batteries, normal fluorescent bulb and switch. But due to it carcinogenic effect, wide variety of choices and enhancement of nowadays technologies, their popularity has decreased.

1.2 Problem Statement

Mercury is one of heavy metal that flow through the wastewater of petrochemical industries. The problem of mercury in the wastewater not only is the concern of the company but also Department of Environment (DOE). Mercury exists in several forms that are elemental mercury, organic mercury and lastly inorganic mercury. Different type can cause different type of illness or hazards. Generally when mercury enters human body, they will attack the central nervous system and liver. Mercury can cause blindness, mental and emotional deterioration, involuntary immobilization and other. Mercury is also mutagenic, teratogenic, carcinogenic and promotes tyrosinemia.

The discharge limit value for mercury in wastewater is about 10 µg/ L and the limit standard value of mercury in drinking water is 2 µg/ L (Zhang et al., 2005). While in the common wastewater from petrochemical industries is about 0.1- 9 mg/ L. This value is way over from the permitted standard and wastewater treatment

should be done to remove the mercury before the wastewater can be discharged into the oceans. With such a high value human being that exposed to the water contaminated with mercury can be affected. One of the examples for disaster that is cause by mercury in the past is in the late 1950s when more than hundreds people are killed and disabled through the intake of fish and shellfish. This disaster was happened in Minamata, Japan.

Many technologies have been identified to be capable of removing mercury from wastewater. They are including several physical and chemical separation processes such as solvent-extraction, ion-exchanged, precipitation, membrane separation, reverse osmosis, coagulation, adsorption and activated carbon. Many researchers have found that adsorption is an effective way to remove mercury while activated carbon is very effective but it is expensive for large scale application. The other techniques stated required either high energy or big amount of chemicals. Furthermore, current technologies used require large space in plant or oil rig but by applying Portable Mercury Removal Rig (PMRR), this problem can be solved. Besides, the benefit of using is it requires fewer workers to operate the rig. Thus the company can save space and cost that can be used for other purposes.

1.3 Objective of Research

The objective of this research is to study the effect of mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR) for petrochemical wastewater.

1.4 Scope of Research

The objective of this research is to study the effect of mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR) for petrochemical wastewater.

Due to the objective is to remove mercury from petrochemical wastewater, thus several components must be studied on.

1. To determine the most influence parameter in mercury removal using PMRR.
2. To determine percentage of mercury removed after treated by PMRR.
3. To compare the quality of wastewater with the standard after it has been treated by PMRR.
4. To determine the most effective method of removing mercury from wastewater either by ion exchange or activated carbon.

1.5 Significances of Research

This research is significance because mercury is a highly toxic material and it can bring many bad effects to the human health. Petrochemical industries are important to Malaysia economy and it can affect many citizens because wastewater that flowing from this type of industry will go directly to the ocean. Mercury can enter the food chain from fish and the higher consumer in the food chain, the higher mercury contamination it can have. This will reflect to human because usually human will be the last consumer in the food chain. This research is also significance because of every wastewater to be released into the sea need to follow or satisfy

Department of Environment (DOE) requirements. Failing to follow the rules, the operation of the petrochemical company may force to stop and what worse is the aquatic ecosystem in the sea may endanger by action taken by the greedy company.

CHAPTER 2

LITERATURE REVIEW

Many have agreed that mercury is hazardous to living thing especially human. Human can consume mercury when they eat fish from the ocean. When mercury has entered the sea, microorganisms will convert the inorganic mercury into methylmercury. Fish then eat this microorganism that result the fish to be contaminated by mercury. Thus, human that consume the fish will also consume the methylmercury. What worsen the situation is methylmercury is more carcinogenic than inorganic mercury. Although inorganic mercury is less harm than methylmercury, Lloyd-Jones et al. (2004) state that high level exposure to inorganic mercury can permanently damage the brains, kidneys and foetus. Such concerns in this topic, many researchers have studied different method to remove mercury in the water. Due to this concern, this literature will review on the effect of mercury concentration and operating parameters to mercury removal using Portable Mercury Removal Rig (PMRR).

2.1 Sources of Mercury

Mercury is a natural occurring element that can be found in rocks, soil and ocean. It can be released into the environment by volcanoes eruption, rocks erosion and soil decomposition. Mercury is commonly used in temperature measurement tools such as thermometer and thermostat but it is also used in pressure measurement devices such as manometer and barometer. Manohar et al. (2002) state that wastewater that comes from industries such as chlor-alkali manufacturing, oil refinery, paint, pharmaceutical and battery manufacturing industries contain mercury. But out of all industries that have been stated, chlor-alkali manufacturing industries have been the main contributor for mercury contamination in environment said Mohan et al. (2001). People may be exposed to mercury from a variety of sources, including drinking water. Inorganic mercury compounds such as mercuric chloride are used in batteries, paper manufacturing and chemical industries. On the other hand, organic mercury compounds such as methyl mercury are found in large fish such as bass, shark, swordfish and tuna. In the past, mercury was used in indoor paints and agricultural pesticides and is used to prevent mildew in outdoor paints.

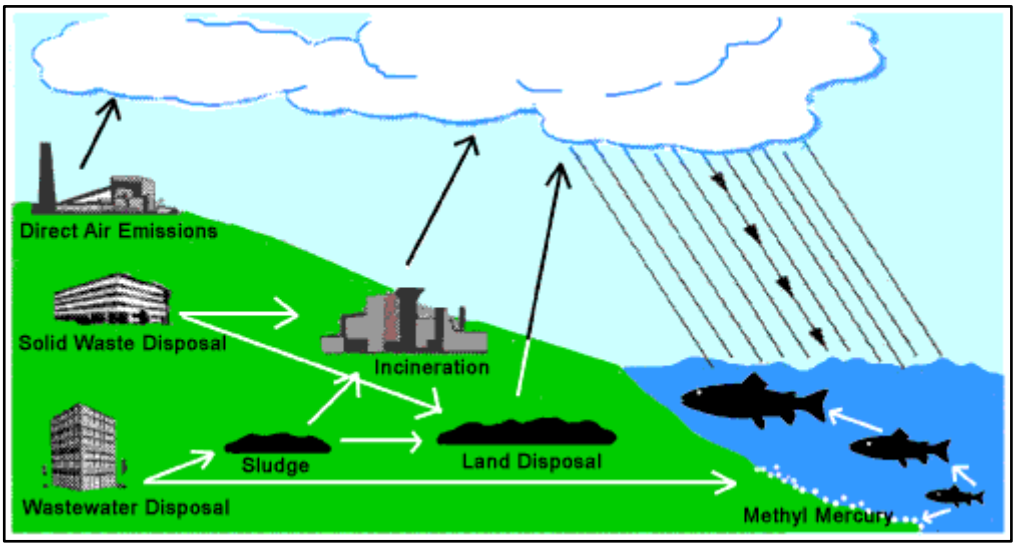

Figure 2.1 Sources of mercury released into the environment

2.2 Hazard that will come out as the Effect from Mercury Contamination

Mercury has been classified as one of the most hazardous element that can be found on the earth. Dabrowski et al. (2004) also agreed with this statement by stating in their research that mercury can spread easily in the environment and will be accumulated by living organisms. Many health effects can be cause by mercury contamination in human body such as brain and kidney damage. In the word of Manohar et al. (2002), high concentration of mercury in the body can cause damage to pulmonary function, chest pain and difficulty to breathe (dyspnoea). They also said that mercury can easily pass brain-blood barrier and damage the brain. Risher (2003) added that mercury also can cause cardiovascular effect, gastrointestinal effect, hepatic effect, irritation and sensitization, genotoxic effect and cancer. One of the examples for mercury hazard come in late 1950s as more than a hundred people life in Minamata bay, Japan were killed and disabled after they eating fish and shellfish that contaminated with methylmercury. Besides that, mercury can also bring negative effect to developing foetus when the mother is consuming foods that are contaminated by mercury. UN Food and Agriculture Organization (FAO) have suggested Provisional Tolerated Weekly Intake (PTWI) for methylmercury to be 1.6 µg/kg body weight in order to prevent the developing foetus be damaged (Malakahmad et al., 2011). According to Langford and Ferner (1999) the toxicity of mercury is different from elemental mercury metal, inorganic mercury salts and organometallic mercury compound. Inorganic mercury compounds are the most common forms of mercury found in drinking water. While organic mercury compounds are the most harmful forms of mercury are rarely found in drinking water.

2.3 Mercury in Drinking Water

Mercury carried by wind and rain is found throughout the environment mostly due to the release of naturally occurring mercury from rock and soil, burning of coal and oil that contains small amount of mercury, release of mercury from metal smelters and incineration of materials that contain mercury such as batteries. There are many ways that mercury can get into drinking water firstly by rain and snow can carry mercury from the air into surface water supplies such as lakes, rivers and reservoirs. Mercury also can seep into underground water supplies from industrial and hazardous waste sites. Improperly disposed household products such as mercury containing outdoor paints also contribute to the problem by moving through the soil and reach private well water supplies. In addition, past application of mercury-based pesticides on agricultural lands such as farm and fruit orchards can wash into nearby surface water or travel through the soil into underground water supplies can worsen the problem.

2.4 Methods to Remove Mercury from Water

There are many methods that can be used to remove mercury from water. Each of the method has their own advantages and disadvantages and the table below will show the results obtained by other researchers.

Table 2.1 Methods of mercury removal from water

Title of literature (authors, year)	Method of removing mercury	Result
Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste (Mohan et al.,2001)	Activated carbon	Adsorption of mercury increased with decrease in temperature and solution pH
Mercury removal from aqueous solutions by complexation ultrafiltration (Barron-Zambrano et al.,2002)	Complexation-ultrafiltation	In acidic medium the mercury retention strongly depends on pH
Mercury removal using a poly(vinylalcohol)/ poly(vinylimidazole) complexing membrane (Bessbousse et al.,2010)	Membrane	When used in the filtration mode, the elimination ratio of mercury was greater or equal to 99.4%
Mercury removal from water by ion exchange resins adsorption (Chiarle et al.,2000)	Ion exchange resins	Sorption capacity is very high and strongly dependent on the initial pH
Sequencing Batch Reactor (SBR) for the removal of Hg2+ and Cd2+ from synthetic petrochemical factory wastewater (Malakahmad et al.,2011)	Micoorganism in batch reactor	The treated wastewater will achieve considerable chemical oxygen demand (COD)
Mercury (II) removal from water by electrocoagulation using aluminium and iron electrodes (Nanseu-Njiki et al.,2009)	Electrocoagulation	More than 99% of pollutant was eliminated and removal efficiencies do not vary significantly on type of electrode.

2.5 Important Operating Parameters in Order to Remove Mercury from Wastewater

Many operating parameters can be assumed to be important to remove mercury from wastewater. From Chiarle et al. (2000), they have stated that the lower the initial pH, the lower the concentration of mercury at the uptake. Thus, the pH of the water can be related to the concentration of mercury at the inlet of PMRR. Besides, the pressure of the PMRR during the treatment process can also have the effect on the efficiency of the adsorption process. The pressure in the PMRR can affect the flow rate of the wastewater containing the mercury. It has been proved that the pressure in the PMRR is directly proportional to the flow rate of the wastewater enter the PMRR from the dilution tank. When the flow rate of wastewater is high, thus the water cannot be treated in a proper time and as the result, the mercury is less efficient to be removed from the wastewater.

2.6 Advantages of using PMRR for Mercury Removal

The current system that is used at the petrochemical industries to remove mercury from their wastewater is requiring large space. Thus by applying PMRR at the petrochemical industries, much space can be saved and used for other things. Secondly, PMRR does not require many workers, thus the company can saved more money. The system used in PMRR is just simple and only need one or two workers. Thirdly, PMRR is easily to move around the workplace. From this advantage, many section of the company can used the same PMRR without adding other piping to connect several sections in order to remove mercury from the wastewater. The

system that currently applied to PMRR is quiet easy thus workers assigned to operate the rig do not require high training as well as the rig is really safe to operate. Now it has been proved although PMRR is just a small system, but it can challenge the current system that used to remove mercury in the petrochemical wastewater.

2.7 Ion Exchange Resins

Rengaraj and Moon (2002) state the removal of heavy metal pollutants at high concentrations from water can be readily accomplished by chemical precipitation or electrochemical method. They also state the removal for low concentrations heavy metal is more effective if implemented by ion exchange or adsorption on solid sorbent such as activated carbon as supported by Sigworth and Smith (1972). For this experiment, Lewatit® MonoPlus TP 214 ion exchange resins are selected to be used. This type of ion exchange is monospherical, and having a high affinity for mercury. It has a good capacity for platinum metals, gold and silver and specially used to remove mercury from flue gas and ground water. This resin offers higher mechanical and osmotic stability, better kinetics, higher capacity and remarkable low leakage according to the process conditions.

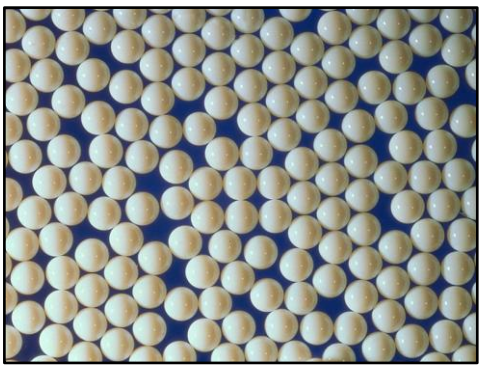

Figure 2.2 Ion exchange resins

2.8 Activated Carbon

Activated carbon can be produced from a variety of carbonaceous raw materials, by either a physical or chemical activation methods. The adsorptive capacity of the final product depends on internal surface area, pore structure and surface chemistry that are defined by the nature of the starting material and production process. According to Skodras et al. (2007), among air pollution control applications, carbon-based processes including both direct injection and fixed bed have been developed for mercury uptake from municipal and hazardous waste incinerators. Yardim et al. (2003) said activated carbons are widely used as adsorbents for removing different pollutants from drinking water. This shows that activated carbon or also known as activated charcoal is commonly used in water purification system. In recent years, activated carbon is derived or prepared from various cheaper and alternative materials such as agricultural by-product and waste of polymer materials thus reducing its cost and can be used in large scale application compared to ion exchange.

Figure 2.3 Activated carbon as solid sorbent in water purification method

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this study, there are several steps that need to be conducted before the experiment, during the experiment and after the experiment. In this chapter, the steps will clearly explained in their section respectively such as the set up for Portable Mercury Removal Rig (PMRR), the installation of absorbent, the preparation for the synthetic mercury wastewater and mercury analysis preparation.

3.2 Research Design

This research is a qualitative research thus it will focus on the concentration of mercury in the water at the outlet of the PMRR. This research proposes to study on the effect of mercury concentration and operating parameters for mercury removal using PMRR. Thus the operating parameters such as temperature, pressure and pH

value also will be investigated to know on how it will affect the mercury concentration that will be removed during the process. At the end, the mercury concentration in the water will be analyzed to make sure whether the PMRR is effective in removing mercury from water or not.

Figure 3.1 Portable Mercury Removal Rig (PMRR)

3.3 Procedures before the Experiment

3.3.1 To prepare stock solution

In this experiment, 1000 ppm of mercury stock solution was prepared before diluted for the purpose of the experiment. Several apparatus were needed to prepare the stock solution such as weighing boat, electronic balance, spatula, 500 mL volumetric flask, dropper, glass rod and beaker. Materials used to prepare stock were

mercury (II) chloride and distilled water. Firstly, 0.5 g of mercury (II) chloride was weighed using an electronic balance. After that, the solids were transferred into a beaker. The weighing boat used was washed by distilled water and the water was transferred into the beaker. 150 mL of distilled water was added into the beaker to dissolve the solids. The solution was stirred using a glass rod until all the solids have dissolved in the solution. Then, the solution was transferred into a 500 mL volumetric flask. Lastly, distilled water was added into the volumetric flask until 500 mL then the volumetric flask was shook to mix the solution thoroughly.

3.3.2 To prepare activated carbon filter

Apparatus needed to preparer the filter that will be installed to the PMRR was weighing boat, electronic balance, sponge and activated carbon holder. The activated carbon used was from extruded activated carbon (EAC). Firstly, the activated carbon was weighed for about 300 g on a weighing boat using the electronic balance. After that, the activated carbon was put into the holder. A sponge was used on top of the activated carbon to prevent the activated carbon from flushed down due to the high pressure of water entering the filter. Then, the filter was installed to the PMRR. After the experiment using EAC was completed, granular activated carbon (GAC) and ion exchange (IE) resins were used in the place for activated carbon.

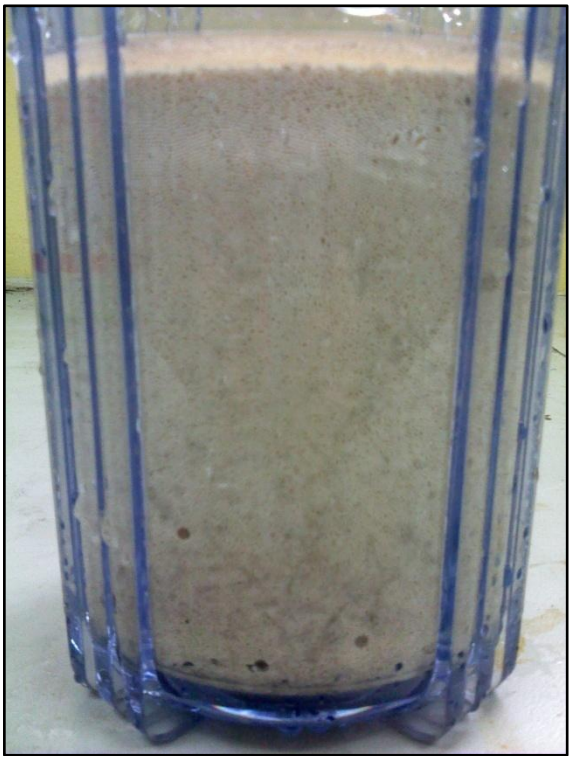

Figure 3.2 Lewatit® MonoPlus TP 214 Ion Exchange Resins

3.4 Procedures during the Experiment

3.4.1 To prepare synthetic mercury wastewater

The 1000 ppm mercury stock solution was diluted to the desired concentration using the simple Equation (3.1):

$$M_1V_1 = M_2V_2 \quad (3.1)$$

The volume of V_2 is 40 L. The inlet concentration of synthetic mercury wastewater to be treated was 2, 4, 6 and 8 ppm. This is due to the common petrochemical wastewater discharge mercury concentration at 1-9 ppm. Thus the volume of 1000 ppm for respective inlet concentration was:

Table 3.1 Volume of 1000 ppm stock solution for respective inlet concentration

M_1 (ppm)	V_1 (mL)	M_2 (ppm)	V_2 (L)
1000	80	2	40
1000	160	4	40
1000	240	6	40
1000	320	8	40

The valve at the outlet of untreated tank was closed before the stock solution as calculated above was pour into the tank. After that, water was added to the tank until the volume was equal to 40 L.

3.4.2 Running the experiment

Before the synthetic wastewater was treated using PMRR, the temperature of the synthetic wastewater was taken using a thermometer and the reading was recorded. Then, 80 mL of the wastewater was taken and stored in a Scott bottle as inlet sample. Make sure the valve at the bottom of treated tank and valve for drain was closed then the pump was turned on. The valve at the bottom of untreated tank was opened then the pump was turned on. Wait until all the wastewater to be treated then the pump was turned off. The temperature of the treated wastewater was taken. After that, 80 mL of the treated wastewater was taken as the treated sample and inserted into a Scott bottle. All the samples were analyzed.

3.5 Procedures after the Experiment

After the PMRR was ran, the PMRR must be cleaned. Firstly, the treated wastewater was drained by opening the valve at the bottom of the tank and the drain valve. After that, all the valves were closed and clean water from the tap was filled into the untreated tank. The PMRR was run as it was run for treating the synthetic wastewater. After that, the treated tank was drained once again. All the apparatus used to run the PMRR were washed and cleaned before they can be used again for the next run.

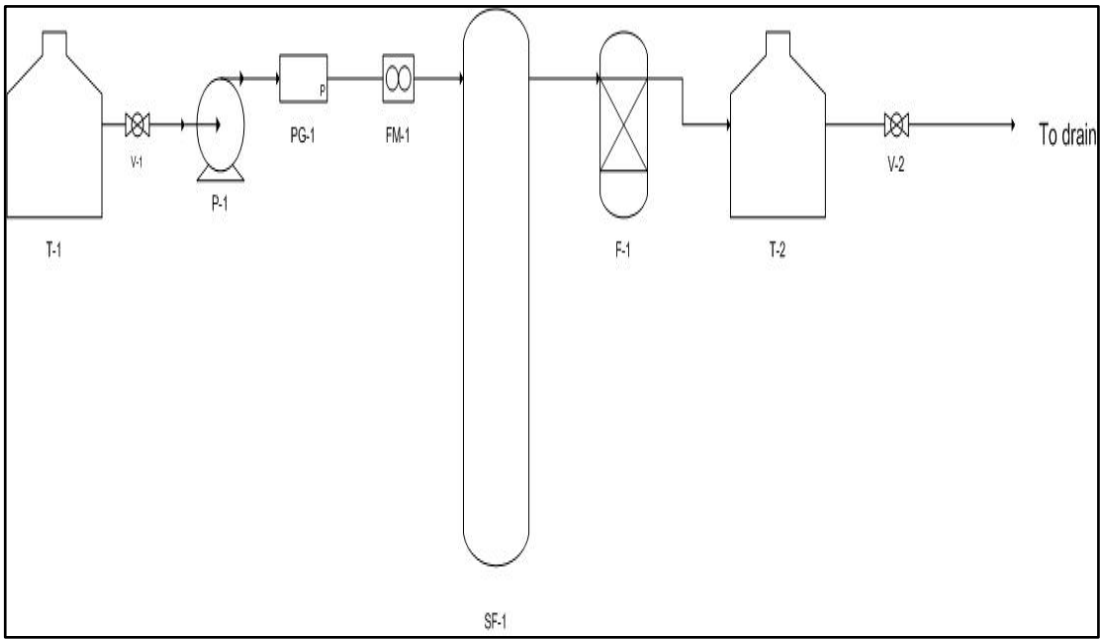

Figure 3.3 Schematic Diagram for Portable Mercury Removal Rig (PMRR)

3.6 Procedures for Mercury Analysis

After all the samples were obtained during the experiment, they were analyzed to measure the mercury concentration before and after the treatment. The methods used to analyze the wastewater samples were using pH value and conductivity value. The

apparatus used were pH meter and conductivity meter. After the conductivity values were got, the percent removal of mercury was calculated using the Equation (3.2):

$$\left(\frac{C_I - C_O}{C_I}\right) \times 100\% \qquad (3.2)$$

3.6.1 Analysis using pH meter

The apparatus used to measure the pH value of the wastewater was pH meter. Firstly, the pH meter must be calibrated to ensure the results obtain is right and do not deviate from the real one. After the pH meter was calibrated, then it can readily be used to test the samples. The probe of the pH meter was inserted into the sample and it was stirred to make sure the hydrogen ions in the samples were equal at all point in the liquid. After the reading was constant and the symbol √A was shown, the reading can be taken and recorded. Before the other samples were tested, the probe need to be washed using distilled water. All the readings were recorded and tabulated.

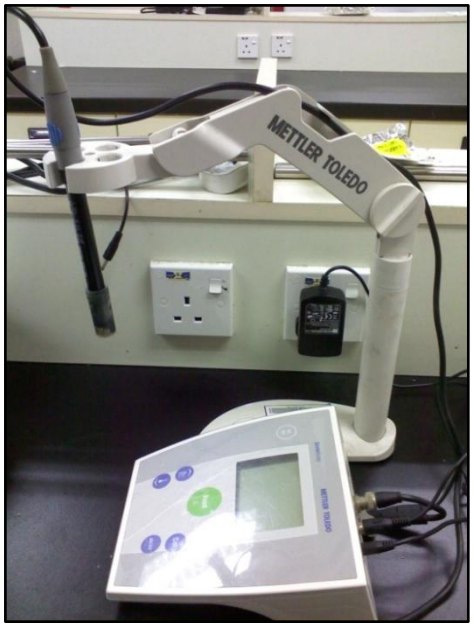

Figure 3.4 Mettler Toledo SevenEasy pH meter

3.6.2 Analysis using conductivity meter

For analysis using conductivity value, a conductivity meter was used in this procedure. The procedures were just the same except the conductivity meter do not required to be calibrated. The probe of the conductivity meter was inserted into the sample and it need to be stirred. After the reading was constant and the symbol √A was shown, the reading can be taken and recorded. Before the other samples were tested, the probe need to be washed using distilled water and all the readings were recorded and tabulated.

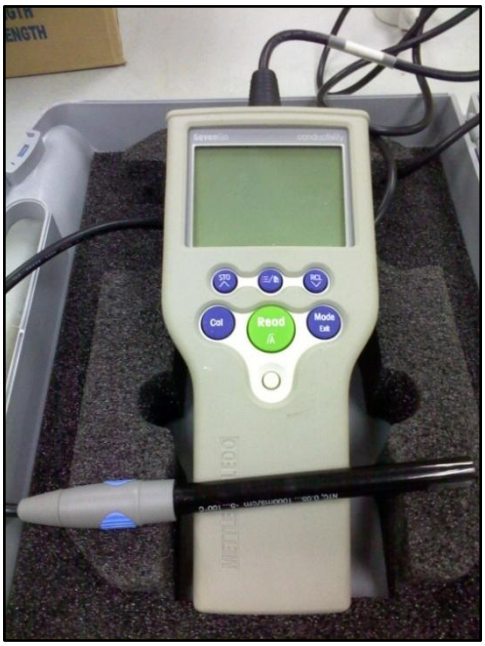

Figure 3.5 Mettler Toledo SevenGo portable conductivity meter

3.7 Process Flow Chart

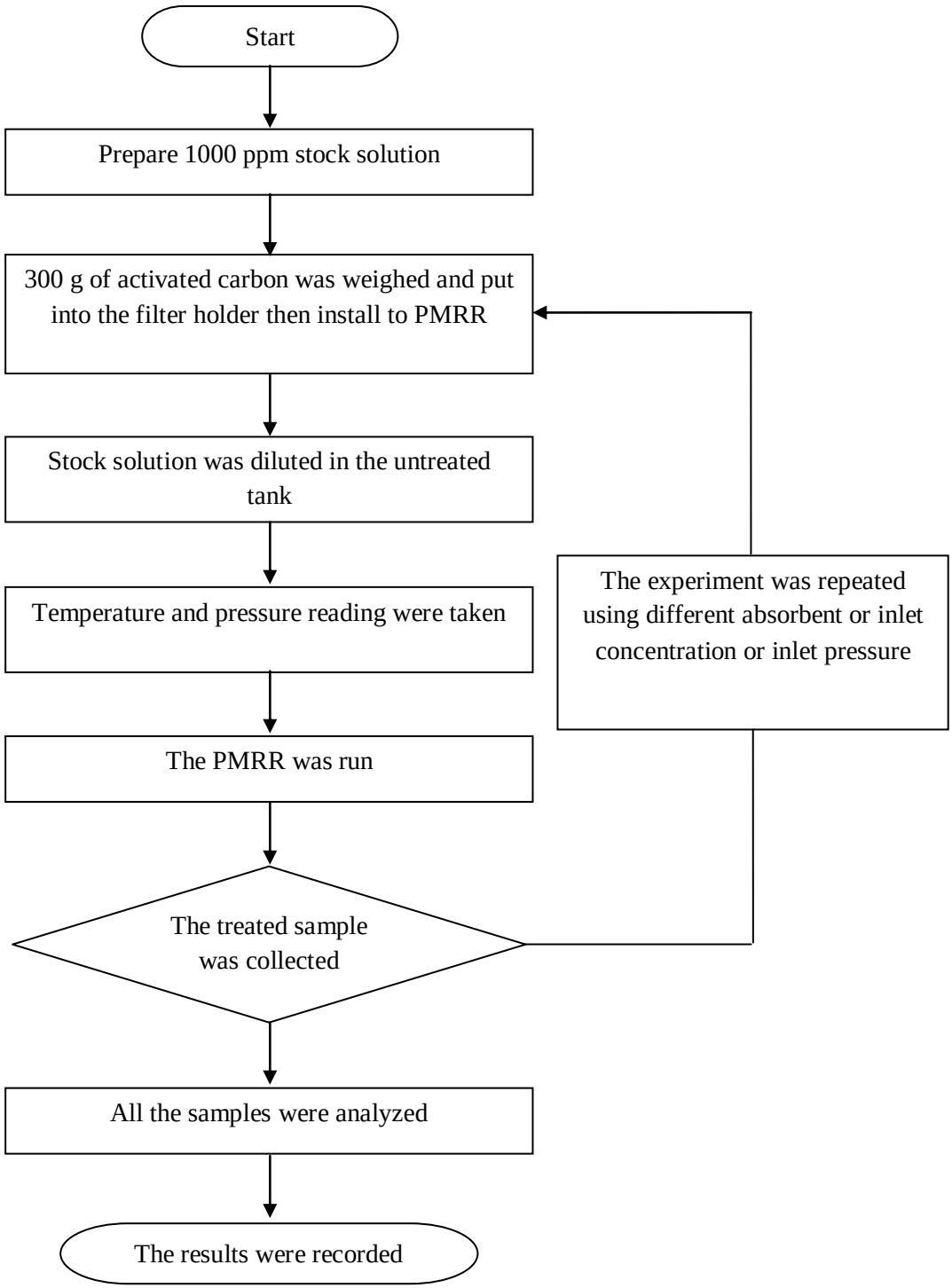

Figure 3.6 Process Flow Chart for Mercury Removal using PMRR

CHAPTER 4

RESULTS & DISCUSSION

4.1 Experimental Studies

In this research, several parameters were investigated to know how much they can affect the efficiency of mercury removal in the wastewater using PMRR. Parameters investigated were the temperature, inlet pressure of the wastewater, inlet concentration of wastewater, type of absorbent and inlet pH of wastewater. This chapter will discuss how significant the parameters in affecting the removal of mercury from the wastewater.

4.2 Effect of Temperature of Synthetic Mercury Wastewater on Mercury Removal

The temperature reading of synthetic mercury wastewater was taken before and after the wastewater is treated in the PMRR. From the observation, all the temperature for

influent wastewater were read about 29-30 ˚C. This is due to the room temperature where the experiment was run and temperature of tap water used to dilute the stock solution. After the PMRR was run, the temperature of effluent wastewater in the tank was measured and the temperature was same as the inlet that is 30˚C. The result showed that the temperature does not change significantly during the water was treated. Mohan et al. (2001) in their research have found that adsorption of mercuric ions is increased with decrease in temperature of the influent wastewater. It is because the increased in mobility of ions and a decrease in retarding forces acting on the diffusing ion results in this phenomenon as they stated.

4.3 Effect of Influent Concentration of Synthetic Mercury Wastewater on Percentage of Mercury Removal

For the effect of initial concentration on mercury removal can be seen in the graph below. The graph below shows the conductivity value of wastewater using granule activated carbon (GAC) as the absorbent.

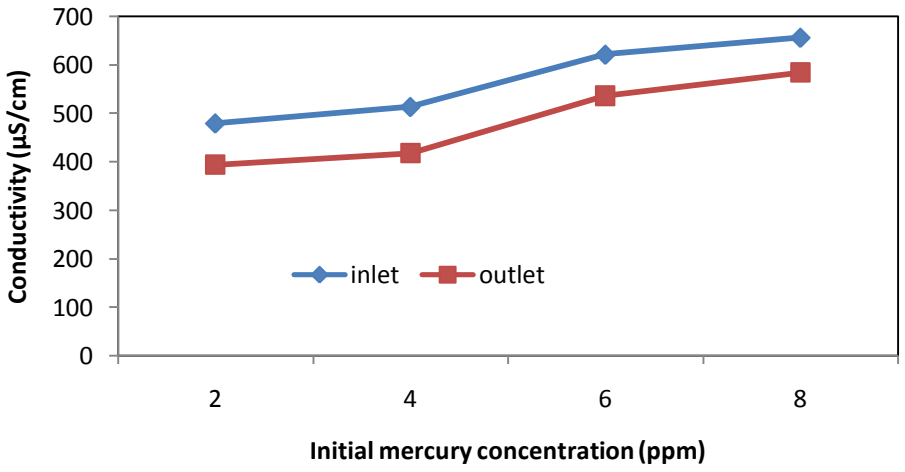

Figure 4.1 Graph of conductivity value vs. initial mercury concentration

From the result above, the graph for percent of mercury removed after the treatment was plotted and shown below.

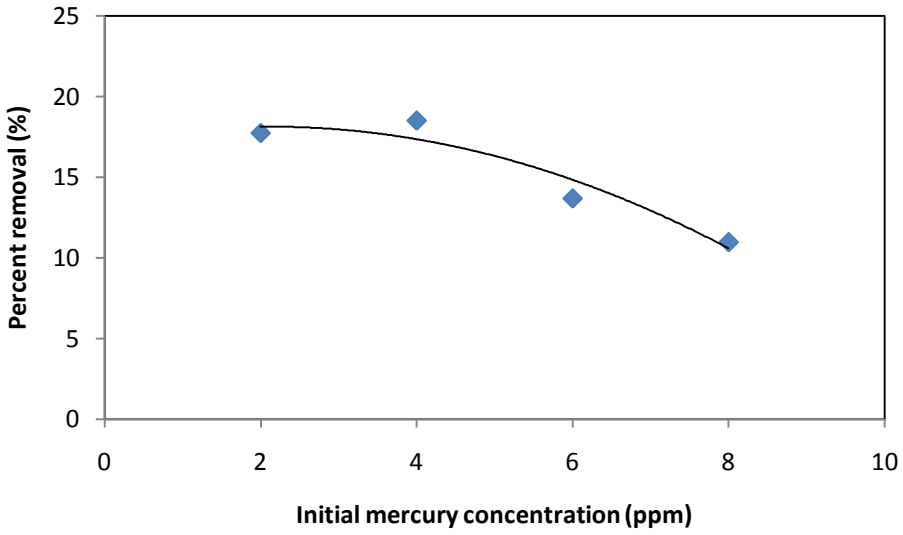

Figure 4.2 Graph of percent removal of mercury vs. initial mercury concentration

As the influent concentration increased, the percent of mercury removal is decrease. The highest percent mercury removed was at the inlet concentration of 4 ppm followed by 2 ppm. This is because of the amount of mercury ion concentration in the aqueous solution that lower compared to 6 ppm and 8 ppm. If the concentration is high, so goes the same as the ion of mercury in the solution thus the absorbent may not has enough sites for absorption to treat the wastewater. This kind of result was also obtained from the other two types of absorbent used for the experiment. Lloyd-Jones et al. (2004) as they state in their research that the mechanisms of mercury sorption by the sorbents are strongly dependent on the solution parameter such as concentration of the solution. Kadirvelu et al. (2004) also agree when they state in batch mode studies, the adsorption was dependent on the initial Hg (II) concentration. Goyal et al. (2009) in their journal state, the breakthrough time of Hg (II) ions on granular activated carbon and activated carbon cloth decreases on increasing the feed concentration. This can really justify that the initial mercury

concentration at the inlet played a very important role in the percentage of mercury ion remove from the wastewater during the treatment.

4.4 Effect of Initial pH value of Synthetic Mercury Wastewater on Percentage of Mercury Removal

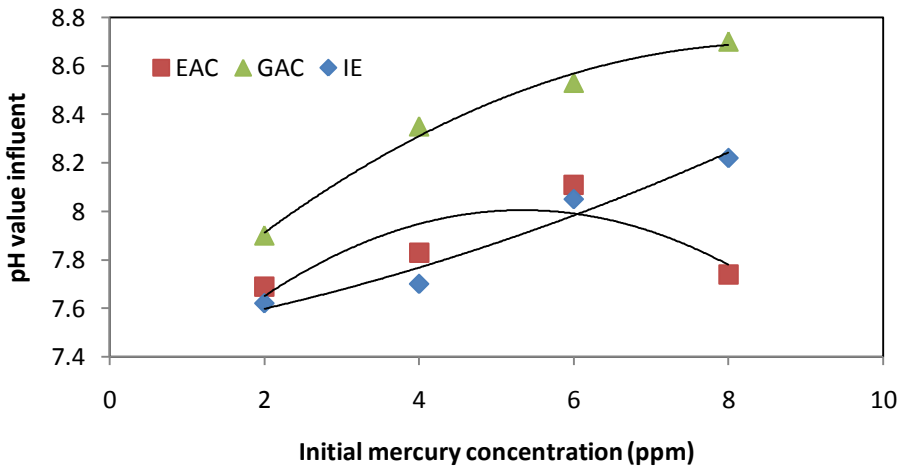

Figure 4.3 Graph of pH value at the influent vs. initial mercury concentration

The graph above shows the pH value of the effluent wastewater vs. the initial mercury concentration. As we all know, the pH value of the aqueous solution is directly proportional to the concentration of the solution. Thus, as the initial mercury concentration was increased, the pH values of the solutions were also increased. After the wastewater was treated, the result was tabulated and the graph below was plotted.

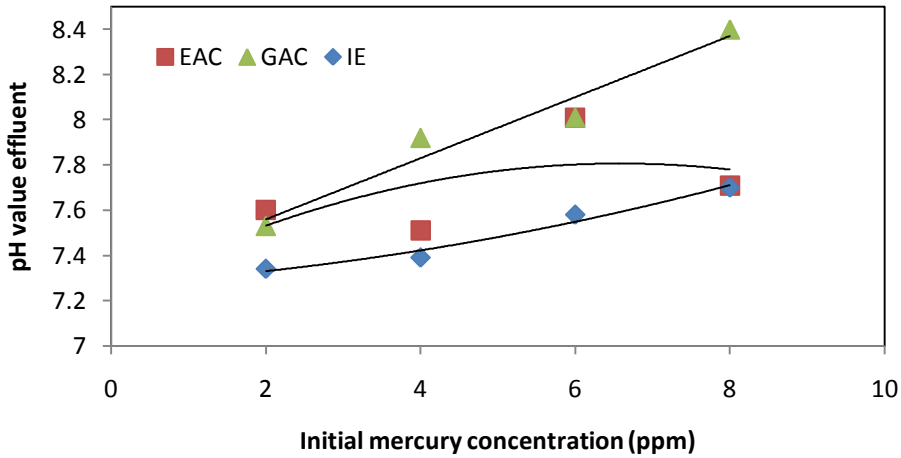

Figure 4.4 Graph of pH value at the effluent vs initial mercury concentration

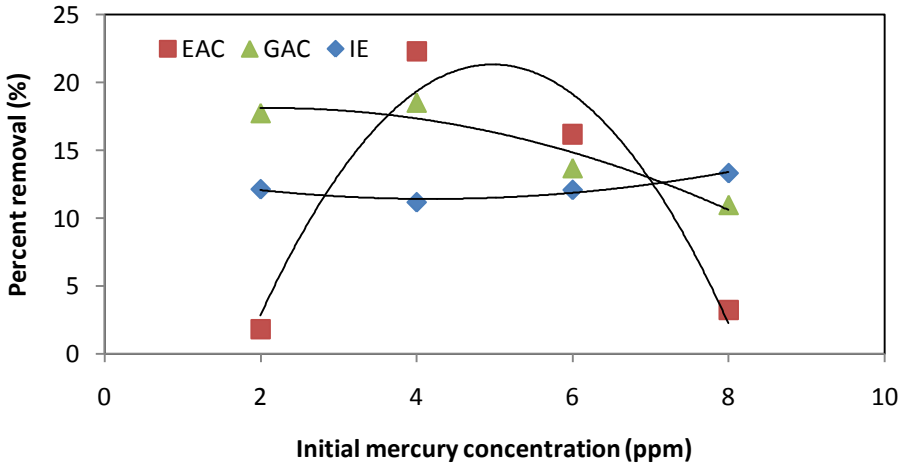

Figure 4.5 Graph of removal of mercury vs initial mercury concentration

As we can observe above, the percent removal of mercury for all types of absorbent was decreased as the initial influent mercury concentration was increased. At concentration 2 ppm using EAC, the percent removal of mercury was very low. This may be due to the low of mercury ions in the wastewater thus the absorbent cannot absorb it effectively. For IE as the absorbent, the percent removals for all the inlet pH values were quiet promising. Although the pH values were increase as the effect of increasing mercury concentration, it still absorbs mercury effectively. This show how

effective ion exchange resins are as the absorbent for mercury removal in PMRR system. Using GAC as the absorbent, the percent removal was decrease as the pH value was increase of the inlet mercury wastewater. The degree of removal strongly dependent on the initial pH of the solution and it decreases as the pH increases (Chiarle et al., 1999). Barron-Zambrano et al. (2002), Lloyd-Jones et al. (2004), Mohan et al. (2001), Rengaraj and Moon (2002), Chojnacki et al. (2004), Rangel-Mendez and Streat (2002), Kadirvelu et al. (2004) and Yardim et al. (2003), all of this researchers agreed that the removal of mercury from aqueous solution or wastewater is strongly influence by the initial pH. In addition, Yardim et al. (2003) wrote that the mercury removal using activated carbon is increases at a pH value greater than pH 4. Then, Llyod-Jones et al. (2004), state that the mercury uptake increases when pH increases from 4 to 6. At pH values below 2, hydrogen ions are likely to compete with mercuric ions and at pH values above 6.5 mercuric ions might precipitate (Mohan et al., 2001). It justified that the removal of mercury is strongly dependent on the initial pH value at the inlet and the optimum pH value is from pH 4 to 6.

4.5 Effect of Inlet Pressure of Synthetic Mercury Wastewater on Percentage of Mercury Removal

The graph below shows the percentage of mercury removed from the wastewater using three different absorbent. In the experiment, it was found that the inlet pressure of wastewater pumped into the system is directly proportional to the flow rate of the wastewater during the experiment.

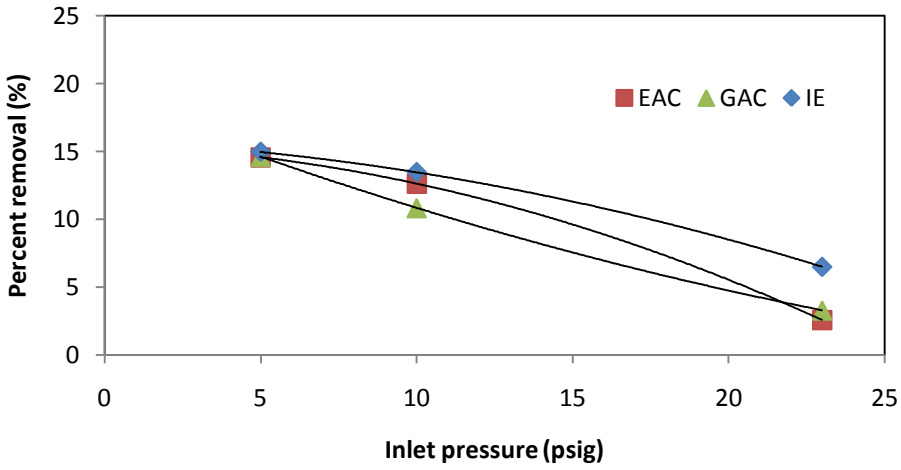

Figure 4.6 Graph of percentage mercury removal vs. inlet pressure

In the graph, we can observe that the highest percent of mercury removed from the wastewater is about 15% at 5 psig. Ion exchange resin has the most promising effectiveness because at pressure gauge of about 23 psi, it still manages to remove mercury at 6.49%. EAC and GAC only manage to achieve about 3.23% and 3.29% mercury removed 23 psig. Overall mercury removals were relatively low due to the less of contact time between the absorbent and the wastewater. Thus the amount of mercury remove was really low. Goyal et al. (2009) in their research said that the breakthrough time of Hg (II) ions on activated carbon increases with decreases on increasing hydraulic loading rate. Bao et al. (1999) also wrote in their paper that the efficiency of GAC filtration depends on the contact time between the activated carbon with the treated water. Thus, it can be justified that the inlet pressure or indirectly the inlet flow rate has a significant influences on the percent of mercury removal using PMRR.

4.6 Effect of Different Types of Absorbent on Percentage of Mercury Removal

To determine which absorbent has the better efficiency in removing mercury, several samples were sent to Central Laboratory at University Malaysia Pahang to measure the exact amount of mercury in the samples. The inlet concentration was same for all the samples that are 14 ppm with 10 psig as the inlet pressure. The concentration of mercury was tested by in-house method using direct mercury analyzer.

Table 4.1 Mercury outlet concentration for various types of absorbent

Absorbent	Outlet concentration (ppb)	Percent removal (%)
Ion exchange	24.718	99.82
Extruded activated carbon	17.398	99.88
Granular activated carbon	19.723	99.86

Based on the result, it can be concluded that extruded activated carbon has a better efficiency in removing mercury in wastewater. This followed by granular activated carbon and lastly ion exchange. The amount of mercury in the treated samples was 17.398 ppb, 19.723 ppb and 24.718 ppb respectively. The effectiveness of extruded activated carbon is due to the amount of carbon at their surface and its high surface area and micro pore volume (Zhang et al, 2005). Lloyd-Jones et al. (2004) in their research found that the mechanisms responsible for mercury removal are predominantly physic-sorption of uncharged species coupled with a reduction reaction and subsequent precipitation on the surface and in the pores of the sorbent. But referring to Figure 4.6, IE is has higher efficiency compared to the other two followed by GAC and lastly EAC. The adsorption onto strong base ion exchange resins has much faster overall adsorption kinetics (Dai et al., 2010). This also agreed by Lloyd-Jones et al. (2004) when the state that the mechanism responsible for

mercury removal by the ion exchange resins in much faster than two-phase reduction-precipitation reaction of mercury.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

The study shows that the removal of mercury from wastewater is strongly dependent on the pH of the wastewater source. As the pH of the water is increased, the percent removal of mercury from the wastewater is decreased.

The other parameters that affect the mercury removal are initial concentration, flow rate or the inlet water pressure and type of absorbent used while temperature only gives small effect to the percent of mercury removal. The optimum initial concentration of mercury that gives highest percent removal is 2-4 ppm while 8 ppm is the most unsuitable inlet mercury concentration to be treated by PMRR.

The inlet water pressure also has significant role in the mercury removal from the wastewater. The recommended pressure is 5 psig while 23 psig is the most unsuitable operating pressure. Ion exchange resins are the best absorbent to be used in the PMRR because of its faster mechanism of mercury removal followed by extruded activated carbon and lastly granular activated carbon.

5.2 Recommendations

For the future improvement, the other physical and chemical properties of water should be tested such as the turbidity, chemical oxygen demand (COD) and biochemical oxygen demand (BOD). This will help to understand how PMRR is treating the water whether it complies with the requirement or not or else the exact performance of PMRR cannot be measured.

In the future, the PMRR should be included with its own control system such as system to control the volume of water into the tank. This is because, if excess water was added to the system instead of the calculated one, it can give huge effect to the result thus hidden the true PMRR performance. For industrial usage, the installation of mercury concentration measurement is much recommended to control the effluent mercury concentration at the outlet to make sure it satisfied the DOE requirement.

The petrochemical wastewater should be analyzed first to determine the state of mercury in the wastewater. This is because organic mercury cannot be removed by ion exchange but activated carbon. But ion exchange has a faster mechanism of mercury removal compared to activated carbon thus this two absorbents should be applied together to get higher percent of mercury removed.

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APPENDIX A-1

Direct Mercury Analyzer DMA-80