EFFECTS OF PH IN MERCURY NITRATE TREATMENT USING MEMBRANE SYSTEM WITH BIOLOGICAL PRETREATMENT

MOHD YUSNIZAM BIN YUSOF

UNIVERSITI MALAYSIA PAHANG

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JUDUL: **EFFECTS OF PH IN MERCURY NITRATE TREATMENT USING MEMBRANE SYSTEM WITH BIOLOGICAL PRETREATMENT**

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EFFECTS OF PH IN MERCURY NITRATE TREATMENT USING MEMBRANE SYSTEM WITH BIOLOGICAL PRETREATMENT

MOHD YUSNIZAM BIN YUSOF

A report submitted in partial fulfillment
of the requirements for the award of
the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resource Engineering
University Malaysia Pahang

APRIL, 2008

"I declare that this thesis is the result of my own research except as cited references. The thesis has not been accepted of any degree and concurrently submitted in candidature of any degree."

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Date	: 29 APRIL 2008

I dedicate the joy of my successful undergraduate project to my beloved family and my precious friends

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Finally, I hope that this report has fulfilled the requirements of the project evaluation. I also hope that the report will give aid to those who wanted to do projects that associated with membrane and mercury in the future.

ABSTRACT

Wastewater come from industry containing mercury is very dangerous. We need to treat the wastewater effectively to avoid the toxic. Membrane usage in wastewater treatment has increase due to its ability to filtrate the unwanted particle. The manipulating of parameters of membrane can give the better result other then changing the type of membrane for filtration of mercury in wastewater. Using *P.putida* as the pretreatment or volatilizing agent and continue with alternation of pH value for mercury solution, this technique seems easily can reach the target of removing mercury to the minimum level of permitted. According to experiment, the pretreatment stage decreases the Hg solution from concentration of 250ppb to 8ppb. Then, continue with Membrane separation, the concentration was decrease to 0ppb within pH8 to pH9. So, as conclusion, the best pH for operating membrane to filtrate mercury wastewater is pH8 to 9. This is because membrane operates at neutral or base condition.

ABSTRAK

Air kumbahan kilang yang datang dari industri dan mengandungi merkuri adalah sangat bahaya. Rawatan air kumbahan dari kilang perlu dilakukan dengan berkesan untuk mengelakkan kesan toksiknya. Penggunaan membrane dalam rawatan air kumbahan kilang telah meningkat kerana keupayaanya untuk menapis bahan yang terbuang. Pengubahsuaian ke atas pembolehubah pada membran boleh memberikan keputusan yang lebih bagus berbanding dengan penukaran jenis membrane untuk menapis merkuri dalam air kumbahan kilang. Dengan penggunaan *P.putida* sebagai rawatan awal atau agen peruap dan disambung pula dengan pemendakkan merkuri dengan menggunakan batu kapur, teknik ini menunjukkan tujuan untuk membuang merkuri dari air kumbahan mudah tercapai. Berdasarkan ujikaji yang dilakukan, rawatan awal menggunakan *P.Putida* telah menurunkan kepekatan larutan Merkuri dari 250 ppb kepada kepekatan 8ppb. Kesinambungan terus kepada penapisan Membran, kepekatan 8ppb telah diturunkan kepada 0ppb pada pH8 ke pH9. Sebagai kesimpulannya, membrane menapis ion-ion merkuri pada pH8 hingga pH9 kerana pada keadaan itu, lubang-lubang membrane mengecil dan bingkai membran menebal. Ini membuktikan yang membran menapis ion-ion merkuri pada keadaan neutral dan beralkali.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Research Background

The pollution of wastewater in Malaysia becomes more serious. Wastewater is the unwanted product yield from the process of cleaning. The contents of wastewater depend on from where the wastewater produced. Usually wastewater came from palm oil industry contain higher level of Chemical Oxygen Demand and Biochemical Oxygen Demand. Wastewater from battery industries and petrochemical industries contains heavy metals such as mercury. The wastewater released must be below the level of mercury permitted limits and if not, it will cause harmful effects to human life and ecosystem. Wastewater treatment system is a factory's owner responsibility. They should provide a plant for wastewater treatment process. Wastewater that contains mercury must be treated effectively to avoid the side effect of mercury pollution.

Historically, one of the largest releases was from the Colex plant, a lithium-isotope separation plant at Oak Ridge. The plant operated in the 1950s and 1960s. Records are incomplete and unclear, but commissions have estimated that some two million pounds of mercury are unaccounted for (Wikipedia, 2007). The toxicity

Figure 1-1: Mercury Waste from Industrial (ERG, 1997)

effect of mercury has long been known to humans like failure brain functions can cause degradation of learning abilities, personality changes, tremors, vision changes, deafness, and muscle incoordination and memory loss (www.osha.gov). Hat makers during the 19th century developed symptom of shaking and slurring of speech from exposure to large amounts of inorganic mercury, which was used to give a metallic sheen to felt halts (Wisconsin, 1999). After that, term "mad as a hatter" rise.

Research on water pollution by heavy metals is essential due to their deadly effects yet at less concentration. For that reason, the elimination and separation of toxic and environmentally related heavy metal ions are a knowledge challenge with respect to manufacturing and ecological applications. Mercury, as one of the most dangerous heavy metal has very high tendency for binding to proteins and it mainly affects the renal and nervous systems; hence mercury content of wastewater streams must be reduce below discharging limits (Yusuf Uludag,*et al*, 1997).

Mercury is one of the most strictly regulated elements, often restricted to less than 1 µg/l (Ebdon *et al*, 2002) and in Malaysia, 0.005mg/l (http://www.aots.org), or less. Mercury is often found in landfill leachate, in petroleum and incinerator (Wisconsin, 1999) scrubber water. It may also be found in research and development laboratory wastewater. Mercury is very dangerous to our lives but there are ways to remove it nowadays. In petrochemical processing, mercury contain in wastewater is at low concentration but somehow this is the problem because it is hard to remove and usually the industrial just ignore it.

1.2 Problem Statement

Previously, mercury has traditionally been treated by the alteration of the pH value using lime or caustic soda in precipitating hydrated metal oxides (Broom *et al*, 1994). Also at that time sulphide compound and other materials are added which result the production of heavy metal compounds with lower solubility products. Both of the methods had because the pH of mercury solution alkaline and to completely remove the mercury, usually settlement and sand filtration was done (IMSTC, 1992).

As the new era has come, the sand filtration is not compatible anymore. With the advent of more stringent environmental legislation regarding the quality of the final disposal stream, the use of cross-flow micro-filtration is becoming a choice to the more usual methods of treatment (settlement). In this study, membrane will be used as replacement of settlement and sand filtration. The adjustment of pH will decrease the Hg concentration.

Sodium hydroxide will change the pH level to higher value and HNO_3 will acidify the mercury solution. So, changing the pH level from acidic (HNO_3) to alkaline (limestone) and membrane filtration (replacing the settlement), the removal of mercury from wastewater is predicted to be more effective. After changing in pH value as above,

precipitation will occur in alkaline and acidify will less the colloidal fouling effect in membrane and the process will continue with filtration and sack the unwanted mercury. The size of mercury ion is 0.1nm (+2) and this ensures the micro-filtration membrane can not filtrate the mercury alone. Refer to table 1.1 for Mercury Properties.

In this study, *Pseudomonas putida* bacterium is used as the capturing and volatile agent. This process is known as pre-treatment process and will proceeds to the major process, membrane filtration which is the final step to overcome the mercury. For pre-treatment with *P.putida,* is set the parameters, pH value and temperature to the best condition of *P.putida.* When mercury is treated with membrane bioprocess, the mercury solutions need to be more alkali. Studies have shown that low water pH (acidic lake) aids the methylation reaction (Winfrey and Rudd, 1990, Xun, Campbell and Rudd, 1987). Adding HNO_3 had decrease the rate of accumulation of mercury and the change of Hg^{2+} to Hg^0

1.3 Research Objective

The objective of this research is to study the mercury removal efficiency with the existence of *P.putida process* and manipulating the pH value.

1.4 Scopes of Work

The scopes of this research are:

1) To remove mercury using cross flow microfiltration system with the absence of pre-treatment stage
2) To study the effects of different pHs on mercury removal efficiency with the absence of pretreatment stage

3) To obtain the best operating pressure, pH for the highest mercury removal efficiency with the absence of pretreatment stage
4) To pre-treat mercury wastewater using *P.putida* bacterium,
5) To remove mercury in the pretreated wastewater using cross flow microfiltration system at pH obtain from scope 3
6) To compare the mercury removal efficiency via crossflow microfiltration system with the absence and the presence of pretreatment stage.

CHAPTER 2

LITERATURE REVIEWS

2.1 Introduction

"Effects of pH in Mercury Nitrate Treatment Using Membrane System with Biological Pretreatment" means research on the effects of pHs parameter on membrane performance only and with the existence pretreatment of bacteria, *Pseudomonas Putida* as the volatile agent. Membrane filtration is a develop technology because of its ability to filtrate even nano-particle. The filtration is based on the particle size and the membrane pore, and also ion attraction. **Section 2.2** in this chapter presents a literature review on mercury and wastewater. The next section, **Section 2.3** is elaboration about the method that will be used to remove mercury. The problem with membrane filtration and pH effects is highlighted in **Section 2.4.** A review on *P.putida* bacterium as captured agent and the best condition in the treatment process is presented in **Section 2.5.** Nowadays, the research on heavy metals removal is a lot but using polymer as captured agent. As the Malaysia is towards the biotechnology process, the usage of bacterium is important and the bacterium usage, *Pseudomonas Putida* will be the pre-treatment process.

If the mercury exists in natural gas, petrochemical and refinery feed streams, it can be removed by using absorbent, HgSIV. This absorbent remove mercury to less than $0.01 \mu g/m^3$ (Corvini *et al*, 2002). Different for liquid phase of mercury, one of technique

very common nowadays is Polymer Enhanced Ultrafiltration, PEUF. In this technique, polymer was added as complexing agent with mercury. To remove mercury from wastewater, Hg^{2+} is converted to metallic form by reduction and separation using reducing agents include hydrazine (http://www.watertreatment supply.com), zinc, stannous chloride and borohydride.

Other than above method, there are a lot of methods, such as apply of precipitation agents (carbonate, phosphate or sulfide), water-insoluble ion exchange resins and organic solvents have been employed for the heavy metal separation from waste streams. But limitations encountered in these methods (Peters *et al*, 1985) such as requirement of extra steps, slower kinetics, and lower capacities due to heterogeneous reactions, and interface transfer lead to search for new techniques for heavy metal separation.

2.2 Mercury as Waste

Mercury is the only common metal liquid at ordinary temperatures. Also is known as quicksilver. It rarely occurs free in nature and is found mainly in cinnabar ore (HgS) in Spain and Italy and in petroleum in Malaysia. In natural gas, petrochemical and refinery feed streams, mercury is often presented. Mercury is a heavy, silvery-white liquid metal. It is poor heat conductor when compared with other metals but is a fair conductor of electricity. Mercury easily alloys with many metals, such as gold, silver, and tin. In petrochemical processing, mercury contains in wastewater is at low concentration and causing the problem in detection and removal. Even though mercury is at low concentration, the effect is still dangerous to ecosystem.

Figure 2.1: Mercury Ore (http://en.wikipedia.org)

2.2.1 Properties

Table 2-1 : Mercury Properties (http://www.lenntech.com)

Class	Properties
Atomic number	80
Atomic mass	200.59 g.mol-1
Electronegativity according to Pauling	1.9
Density	13.6 $g.cm^{-3}$ at 20°C
Melting Point	- 38.9 °C
Boiling point	356.6 °C
Vanderwaals radius	0.157 nm
Ionic radius	0.11 nm (+2)
Isotopes	12
Electronic shell	[Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$
Energy of first ionization	1004.6 $kJ.mol^{-1}$
Energy of second ionization	1796 $kJ.mol^{-1}$
Energy of third ionization	3294 $kJ.mol^{-1}$
Standard potential	+ 0.854 V (Hg^{2+}/ Hg)
Discovered by	The ancients

Figure 2.2 – Mercury (http://www.webelements.com)

2.2.2 Mercury's Types

Mercury was classified according to the different health hazard. There are three classes:

1. The pure element.
2. Inorganic compounds (such as mercuric chloride).
3. Organic mercury compounds (such as phenyl mercuric propionate).

Elemental mercury known as **Hg^0** is a liquid and at the temperature room, this type of mercury will volatile. This elemental mercury will absorbed into lungs and enter the blood stream. Elemental mercury can also pass through the skin and continue to the blood stream. However, if swallowed this elemental mercury usually passes out of the body without harm because it is not absorbed out of the stomach (http://www.pp.okstate.edu/ehs/).

Inorganic mercury compounds can also be inhaled and absorbed through the lungs, and may pass through the skin. But the compounds can also be absorbed through the stomach if swallowed (http://www.pp.okstate.edu/ehs/). Many inorganic mercury

compounds are irritating or corrosive to the skin, eyes and mucus membranes as well and had cause many injuries.

Organic mercury compounds can enter the body readily through all three routes-lungs, skin and stomach (http://www.pp.okstate.edu/ehs/).

2.2.3 Usage

In dentistry, for example, mercury usage is in fillings because of its strength and ability to accommodate temperature ranges foods (http://www.ecy.wa.gov/). Including thermometers, switches, thermostats and fluorescent light bulbs or tubes, mercury also been used for these products subjected to temperature fluctuations. The high rate of thermal expansion that is fairly constant over a wide temperature range is something special about mercury (http://www.lenntech.com). Mercury also is used to produce some pharmaceuticals, chemical and cosmetics.

Mercury metal has many other uses. Because of property that does not attract to glass surface and high density, mercury is used in barometers and manometers. . In amalgamating with gold, mercury is used in recovery of gold from ores because of its simplicity.

Mercury metal in industrial was used as a liquid electrode in the produce of chlorine and sodium hydroxide by electrolysis of brine (http://www.lenntech.com). Mercury is also still used in some electrical gear, such as switches and rectifiers, which need to be reliable, and for industrial catalysis. Much less mercury is now used in consumer batteries and fluorescent lighting, but it has not been entirely eliminated.

Mercury also exists in natural gas and petroleum. The reason for removing mercury from natural gas is to protect downstream aluminum heat exchangers because mercury amalgamates with aluminum, resulting in a mechanical failure and gas leakage (ERG, 1997).

2.2.4 Effects to Health

Mercury has a number of effects on humans that can all of them be simplified into the following main effects (http://www.lenntech.com):

a) Disruption of the nervous system
b) Damage to brain functions
c) DNA damage and chromosomal damage
d) Allergic reactions, resulting in skin rashes, tiredness and headaches
e) Negative reproductive effects, such as sperm damage, birth defects and miscarriages.

Failure brain functions can cause degradation of learning abilities, personality changes, tremors, vision changes, deafness, and muscle incoordination and memory loss (http://www.lenntech.com).

A very high exposures to mercury vapor in the air can cause acute poisoning. Symptoms usually begin with cough, chest tightness, trouble breathing and upset stomach (http://www.pp.okstate.edu/ehs/). This may go on to pneumonia, which can be fatal. If the inorganic mercury compounds are swallowed, nausea, vomiting diarrhea and severe kidney damage can occur (http://www.pp.okstate.edu/ehs/).

Contact to any form of mercury on a repeated basis, or even from a single, very high exposure can lead to the disease of chronic mercury poisoning. There are three main symptoms (http://www.pp.okstate.edu/ehs/):

1. Gum problems. The gums become soft and spongy, the teeth get loose, sores may develop, and there may be increased saliva.
2. Mood and mental changes. People with chronic mercury poisoning often have wide swings of mood, becoming irritable, frightened, depressed or excited very quickly for no apparent reason. Such people may become extremely upset at any criticism, lose all self-confidence, and become apathetic. Hallucinations, memory loss and inability to concentrate can occur.
3. Nervous system. The earliest and most frequent symptom is a fine tremor (shaking) of the hand. A tremor may also occur in the tongue and eyelids. Eventually this can progress to trouble balancing and walking.

There are a number of other symptoms that may be caused by exposure to mercury and mercury-containing compounds (http://www.pp.okstate.edu/ehs).

1. A skin allergy may develop. If this happens, repeated exposure causes rash and itching.
2. Exposure to mercury vapor can cause the lens of the eye to discolor.
3. Some of the inorganic mercury compounds can cause burns or severe irritation of the skin and eyes on contact.

Effects on the Reproductive System Some organic mercury compounds (methylmercury) are known to cause birth defects in children born of exposed mothers (http://www.pp.okstate.edu/ehs). It is not known whether inorganic compounds or elemental mercury have this effect.

2.2.5 Safety and Precaution

Students should use appropriate personal protective clothing and equipment that must be carefully selected, used, and maintained to be effective in preventing skin contact with mercury vapor. The selection of the appropriate personal protective equipment (PPE) (e.g., gloves, sleeves, encapsulating suits (http://www.osha.gov)) should be based on the extent of the worker's potential exposure to mercury vapor. There are no published reports on the resistance of various materials to permeation by mercury vapor.

To estimate the use of PPE equipment with mercury vapor, users should check with the best available performance data and manufacturers' recommendations. Major differences have been demonstrated in the chemical resistance of generically similar PPE materials (e.g., butyl) produced by different manufacturers (http://www.osha.gov). In addition, the chemical resistance of a mixture may be significantly different from that of any of its neat components.

Any chemical-resistant clothing that is used should be periodically evaluated to determine its effectiveness in preventing dermal contact. Safety showers and eye wash stations should be located close to operations that involve mercury vapor. Splash-proof chemical safety goggles or face shields (20 to 30 cm long, minimum) should be worn during any operation in which a solvent, caustic, or other toxic substance may be splashed into the eyes (http://www.osha.gov).

Protective clothing should be kept free of oil and grease (http://www.osha. gov) and should be inspected and maintained regularly to preserve its effectiveness. Protective clothing may interfere with the body's heat dissipation (http://www.osha.gov), especially during hot weather or during work in hot or poorly ventilated work environments.

2.2.6 Rejection Mercury in Wastewater

Removal of metal ions from low concentrated wastewater in a cost effective manner is an important challenge. Discharge of metals to the environment causes serious damages and is also a waste of dwindling and valuable resources. Moreover, financial benefit could be gained from water saving and lower disposal costs.

Mercury rejection in wastewater is usually come from mining, mineral processing, battery, petrochemical and metal finishing industries. Mercury in wastewater is in ion form. Actually, mercury ion can be attracted by using positive-negative electrical charge but there are many others cation and anion in wastewater. To be more selective on mercury ion, membrane usage is applied. Membrane that will be used also known as micro and ultra filtration (MF&UF). The major disadvantages of these materials are low metal loading and small metal-ion binding
constants.

2.3 Membrane as Treatment Process

In this experiment, the method that will be used is control the parameters of membrane, pH and also using the microbial as pretreatment. Membrane cross-flow will be used in this experiment because its are continuous process, offers several advantages such as relatively high mass transfer coefficients, minimized shell-side channeling and lower shell-side pressure drop when compared to the parallel flow contactors (Wickramasinghe *et al*, 1992). As the pH of solution increases, generally retention of metal cations also increases in the acidic region up to certain pH values**.** It should be noted that many heavy metals form hydroxides with very low solubility at high regions (Volchek *et al*, 1993). After the pretreatment with *P.putida,* the change in pH value will

be made to precipitate mercury ion using lime (Broom *et al*, 1994) and using the membrane, precipitated mercury will be filtrated.

The cross-flow micro-filtration system is based upon the idea of using a dynamic membrane to form the filtration medium. This membrane is laid down on the internal wall of a woven fabric cloth and may be formed by either the solids naturally present in the feed suspension or by the deposition of materials such as diatomaceous earth, metal hydroxides or kaolin (Broom *et al*, 1994). In this use the heavy metal precipitate provides a suitable membrane without the introduction of filter aids.

Mercury removal via crossflow microfiltration was reported for a full-scale plant designed to process 200 m3/day of mixed plating wastewater (Broom *et al*., 1994). The filtrate from the rotary vacuum filter pH was adjusted to 11 to 12, primarily to precipitate cadmium. Sodium hydrogen sulfide (NaHS) was also added to precipitate any soluble metals remaining. This conditioned filtrate was then pumped to the crossflow microfiltration unit. The reject flow was effectively a concentrate produced by the passage of clean permeate through the filter. With mercury feed concentrations to the microfiltration plant of 1.27, 0.967, 0.15, and 2.28 mg/L, permeate concentrations of 0.015, 0.015, 0.088, and 0.03 mg/L were achieved, respectively. This represents a removal efficiency of about 95 %. Removal may have been enhanced by mercury co-precipitation in the balance tank.

2.3.1 Bacteria as Volatile Agent

The pre-treatment process, removal of mercuric chloride by *Pseudomonas putida* was studied using peptone water medium in the concentration range 1-120 mg L^{-1}(http://www.nies.go.jp). Two processes, adsorption on the cell surface and bioaccumulation have been observed. Maximum removal capacity for the bacterium

was found to be 98%. Thus, bacterial removal of mercury is a potential biological treatment for mercury waste.

Under optimum conditions, nearly 100% of the 40 mg L-1 of mercuric chloride was removed from contaminated water and 70% were removed from soil slurry. The *P. putida* cells were motionless on various carriers to maintain the mercury removal activity and to avoid the exposure to environment. After the experiments, bacterial cells and mercury droplets can be found in the membrane.

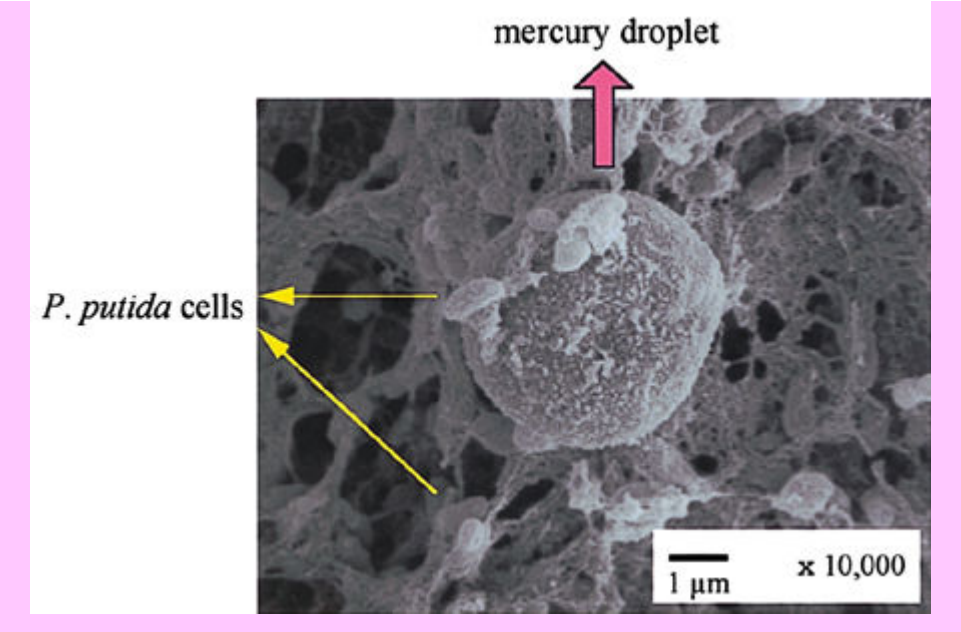


Figure 2-3: *P.putida* Cells

2.4 Membrane

In this experiment, membrane was use as filter of ion mercury. According to mercury ion size, Nano-Filtration Membrane is the most suitable but this membrane is not available yet. So, we will replace this membrane with ultrafiltration membrane with

the adjusting of pH. The crossflow ultrafiltration system is based on the concept of using a dynamic membrane to form a filtration medium. This process, whose patented form is called Exxflow, is a solid-liquid separation process in which the feed suspension sweeps across the face of a filter membrane while pressure differences cause the liquid phase to pass through the membrane, leaving the solids to be flushed away in the residual flow. By this means, the solids are concentrated up in the suspension flow, which is commonly recycled to the feed end. This contrasts with "barrier" filtration systems in which the solids build up on the filtering surface, gradually restricting the flow through the filter (Squires, 1992).

2.4.1 Membrane Performance

The performance of membrane depends on the permeate flux and retention of species (mercury). Flux values were determined from the permeate flow rates measured during experiments. To measure the flow rate, use the measurement cylinder to collect the permeated for a minute. After the mercury ion concentrations of permeate and feed solutions were obtained, retention values were calculated from the formula.

$$R = 1 - \frac{Cp}{Cf} \tag{2-1}$$

Where Cp and Cf are mercury ion concentration of the permeate and the feed solutions, respectively. To determine the concentration of mercury in the sample, use the Mercury Analyzer.

2.4.2 Parameters

Let's take a look on pressure as parameter. Pressure does have effect on membrane performance. The applied pressure will increase and decrease the permeate flux. Permeate flux is the flow in a minute of the filtrate of wastewater per area of membrane (m/min). How does it effect? Increasing the pressure will increase the force on the wastewater within the membrane (Muslehiddinoglu *et al*, 1998). This will cause the water to pass through the membrane and left the refinate on the membrane. The refinate included mercury and others ion. What makes mercury and other unwanted particle filtrated? It is the retention of membrane over the refinate

Transmembrane Pressure is the difference in pressure between the filtrate side of the membrane and the permeate side of the membrane. This parameter is the driving force for the membrane separation. In general, an increase in the transmembrane pressure increases the flux across the membrane (www.rpi.edu).

2.4.3 Effect of pH

The pH value of mercury solution is pH 2-3. The changing in pH value can cause the change in permeate flux of membrane. pH of solution affects numerous biological processes and some membranes are exposed to extreme pH environments. At pH 2 the elastic area compressibility was reduce by 30% and none between pH 3-9. The membrane bending stiffness, k_c, increased by ~40% at pH 4 and pH 9 over the control value at pH 6.5. These mechanical studies lead to the conclusion that the effect of pH on membrane bending stiffness results from alterations in interfacial, as opposed to intramembrane, electrostatics.

The change of flux with feed pH was not great generally. The permeate flux was minimum around the isoelectric points of the membranes. The rejections for the feed with pH more than 7 were greater than that for the feed with pH less than 7 (Zhi Wang , Guangchun Liu, Zhifeng Fan, Xingtao Yang, Jixiao Wang, Shichang Wang, 2007)

2.4.4 Mercury Removal pH

At pH 6.0, the removal of mercury using gel beads was fast; 90% of adsorption occurred within 45 min and equilibrium was reached at around 1h (Adil Denizli *, Serap Senel , Gu¨leren Alsancakb, Nalan Tu¨zmenb, Ridvan Sayc). The maximum Hg adsorption capacity obtained was 1.67 mmol/g at a pH of about pH 5.

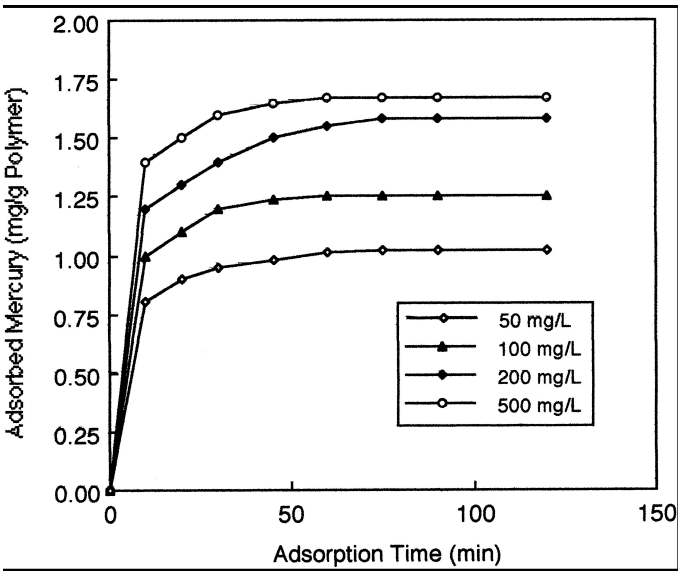


Fig. 2-4. Adsorption rates of Hg on the PEI-attached PHEMA gel beads. PEI loading: 50 mg/g; *T*520 8C and pH 6.0

According to the below table, higher pH can cause the crystallization or colloid. So, to treat mercury, we need to increase the pH value, or alkaline the mercury solution.

Table 2-2: pH Effect on Membrane (D.R. Kasper)

	Value	Crystallization	Cause
pH	Higher	Increased	Solubility Decreased
Pressure	Higher	Increased	Increasing Osmotic Pressure

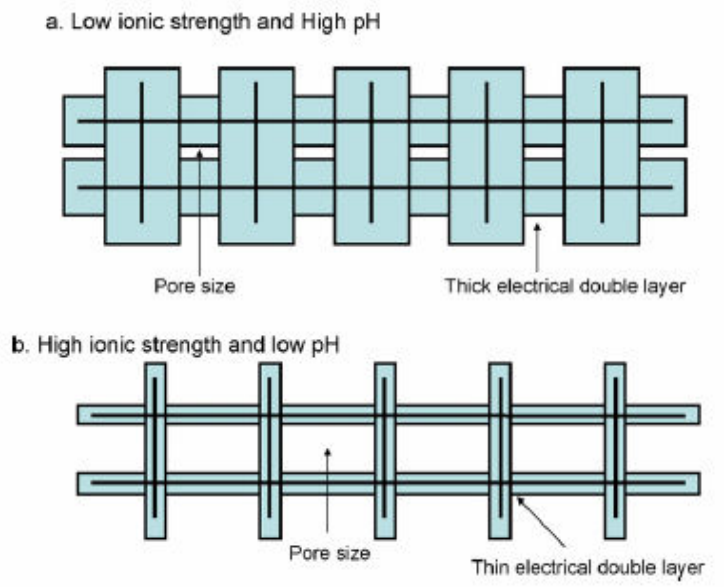


Figure 2-5: pH effect on membrane (Kasper)

The apparent membrane surface structured in the solution is a function of pH and ionic strength. Fig. 6 shows the potential impact of high and low ionic (high pH) strength on membrane structure. At high ionic strength, the membrane pore size was found to exhibit larger pore size compared at low ionic strength.

The alternation of the pH value for Mercury can be precipitated to low levels using carbonate, phosphate or sulfide (http:// www.rwaterguy.com). When mercury is precipitated and becoming mercury sulfide, the high residual of mercury can be observed. This effect is due to the reduction of the mercury to the metallic mercury by

the sulfide. Once in the metallic form, the mercury cannot form the insoluble sulfide (http:// www.rwaterguy.com). Metallic mercury is soluble in water at about 25ug/l (http:// www.rwaterguy.com), which is above the regulatory limits. It may be visible as a lake floating on the surface of the reactor during the settling step. The residual mercury in the treated water must by oxidized to mercury 2 and then retreated to achieve low residual concentrations (http:// www.rwaterguy.com). The oxidation step should be done prior to the precipitation step when treating mercury to form mercury phosphate. Following the initial precipitation step, the residual phosphate must be precipitated by the addition of calcium ion.

Effect of increasing hydrogen ion (H+) concentration on the uptake of mercury (Hg(II)) by an aquatic bacterium even small changes in pH (7.3-6.3) resulted in large increases in Hg(II) uptake, in defined media. Lowering the pH of Hg solutions mixed together with natural dissolved organic carbon, or with whole lake water, also increased bacterial uptake of Hg(II). Thus, pH appeared to affect a facilitated mechanism by which Hg(II) is taken up by the cells. These findings have several potential implications for mercury cycling, including effects on elemental mercury production, mercury sedimentation, and microbial methylation of Hg(II) (C. A. Kelly and J. W. M. Rudd).

As conclusion, changing the pH to the higher value can cause the rate of filtration mercury increase and changing to the low value can cause the decrease in filtration and increase in flow rate. Alkalization had causing the colloid in particle and thickens the membrane web. Acidification had causing the membrane web thinner and the pores size bigger. So, within this experiment to alter the pH value, lime stone and acid nitrate will be used.

2.5 Pseudomonas putida

Pseudomonas putida is a gram-negative rod-shaped saprophytic soil bacterium (http://en.wikipedia.org). Based on 16S rRNA analysis, *P. putida* has been placed in the *P. putida* group, to which it lends its name.

It demonstrates very diverse metabolism, including the ability to degrade organic solvents such as toluene (http://en.wikipedia.org). This ability has been put to use in bioremediation, or the use of microorganisms to biodegrade oil. Use of *P. putida* is preferable to some other *Pseudomonas* species capable of such degradation as it is a safe strain of bacteria, unlike *P. aeruginosa* for example, which is an opportunistic human pathogen.

2.5.1 Uses

The diverse metabolism of *P. putida* may be exploited for bioremediation; for example, it is used as a soil inoculant to remedy naphthalene contaminated soils (http://en.wikipedia.org). *P. putida* is capable of converting styrene oil into the biodegradable plastic PHA (http://en.wikipedia.org). This may be of use in the effective recycling of Polystyrene foam, otherwise thought to be non-biodegradable.

2.5.2 Mercury Treatment

Genetically engineered *Pseudomonas putida* can grow in high concentrations (up to 100 mg/l) of mercuric chloride and can volatilize mercuric ions to elemental mercury [29]. A developed mercury removal-recovery system that can effectively recover

volatilized elemental mercury. With this system, a studied on removal of mercuric chloride from a mercury-containing solution without nutrients by resting cells of *P. putida*.(http://www.nies.go.jp).

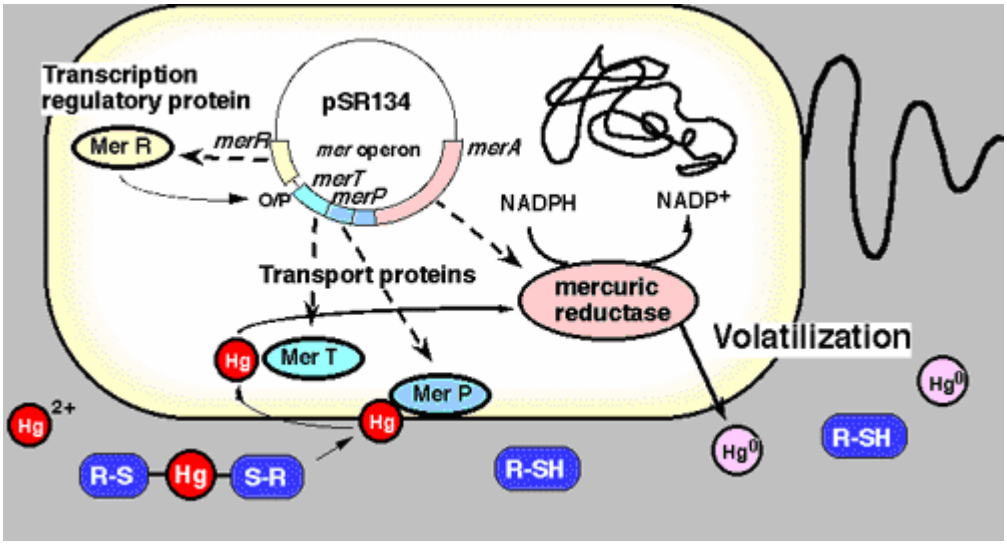


Figure 2-6 P.*Putida* Process (http://www.nies.go.jp)

The process will use *P. putida* as the pretreatment then continued with membrane filtration.

CHAPTER 3

METHOD

3.1 Introduction

In this chapter, there are 3 sections which are **section 3.2** describing the material needed, **section 3.3** listing the equipment that will be used and **section 3.4** is the methodology of research. In section 3.4, there are 4 subchapters that are Preparing stock solution, Membrane Separation, *P.Putida* Growth and continue with membrane separation. For **section 3.5** is analyzing method

3.2 Materials

The materials to be used in this research are 1000ppm Mercury Nitrate, Stanum Chloride, Hydrogen Sulfide (97%), Ultra pure water and 65% Hydrogen Nitrate and 65% Natrium Chloride, Nutrient Browth and Stock of *P.Putida*. Ultra pure water will be used for dilution, cleaning and preparing blank test.

3.3 Equipments

The equipment that was used in this experiment for Preparing Stock Solution are measurement cylinder and 2L volume metric flask. The equipments for Membrane Separation are Quixstand Crossflow Membrane, 1L beaker, stopwatch, 500ml measurement cylinder and 12 Schott Bottles 250mL.

For growth experiment, Fermenter 2L, Autoclave, Incubator Shaker, 250mL Conical Flask, 100mL measurement cylinder, Laminar Flow, 4 Schott Bottles 250mL, Vacuum Pump, Syringe, 20 Covered Test Tubes, Aluminim Foil and Cotton Wool were used.

For analyzing 50mL beaker, Glass Rod, spatula, 2mL pipette, 20mL measurement cylinder, 3 Volume metric flask 100mL, 10mL pipette, test tubes and special mask..

The Cross-Flow membrane is in a spiral shape. The waste will flow from inside to outside of the membrane. The membrane is equipped with Pressure Gauge for inlet and outlet of flow. The only weakness of this machine is it does not have the flow-rate measurement. So, use the stopwatch and measurement cylinder to take the value of flow-rate. With this, the accuracy is decreased because using human as sensor is not very accuracy. The Flat Sheet membrane is in a sheet shape. The waste will flow in one direction only.

For Fermenter 2L, it was equipped with pH controller, stirrer, temperature controller and Dissolve Oxygen measurement. The objective using this equipment is to culture *P.Putida* in Mercury Solution with pH adjustment. When culturing *P.Putida*, air is supplied because this bacteria is aerobic type which means need O_2 for living. The probe that used to measure pH was contaminated. So the measurement of pH was not

really accurate. The pH measurement was assumed to be qualitative and not quantitative.

Mercury Analyzer was used for analyzing the concentration of Mercury Ion. The range for the Mercury Analyzer concentration is 15ppb and under. This sensitive equipment will broke down if the sample is higher then the permitted range. So every sample need to be diluted under 15ppb before analyzing. Sometime, dilution had caused the data for concentration was far away from others. This was the weak ness of this analyzer.

3.4 Methodology of Research

There are 4 stages of this study, which are

a) Preparation and Hg solution

b) Membrane Filtration

c) Growth of *P.Putida*

d) Analyzing

3.4.1 Preparation and Hg Solution

To replace the real wastewater, the synthesize wastewater will be used. The preparation of 20ppm, 10ppm and 5ppm Mercury Nitrate will be done.

Mercury Nitrate 1000ppm was diluted from raw material to 100ppm (stock solution) for about 2L.

↓

Through this calculation:

$$m1 \bullet v1 = m2 \bullet v2$$

$$\frac{1000\,ppm}{1\%} \bullet v1 = 100\,ppm(2000ml)$$

$$v1 = \frac{100(2000)}{10000}$$

$$= 200ml$$

↓

Mercury Nitrate 100ppm is diluted to 20ppm (sample) for 2liter.

↓

Through this calculation:

$$m1 \bullet v1 = m2 \bullet v2$$

$$100 \bullet v1 = 20(2000)$$

$$v1 = \frac{20(2000)}{100}$$

$$= 400ml$$

↓

200 ml of Mercury Nitrate is measured using measurement cylinder

↓

The solution is poured into volumetric flask 2 liter.

↓

Ultra pure water is top upped till 2 liter to dilute the solution to 100ppm.

↓

400ml of Mercury Nitrate 100ppm is measured using measurement cylinder

↓

The solution is poured into volumetric flask 2 liter.

↓

Ultra pure water is top upped till 2 liter to dilute solution to 20ppm.

↓

The dilution step is repeated from 100ppm to 10ppm and 5ppm

↓

Calculation for 10ppm:

$$m1 \bullet v1 = m2 \bullet v2$$
$$100 \bullet v1 = 10(2000)$$
$$v1 = 200ml$$

↓

Calculation for 5ppm:

$$m1 \bullet v1 = m2 \bullet v2$$
$$100 \bullet v1 = 5(2000)$$
$$v1 = 100ml$$

Figure 3.1: Preparing Stock Solution

For preparing stock solution from 1000ppm of $HgNO_3$, equation 4-1 was used

$$m_1 v_1 = m_2 v_2 \qquad (4\text{-}1)$$

After get the value of volume, pour into 2L volume metric flask. Before pouring, add some DI water first for complete and faster dilution. The dilution was done in fume hood to avoid the Hg evaporate in lab. Top up with DI water until 2L.

3.4.2 Membrane Filtration

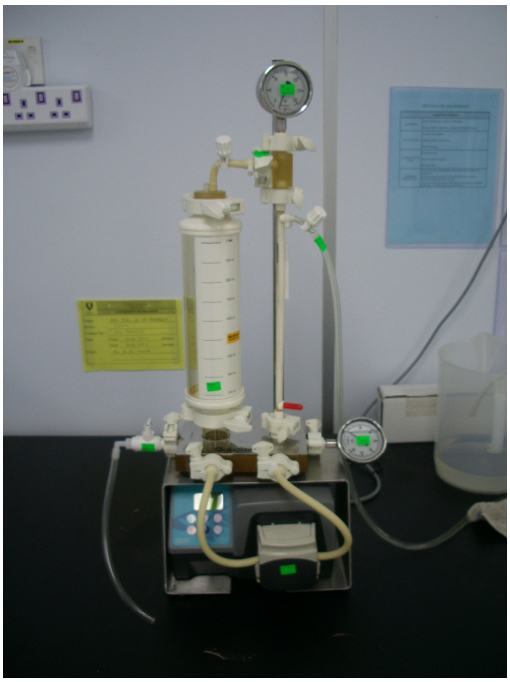


Figure 3.2: Cross-Flow Membrane

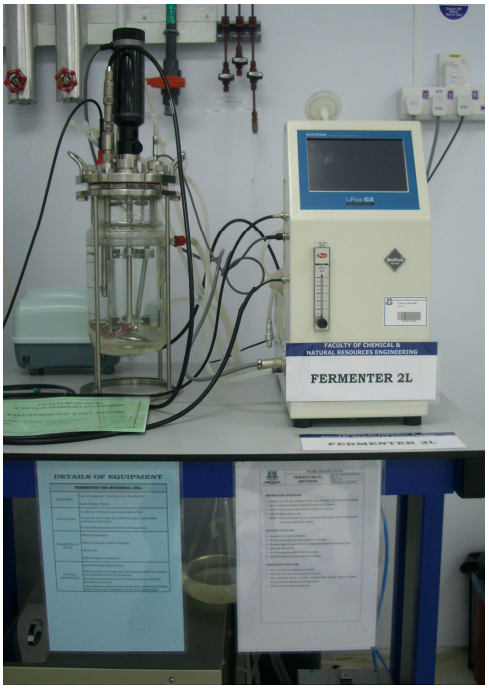


Figure 3.3: Fermenter 2L

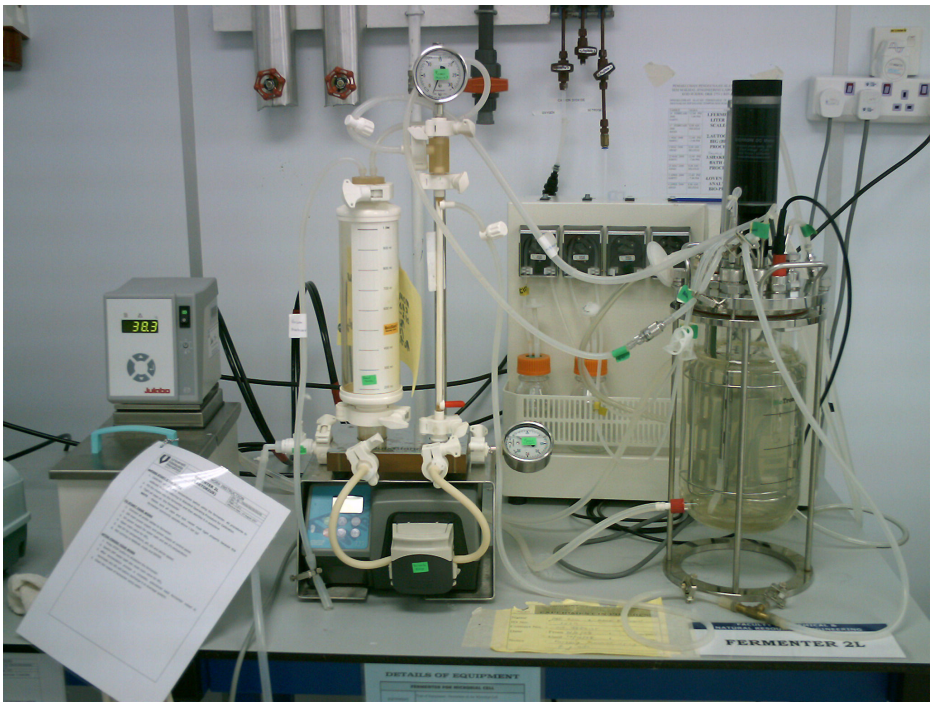


Figure 3.4 Membrane Bioreactor

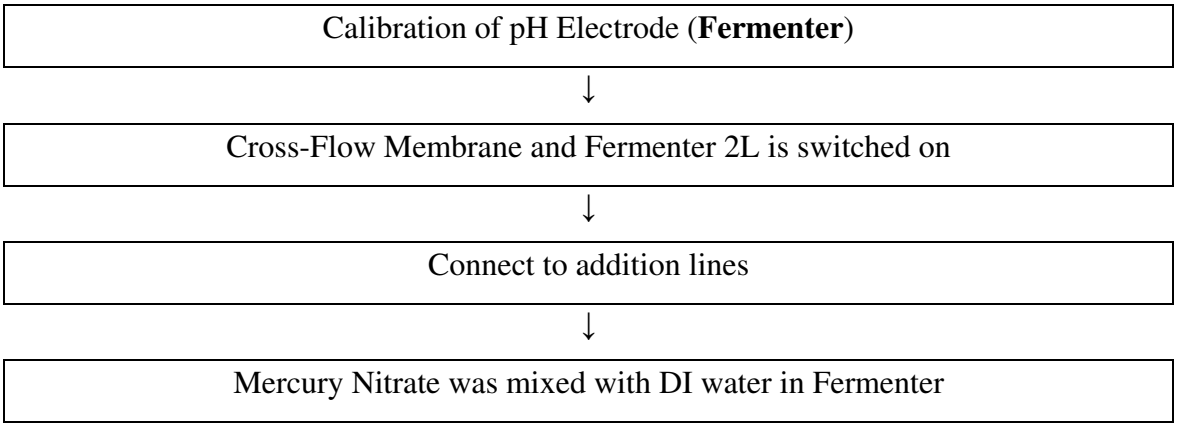
Quixstand Cross Flow Membrane is spiral type membrane. Sample was added in the reservoir tank before push to flow through the spiral membrane. Pressure was taken from pressure indicator before and after the membrane. Maximum allowed pressure is 35psi. Permeate sample was taken from permeate valve at the upper side of membrane. Membrane area is $0.011m^2$.

Fermenter 2L was used as culturing and growing the *P.Putida.* The purpose of using this equipment are to set the maintain temperature, pH and dissolved oxygen at *P.Putida* best condition in growing.

Combining these two equipments as one using piping, Membrane Bioreactor was invented. Fermenter was used as first treatment, growing *P.Putida* with Mercury and Membrane was used as second treatment for filtration Mercury. It was assumed that *P.Putida* was dead before the sample going through the membrane as the dissolve oxygen value increasing.

3.4.2.1 Membrane Treatment: pH determination

Both of these machines will be connected through piping. Using Fermenter 2L, temperature is set to 37^oC and pH is depend on Mercury solution pH.



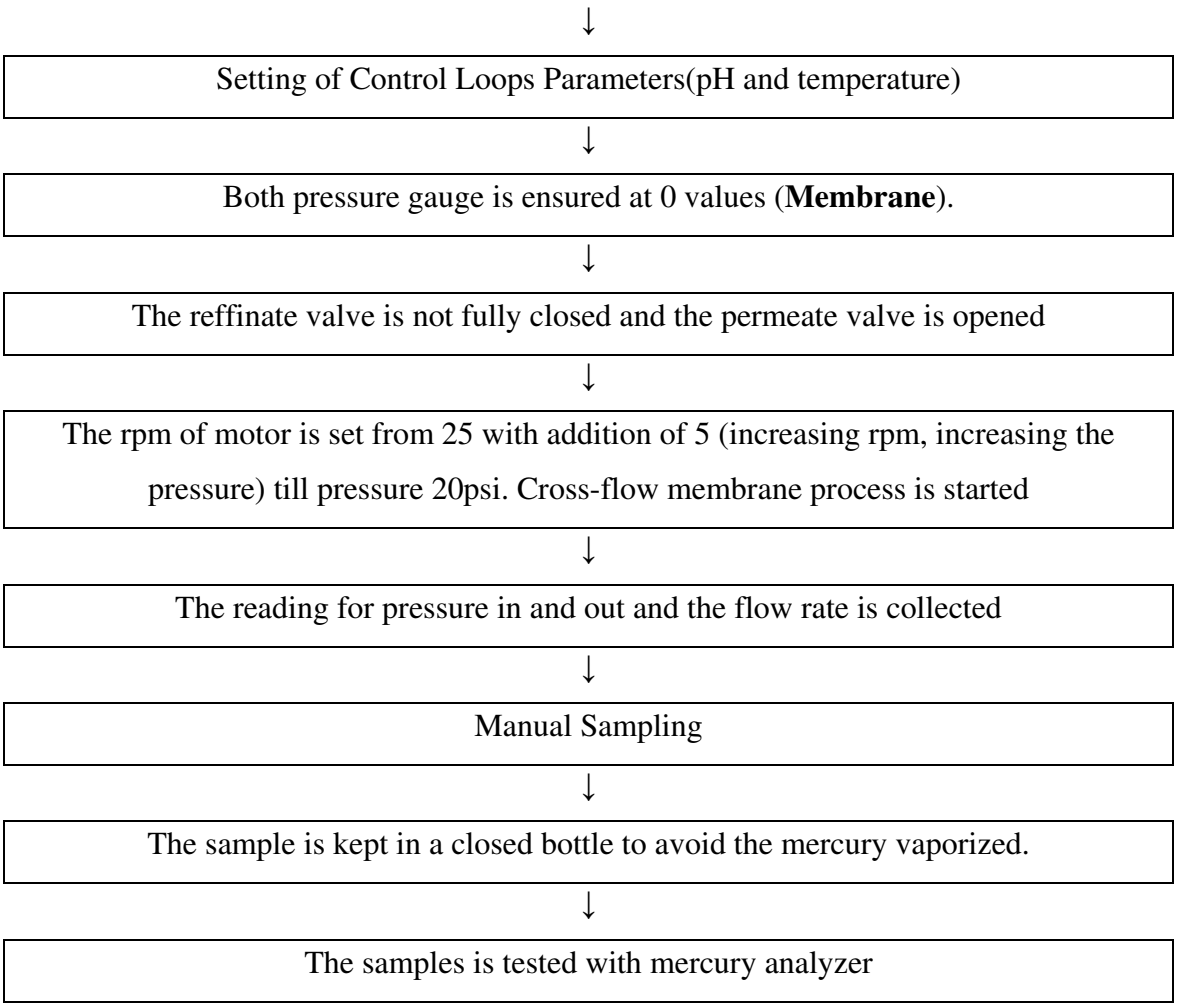


Figure 3.5: Membrane separation Procedure

For membrane separation, the usage of Fermenter was for pH adjustment and also Temperature stabilizer. There is no need for autoclave the fermenter in this stage because no need for growing of *P.Putida* and the medium was DI water. First step for membrane operation was close sampling/drain valve, secure cartridge in upper and lower manifolds and ensure the pump tubing was correctly positioned and tensioned within the pump head. Confirm flexible tubing was connected from the retentate outlet on the upper manifold to one of the tubing barbs on the reservoir caps. If the process solution tends to foam, retentate downcomer pressed was ensured into the reservoir cap for the retentate line. Flexible tubing was directed from the upper permeate line to a collection flask. The sanitary clamp from the reservoir cap and slide the reservoir cap was removed to one side. The feed solution was added to the reservoir. The reservoir

cap on the silicone gasket was repositioned and clamps it in place using the sanitary clamp. The backpressure tubing valve was opened for several times. Pump was started at slow speed and wait for 30 seconds for the pressure to build up. The pressure gauges mechanically dampened and respond slowly. The pump speed increased slowly. The inlet pressure will build up, while the outlet pressure gauge may still read zero. Backpressure was applied by slowly closing the tubing valve. Inlet pressure gauge was watched. If the pressure rises too high, the pump seed was lowered. Upon completion recover product from reservoir via the drain/recovery valve.

3.4.2.2 Membrane Treatment with Pretreatment Stage

pH is fixed based on 3.4.2.1

Calibration of pH Electrode (**Fermenter**)

↓

Equipping of Culture Vessel (DI water)

↓

Preparing Culture Vessel and Accessories for Autoclaving

↓

Cross-Flow Membrane and Fermenter 2L is switched on

↓

Polarization of pO_2 Electrode for at least 6 hours

↓

Calibration of pO_2 Electrode

↓

Connect to addition lines

↓

Inoculation of Inoculum

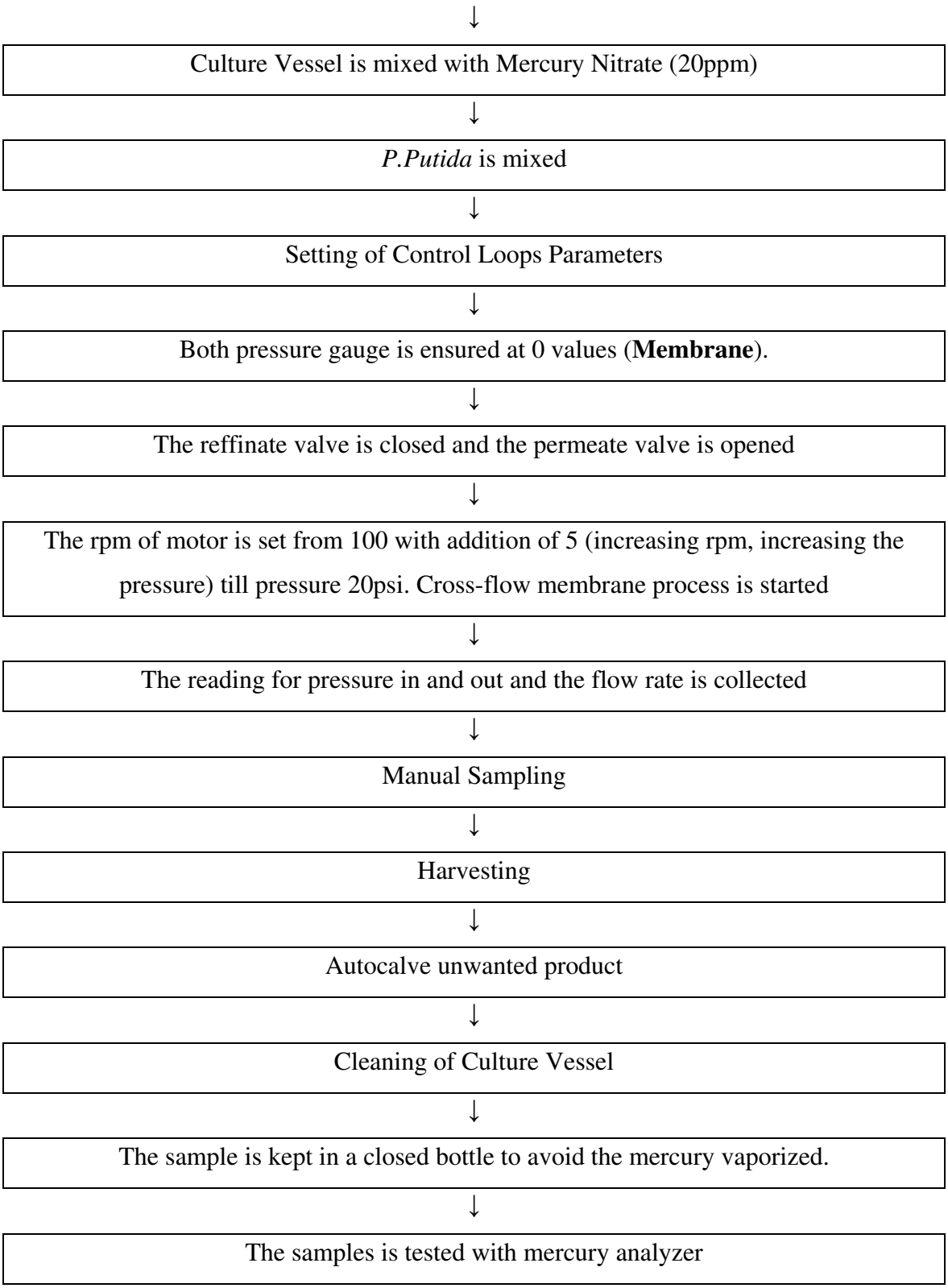


Figure 3.6: Membrane with pretreatment stage

For pretreatment, we need to growth *P.Putida* conical clask first as subchapter 3.4.3 before growth in Fermenter. Calibrate pH and temperature according to Fermenter standard. For 2L Fermenter, pH 4 and 7 is the standard calibration. Adjust the Hg solution pH from acidic to neutral using $NaCl_3$. After pouring the cultured *P.Putida* in Fermenter, take sample after 5minutes of initial mixing as the 0 minute. Every 30 minutes, take the sample for 4 hours as for growing and mercury concentration analyzing. After 4hours, the remain medium were go through the membrane separation. As the above experiment, the method is the same. Keep the sample in freezer

3.4.3 Culturing *P.Putida*

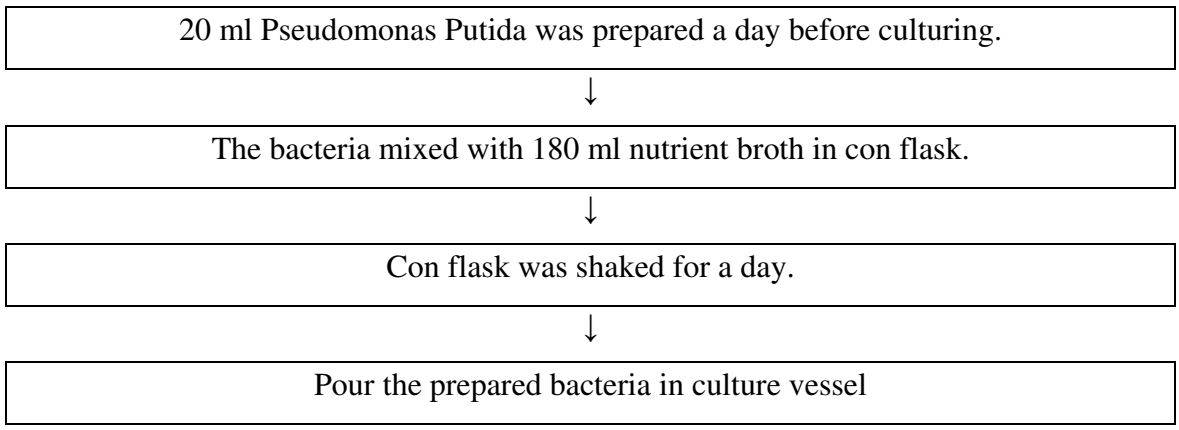


Figure 3.7:Culturing *P.Putida*

P.Putida was cultured with Nutrient Broth before mixed with Mercury solution. This step was to growth *P.Putida* in small scale and to ensure that only *P.Putida* was grown as the Nutrient Broth only prepared for *P.Putida*. 20mL *P.Putida* was prepared a day before culturing. *P.Putida* then mixed with 180mL of Nutrient Broth in conical flask. The flask was shaking in incubator shaker at 180rpm and 37^{o}C for a day. Then, pour the cultured *P.Putida* in the Fermenter for mixed with Hg Solution. Set the Fermenter at 180rpm and 37^{o}C.

3.5 Analyze Hg solution

Figure 3.8: Mercury Analyzer

Analyze the Hg solution using the Mercury Analyzer to detect he concentration of mercury.

A solution containing hydrogen sulphate (97%) and ultra pure water is prepared with 1:1 mixture

↓

40ml hydrogen sulphate (97%) is measured and mixes with 40ml ultra pure water using measurement cylinder. The solution is poured into cleaned glass bottle.

↓

A mixture of stanum chloride and hydrogen sulphate is prepared.

↓

2g of stanum chloride is weighted in beaker using electronic weight measure.

↓

19ml ultra pure water and 1ml hydrogen sulphate (97%) is poured into the beaker.

↓

The mixture is stirred till the solid stanum chloride dissolved using glass rod.

↓

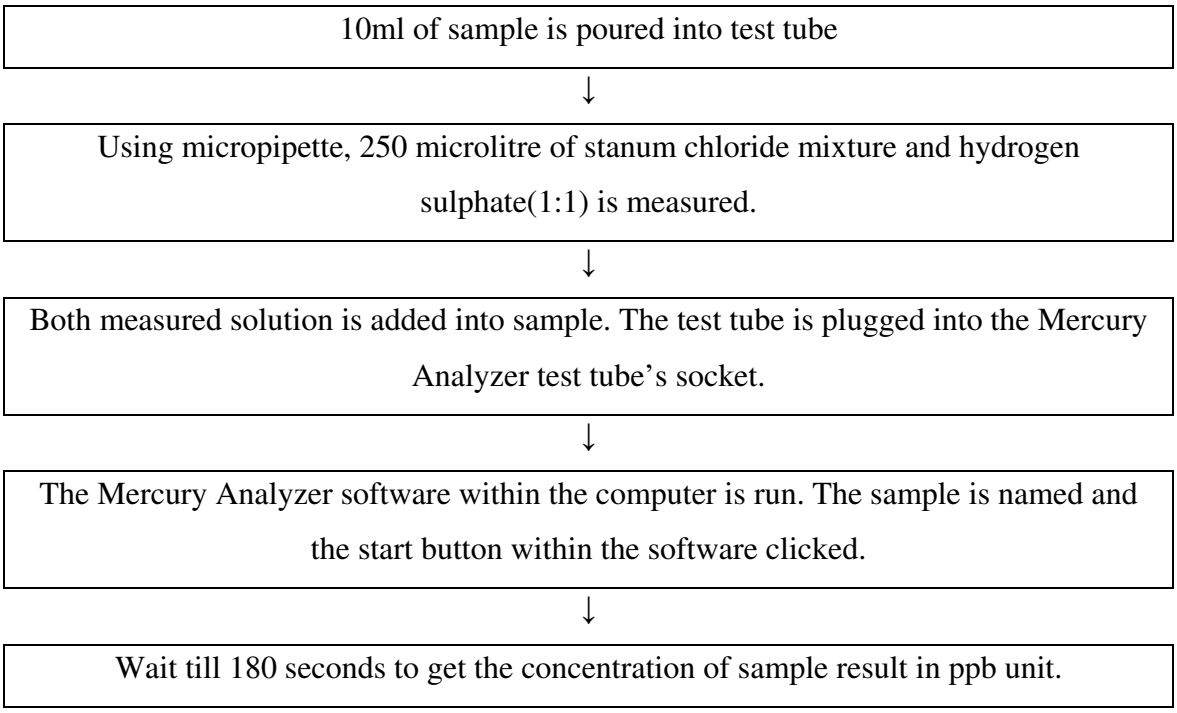


Figure3.9:Analyzing

For analyzing, Mercury Analyzer will be used. Firstly, solution stanum chloride needs to be prepared. 2gram of stanum chloride was weighed and placed in beaker. 1mL of 97% H_2SO_4 and 19mL of DI water was mixed in the beaker. The solution stirred using glass rod. Prepare the solution 1:1 H_2SO_4 and DI water with 50mL 97% H_2SO_4 and 50mL DI water. Dilute the sample from ppm concentration into ppb concentration using equation 4-1. Pour the sample in test tube and start the mercury analyzer. Run the test 3 times for each sample.

CHAPTER 4

RESULT & DISCUSSION

4.1 Pretreatment

It is predict that 98% mercury of the Hg solution will be removing in the pretreatment process. Before proceed with mercury treatment, *Pseudomonas Putida* was growth in Fermenter 2L for a day.

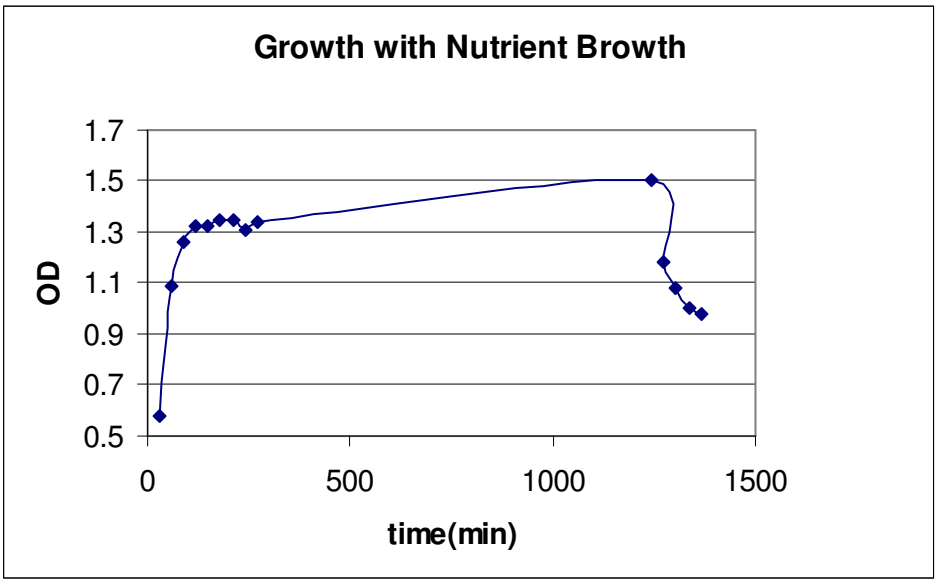


Figure 4.1:Growth with Nutrient Browth

For growth, we used Nutrient Browth as the medium. This was to ensure that *P.Putida* can growth in fermenter condition and avoid any chances of others bacteria to mix with the medium in fermenter. So from this experiment we can trace whether the bacteria was live or not. Absorption represents the qualitative amount of the bacteria. The highest amount is 1.502 compared to blank (0 min, 0 abs).and the increasing value had prove the bacteria growth. So, the objective to growth *P.Putida* in fermenter is achieved with Nutrient Browth as the medium. From graph, the increasement of absorption value was detected within 1200 min of operation. Then the data start to fall down on minutes 1200. It was believe the data was wrong. So, we can conclude that time for bacteria growth is within 500 minutes.

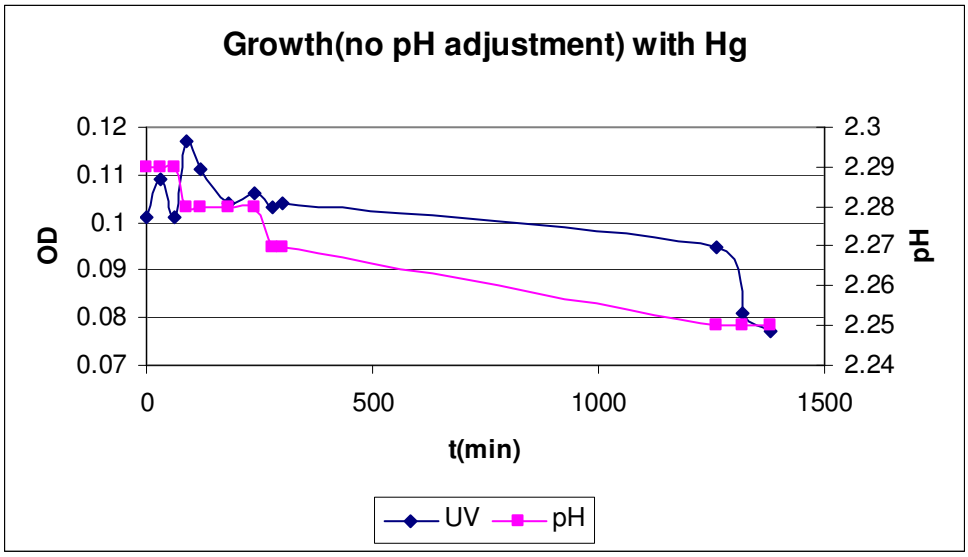


Figure 4.2:Growth (no pH adjustment) with Hg

In this experiment, Hg solution was the medium. The pH shows that the solution is acidic (pH 2). The problem in this experiment is according to the literature review, the bacteria were growth in neutral condition (pH 7). So theoretically *P.Putida* will die at the moment in contact with Hg solution. As above graph, the re are a little bit increasing value of absorption at minutes 90 and after that the *P.Putida* were died. This experiment was just to confirm the theory and it is confirm that *P.Putida* could not growth normally in Hg solution as Figure 4-2 shows compared to Figure 4-1. So to overcome this

problem, we will increase the pH value of Hg solution from ph 2 to pH 7 with NaCl. We used NaCl because it is also agent for adjusting Hg solution before flow through the membrane.

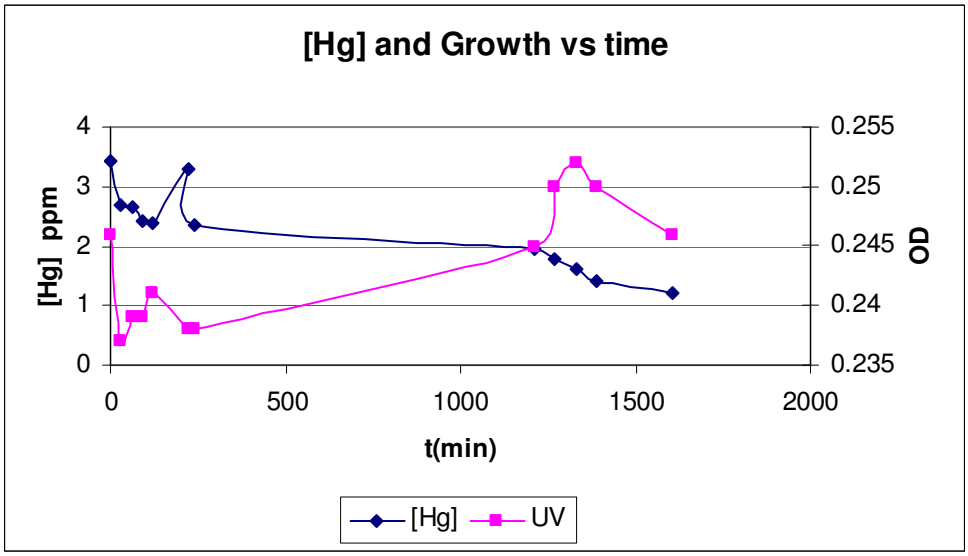


Figure 4.3:[Hg] and growth vs time

In this experiment, without changing the pH (3.5), the growth was studied in acidic solution with the [Hg] is analyzed. With initial concentration 4ppm, the concentration was decrease after mixed with *P.Putida*. As in the graph, *P Putida* showed increasing value in the middle graph but for first one hour, the graph shows that absorption value was down almost to zero. It is assume that for solution with starting pH 4, the *P. putida* need adaptation mode where only *P.Putida* with high strength will survive in such condition. On the 6^{th} reading, it was assume to be wrong because the data was out off graph line. From 4ppm the concentration decreased to 1.215ppm. This prove that *P.Putida* decrease Hg^{2+} to Hg^{0}. The maximum growth was 0.252 abs. The bacteria were assumed to die after the maximum reading. When *P. putida* increase with the time, the [Hg] decrease with time. This conclude to *P. putida* growth is inversely to [Hg]

$$P.Putida(abs) \propto [Hg] \qquad (4\text{-}1)$$

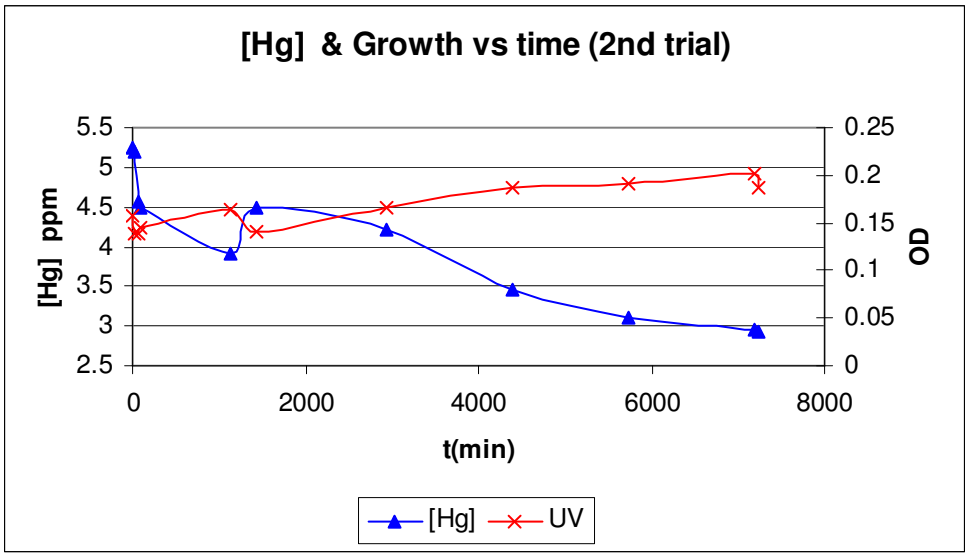


Figure 4.4:[Hg] & Growth vs Time

In this experiment, the [Hg] is 6ppm (pH 2). The stabilize concentration and growth reading only after 2 days. This may because of the pH of solution. After the bacteria adapt the low pH condition, it will growth and use the Hg as "food". The concentration decreased from 6ppm to 2.932ppm and growth reading increased from 0.158abs to 0.202abs. Even though this is small amount of growing, it still effect the Hg concentration. The concentration of Hg is unstable. This is because due to sensitive of the analyzer machine. Mercury analyzer is very sensitive instrument that can detect [Hg] only in range of 15-0 ppb. So, we have to dilute the sample each time before the analyzing. Hg solution can not be stored more then a week because Hg^{2+} density is higher then water. It will settling to the lower part of storage bottle and causing the concentration change even after we shake it.

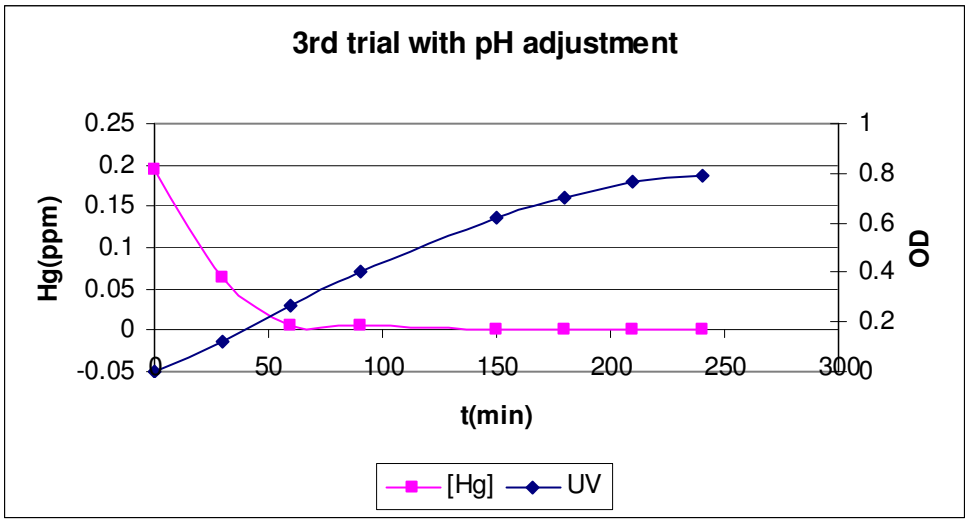


Figure 4.5: pH adjustment(Growth)

In this experiment, the pH was first adjusted to pH 6.5 with initial concentration 200ppb (0.2ppm). The growth curve is smooth. From this graph we can see that *P Putida* growth is inversely to Hg concentration. Only after we trial with concentration under 1ppm, the graph will become smooth like this. Unlike other graph, the concentration is sometime too difficult to be accepted. Within 250 minutes, the *P.Putida* growth with stable even though the concentration is almost at zero

As conclusion for pretreatment growing *P.Putida* in Hg solution, we have to neutralize the pH in purpose of giving best condition for bacteria or decrease the concentration to below then 1ppm.

4.2 Membrane Pressure

Pressure will only increase the permeate flux. Flux is the flowrate over area of membrane. The higher the pressure or flow of solution, the higher the permeate flux. It does not effect the mercury filtration. So, the study will take medium pressure of membrane (15bar) as the best pressure.

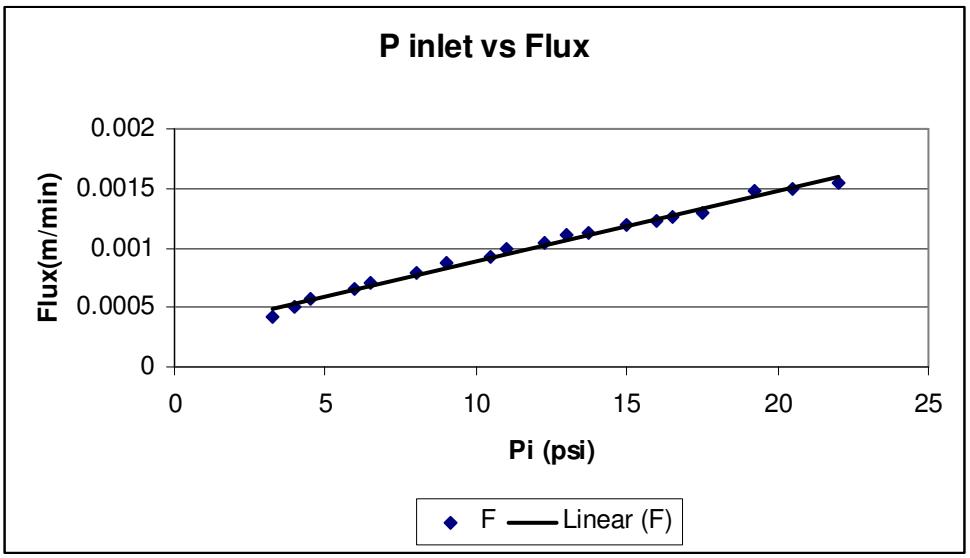


Figure 4.6: P inlet vs Flux

In this experiment, $HgNO_3$ was used as the material. The purpose of this experiment is to study the membrane pressure effect from flux. As the increasing of inlet pressure of Membrane, the value of flux also increase. According to literature, increasing the pressure will increase the force on the wastewater within the membrane. This had cause the sample to go through the membrane faster. So this proves that P is proportional to flux of membrane.

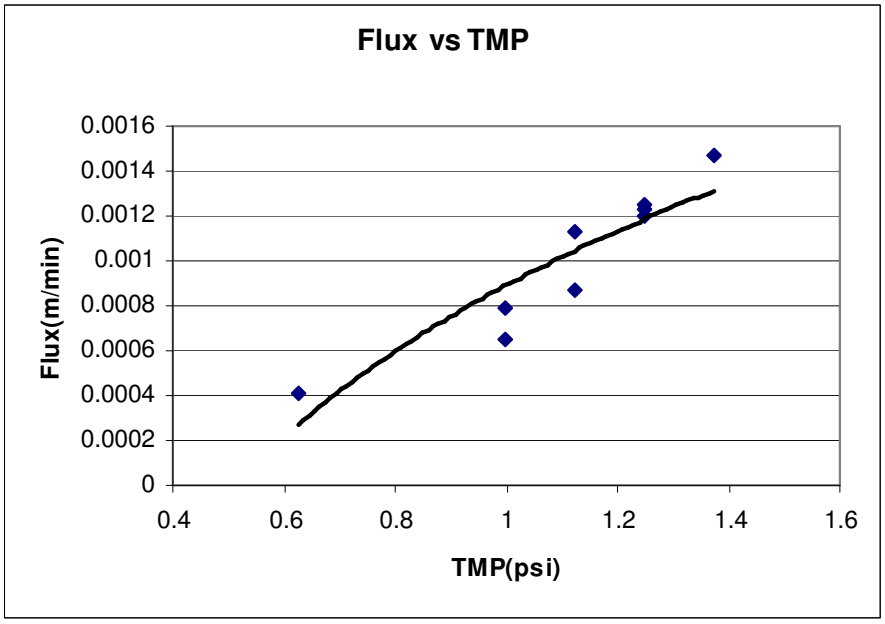


Figure 4.7: Flux vs Transmembrane Pressure

From literatue, it is stated that increasing the flux will increase the Transmembrane Pressure (TMP). As the above figure, the increasing graph shows that flux is proportional to transmembrane pressure. The transmembrane pressure is the driving force for sample to go through the membrane. The increasing of flux is somehow will maintain or drop as the Hg will stuck at the membrane pores and membrane cleaning need to be done with $NaCl_3$.

$$Flux \propto TMP \qquad (4\text{-}2)$$

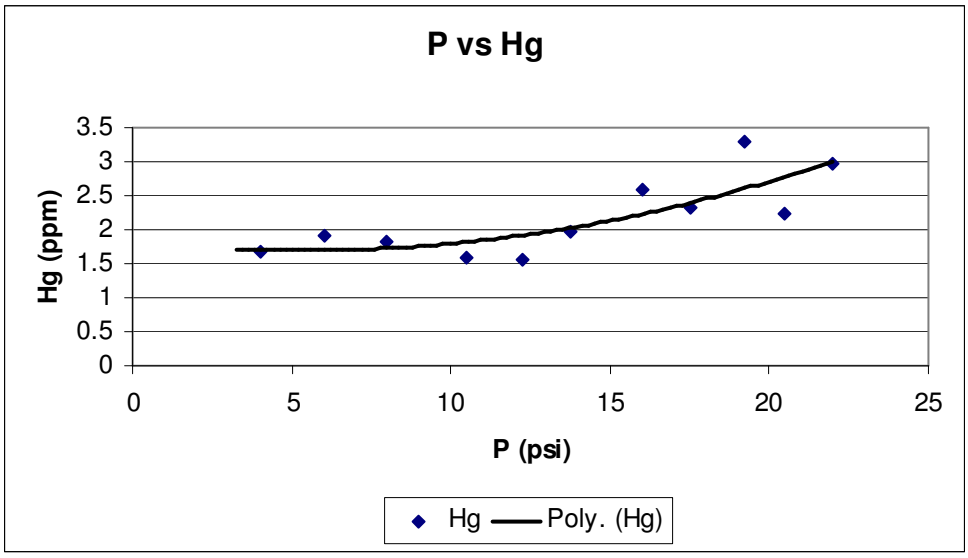


Figure 4.8: Effect of Membrane Pressure on [Hg]

In this experiment, the parameter that was studied is pressure. The pressure was studied from 4 to 23psi in purpose to get the lowest value of Hg concentration. From the above graph, it shows that the best concentration is around 10-15 psi. Increasing the pressure will increase the Hg concentration in the permeate value. This is because the increasing pressure will force the Hg ion to go through the membrane pores. As stated in literature, the ion size of Hg is 0.11nm but this is Ultra Filtration Membrane (10^{-6} m) so the ion will filtrated only in small amount. So to get the best pressure and concentration is 13psi. So the next experiment will be used this pressure value for separation of Hg from the solution.

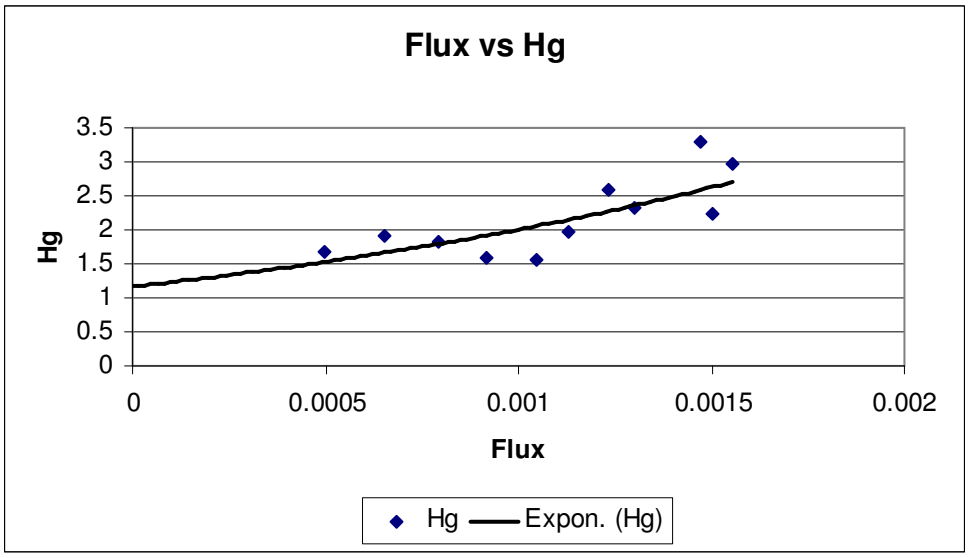


Figure 4.9: Flux vs Hg

In this graph, it is shows that increasing the flux will increase the Hg concentration in permeate sample. When increasing the flux, the value of pressure and transmembrane pressure also increase. So the force on the Hg ion also increases. This had cause the Hg ion forced to get through the membrane as it was stuck at the membrane pores.

4.3 pH effect on Membrane

In adjusting the pH value, it will cause the mercury to precipitate. From previous study, the pH range is around 5-7 (Kelly *et al*, 2003). It is assume 70% mercury will be removed.

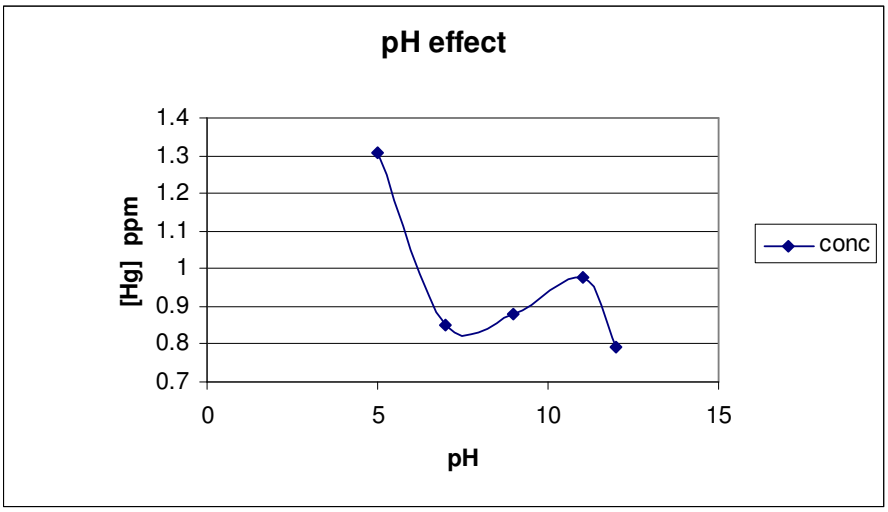


Figure 4.10:pH effect on Membrane without Pretreatment

With concentration 1.5ppm, the pH value is 5. Starting from that point, the pH is increased up to pH 12. at pH 7 or neutral, the concentration is falling down. As the literature review, increasing the pH will increase the thickness of the membrane and the pores become smaller. This concentration remains lower until pH 9. At this level, it is believe that NaCl start to clean the membrane. NaCl as the cleaning agent for membrane will give effect on pH higher then 9. So, between pH 7-9, it will increase the membrane thickness and pH 9-14 NaCl will react as cleaning reagent for membrane.

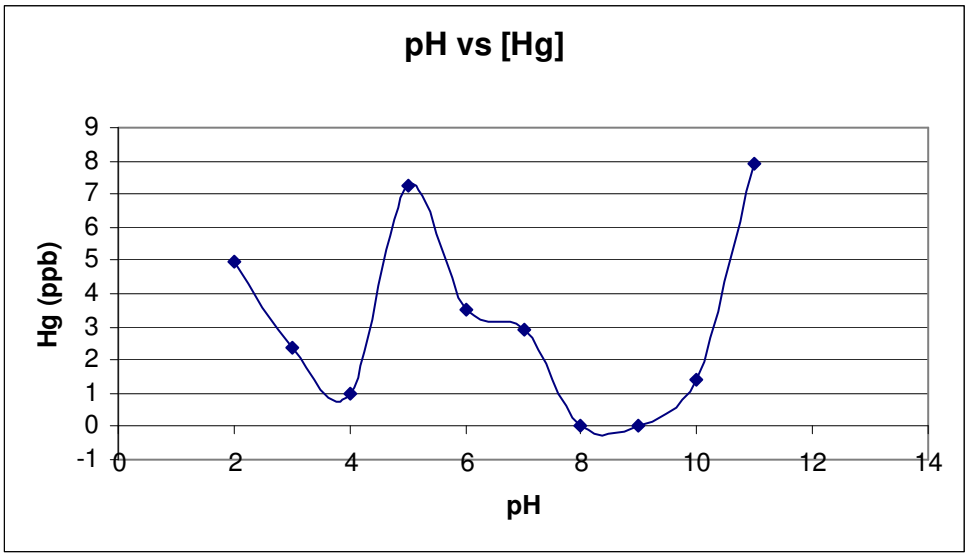


Figure 4.11: pH effect on Membrane Separation with Pretreatment

In this experiment the best pH is 8-9. This is because when in base condition, the membrane pores thickening and block the Hg ion from penetrate the membrane (prove the theory from literature). For pH beyond the pH 9, the attraction between base and membrane are losing and that is why the Hg concentration is increasing. The explanation for lower concentration at pH4 is Hg accumulate at low concentration. Hg ion can accumulate at protein cell (*P.Putida*) and filtrated together, causing the lower concentration. The accumulation is around pH 4 and decreasing pH cause the increasing Hg concentration.

As conclusion, pH does effect on membrane performance filtration on Hg ion at pH 8-9.

CHAPTER 5

CONCLUSION

The usage of membrane in filtrating the mercury from wastewater give a high impact because of its ability to filtrate even though its ion by manipulating the pH level with existence of pretreatment. The pH value from this study is in range pH 8-9

Mercury can be removed using the ultra-filtration membrane. Even though the pores size is differ in large scale, ultra-filtration still can be used as mercury filtration with the changing of pH.

Using *P.Putida* as pretreatment, the concentration drop from 250ppb to8ppb. Continue with membrane separation, the remain concentration in the medium decrease to 0ppb.

As conclusion, mercury can be remove using Ultrafiltration Membrane by adjusting the pH of medium to range pH8-9 and to increase the ability, pretreatment stage is advise.

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APPENDIX

THIRD SCHEDULE

ENVIRONMENTAL QUALITY ACT 1974

ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1979

(REGULATIONS 8(1), 8(2), 8(3)

PARAMETER LIMITS OF EFFLUENTS OF STANDARDS A AND B

Parameter		Unit	Standard	
			A	B
(i)	Temperature	°C	40	40
(ii)	pH value	-	6.0 - 9.0	5.5 - 9.0
(iii)	BOD at 20°C	mg/ l	20	50
(iv)	COD	mg/ l	50	100
(v)	Suspended Solids	mg/ l	50	100
(vi)	Mercury	mg/ l	0.005	0.05
(vii)	Cadmium	mg/ l	0.01	0.02
(viii)	Chromium, Hexavalent	mg/ l	0.05	0.05
(ix)	Arsenic	mg/ l	0.05	0.10
(x)	Cyanide	mg/ l	0.05	0.10
(xi)	Lead	mg/ l	0.10	0.5
(xii)	Chromium Trivalent	mg/ l	0.20	1.0
(xiii)	Copper	mg/ l	0.20	1.0
(xiv)	Manganese	mg/ l	0.20	1.0
(xv)	Nickel	mg/ l	0.20	1.0
(xvi)	Tin	mg/ l	0.20	1.0
(xvii)	Zinc	mg/ l	2.0	2.0
(xviii)	Boron	mg/ l	1.0	4.0
(xix)	Iron (Fe)	mg/ l	1.0	5.0
(xx)	Phenol	mg/ l	0.001	1.0
(xxi)	Free Chlorine	mg/ l	1.0	2.0
(xxii)	Sulphide	mg/ l	0.50	0.50
(xxiii)	Oil and Grease	mg/ l	Not Detectable	10.0