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Effects of pH in Mercury Nitrate Treatment Using Membrane System with Biological Pretreatment

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Abstract

Wastewater from industry containing mercury is very dangerous. Hence we need to treat the wastewater effectively to avoid its toxic effects. The usage of membrane in wastewater treatment has increased due to its ability to filtrate unwanted particle. Modification of the membrane parameters may produce better result than changing the type of membrane for filtration of mercury in wastewater. Using *P.putida* as the pretreatment or volatilizing agent and continue with the alternation of pH value, this technique seems to be able to remove mercury (Hg) to the minimum permitted level easily. Based on the study conducted, the pretreatment stage decreased the concentration of Hg solution from 250 ppb to 8 ppb. The concentration was further decreased to 0 ppb within the pH of 8 to 9, following the membrane separation. As a conclusion, pH 8 to 9 is the best pH for operating membrane to filtrate mercury wastewater since the membrane operates at neutral or base condition.

Keywords: *pseudomonas putida*; growth kinetic; biosorption; mercury; petrochemical wastewater

1. INTRODUCTION

Wastewater pollution has become very serious in Malaysia. Wastewater is the unwanted product yield from the process of cleaning and the contents depend on where it is produced. Wastewater that comes from palm oil industry usually contains 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 have level of mercury below the permitted limits or it will bring harmful effects to human life and the ecosystem. The wastewater treatment system is the responsibility of factory owners and they should provide a plant for wastewater treatment process. Wastewater that contains mercury must be treated effectively to avoid the side effects of mercury pollution.

Research on water pollution by heavy metals is essential due to their deadly effects even at low concentration. The toxic effects of mercury has long been known to humans like failure of brain functions can cause degradation of learning abilities, personality changes, tremors, vision changes, deafness, and muscle in-coordination and memory loss [1].

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 metals has a very high tendency to bind to proteins and it mainly affects the renal and nervous systems; hence mercury content of wastewater streams must be reduced below the discharging limits [2].

Mercury is one of the most strictly regulated elements, often restricted to less than 1 µg/l [3] and 0.005mg/l or less in Malaysia [4]. Mercury is often found in landfill leachate, in petroleum and incinerator [5] and 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 content in wastewater is at low concentration but somehow this is a problem because it is hard to be removed and usually the industries just ignore it.

Previously, mercury has traditionally been treated by the alteration of the pH value using lime or caustic soda in precipitating hydrated metal oxides [6]. In addition, at that time sulphide compound and other materials were also added which resulted in a production of heavy metal compounds with lower solubility products. Both of these methods caused the pH of mercury solution to be alkaline and to completely remove the mercury, usually settlement and sand filtration were done [7].

As the new era has come, 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 compared to the more usual methods of treatment (settlement). In this study, membrane will be used as a replacement of settlement and sand filtration. The adjustment of pH will decreased the mercury (Hg) concentration.

Sodium hydroxide (NaOH) will change the pH level to higher value while nitric acid ($HNO_{3)}$ will acidify the mercury solution. Removal of mercury from wastewater is predicted to be more effective by changing the pH level from acidic (HNO_3) to alkaline (limestone) and using membrane filtration (replacing the settlement). The pH value changes will cause precipitation to occur in alkaline solution while acidic solution will lessen the colloidal fouling effect in membrane and the process continued with filtration and removed the unwanted mercury. The size of mercury ion is 0.1nm (+2) hence the micro-filtration membrane cannot filtrate the mercury alone.

In this study, *Pseudomonas putida* bacterium is used as the capturing and volatile agent. This process is known as pre-treatment process and will proceed to the major process, membrane filtration which is the final step to overcome the mercury. When mercury is treated with membrane bioprocess, the mercury solution needs to be more alkali as studies have shown that low water pH (acidic lake) aids in the methylation reaction [8,9]. Addition of acid (HNO_3) will decreased the rate of mercury accumulation and also the changes of Hg^{2+} to Hg^0

2. METHODOLOGY

2.1 Experimental Procedures

In the pretreatment phase, 20mL *P.Putida* was cultured with 180mL Nutrient Broth in a conical flask. Next, the flask was incubated in an incubator shaker at 180rpm and 37^{o}C for one day. Fermentar was used to culture *P.Putida* with adjusted pH and was supplied with air. The growth rate of the bacteria in Nutrient Broth media was recorded. The cultured *P.Putida* was then mixed with Hg solution in the Fermenter. The growth rate of bacteria and Hg concentration were observed in the acidic solution. Later the pH was adjusted from pH 2 to pH 7 with sodium chloride (NaCl) and the growth rate and Hg concentration were measured.

Sample was taken after 5 minutes of initial mixing to determine the growth rate at 0 minute and every 30 minutes for 4 hours to measure the growth rate as well as to analyse mercury concentration. After the 4 hours, it was continued with the membrane separation phase with the remaining sample.

Cross-flow membrane was used in the membrane separation phase. The Cross-Flow membrane is in a spiral shape and the waste will flow from inside to the outside of the membrane in one direction only. The membrane was equipped with Pressure Gauge for inlet and outlet of flow. The feed solution was added to the reservoir and later the end product was recovered from the reservoir via the drain/recovery valve upon completion.

2.3 Analysing Hg Solution

Mercury Analyzer was used to analyse the concentration of Hg ion. The range for the Mercury Analyzer concentration is less than or equal to 15 ppb hence every sample needs to be diluted before analyzing.

Firstly, a solution of stanum chloride ($SnCl_2$) was prepared by diluting 2 g of $SnCl_2$with 1mL of 97% Sulphuric Acid ($H_2SO_{4)}$ and 19mL of Diionised (DI) water in a beaker. The solution was stirred using glass rod. Next sample was diluted using a prepared solution of 1:1 H_2SO_4 and DI water. This solution was prepared from 50mL of 97% H_2SO_4 and 50mL of DI water. The diluted sample was poured in a test tube and the mercury analysis started. The test was run 3 times for each sample.

3. RESULT AND DISCUSSION

3.1 Pretreatment

It is predicted that 98% of mercury in the Hg solution will be removed during the pretreatment process. Before continuing with mercury treatment, *Pseudomonas Putida* was grown in Fermenter 2L for a day using nutrient broth as media. This is to ensure that P.Putida is able to grow under the Fermenter conditions and to avoid any chances of other bacteria to mix with the media. Absorption value represents the qualitative amount of the bacteria. The increment of absorption value was detected within 1200 min of operation (Figure 1). Then the value started to fall down during minute 1200. The highest amount of bacteria growth was 1.502 as compared to blank (0 min, 0 abs). The increasing value proved that *P.Putida* is able to grow in the Fermenter.

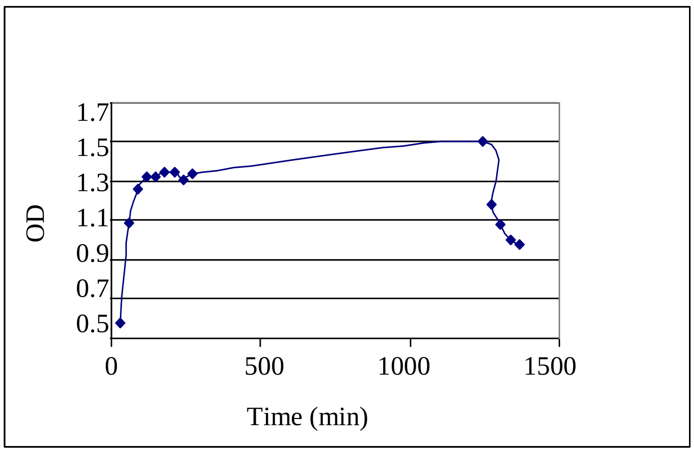

Figure 1: *Pseudomonas Putida* Growth Rate in Nutrient Broth

In Figure 2, there was an increment in the value of absorption at minutes 90 and then the *P.Putida* died. Hg solution was used as media with no adjustment made to the pH. The pH shows that the solution was acidic (pH 2). According to literature review, bacteria able to grow in neutral condition (pH 7). So theoretically *P.Putida* will die the moment it made contact with Hg solution. This experiment confirmed the theory that *P.Putida* could not grow normally in Hg solution. So to overcome this problem, the pH value of Hg solution was increased from ph 2 to pH 7 using NaCl. NaCl was used because it is also an agent for adjusting Hg solution before it was flowed through the membrane.

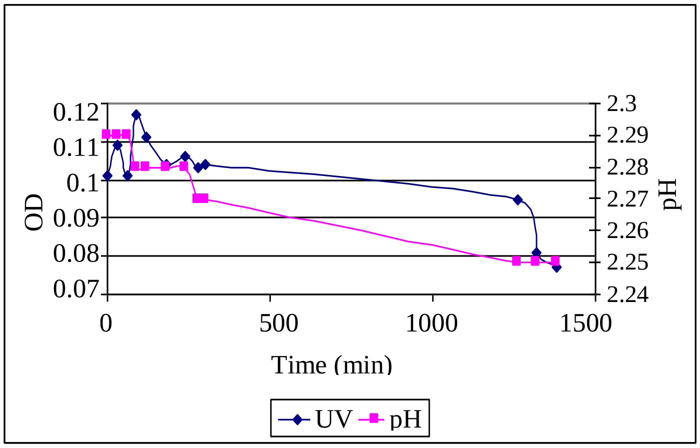

Figure 2: *Pseudomonas Putida* Growth rate (no pH adjustment) in Hg

Figure 3 shows *P.Putida* growth rate and the concentration of Hg in the solution without changing the pH (3.5). A decreasing growth rate was observed in the first one hour and the Hg concentration was decrease from its initial concentration of 4ppm after mixing with *P.Putida*. It was assumed that the *P. Putida* need adaptation for solution starting with pH 4 and only *P.Putida* with high strength will survive in such condition. The Hg concentration continued to decrease from 4ppm to 1.215ppm between minute 1500 and 2000. This proved that *P.Putida* decreased Hg^{2+} to Hg^{0}. The maximum growth rate of *P.Putida* was 0.252 abs. When *P. Putida* increased with time, the Hg concentration decreased with time. Hence it can be concluded that to *P. Putida* growth is inversely proportional to Hg concentration.

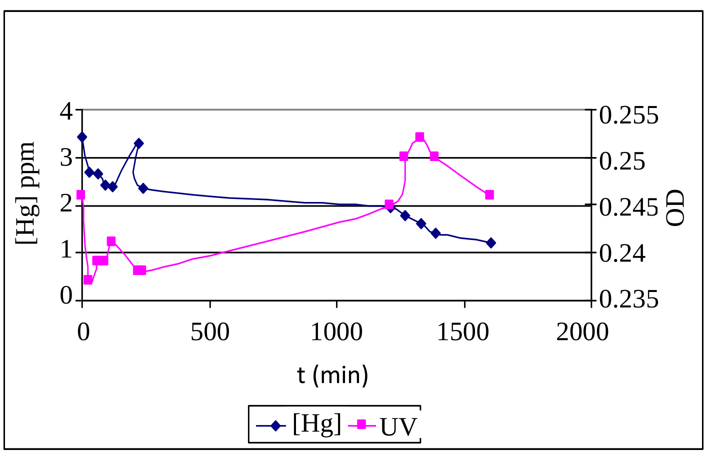

Figure 3: Hg concentration and *Pseudomonas Putida* growth rate

A stabilize Hg concentration and bacteria growth reading was observed only after 2 days (Figure 4). Once the bacteria adapted to the low pH condition, it will grow and used the Hg as “food”. The concentration decreased from 6ppm to 2.932ppm and the growth reading increased from 0.158abs to 0.202abs. Even though the growth rate is low, it still effects the Hg concentration.

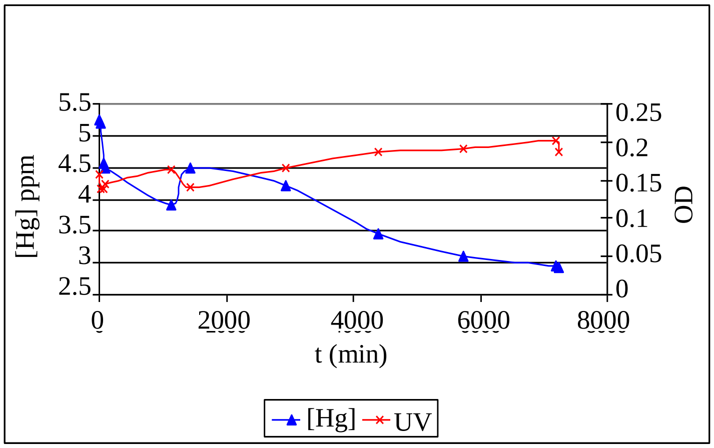

Figure 4: Hg concentration and *Pseudomonas Putida* growth rate against time (Second Trial)

In Figure 5, the pH was first adjusted to pH 6.5 with initial concentration of Hg was 200ppb (0.2ppm). It can be observed that the P *Putida* growth rate was inversely proportional to Hg concentration. Within 250 minutes, the *P.Putida* showed stable growth rate even though the Hg concentration was almost zero.

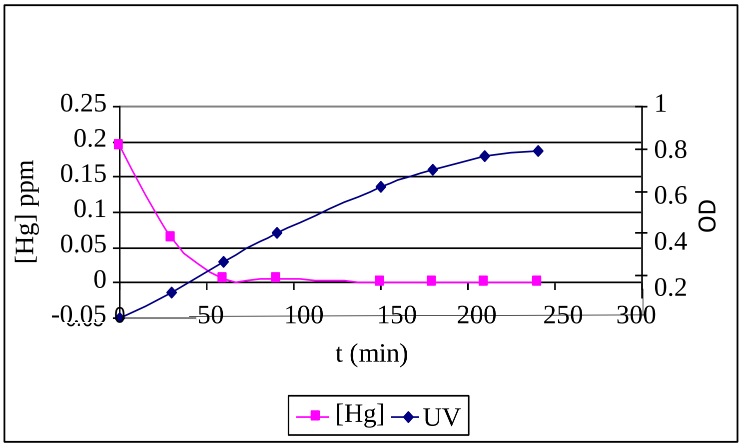

Figure 5: Hg concentration and *Pseudomonas Putida* growth rate against time with adjusted pH (Third Trial)

3.2 Membrane Pressure

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

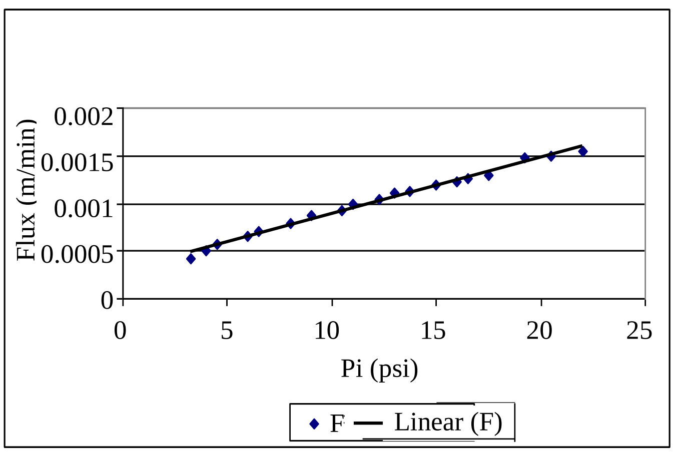

Figure 6: Effect of Inlet pressure on flux

According to literature, increasing the pressure will increase the force on the wastewater within the membrane. From Figure 6, as the inlet pressure of membrane increased, the value of flux also increased. Hence, the sample went through the membrane faster.

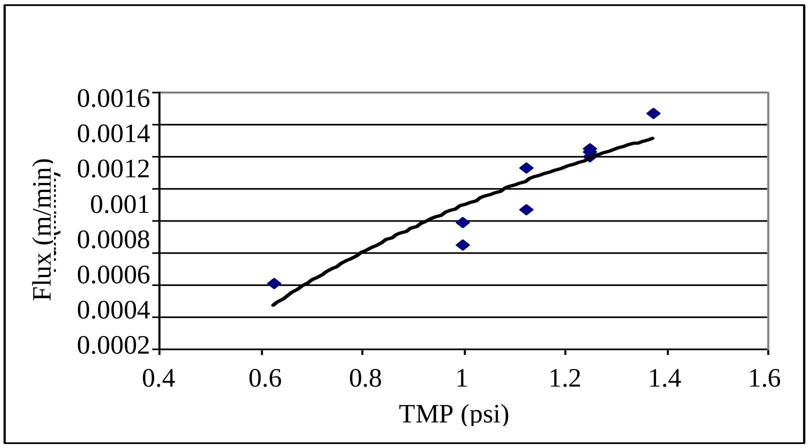

Figure 7: Effect of Transmembrane Pressure on Flux

Figure 7 shows that flux was directly proportional to transmembrane Pressure (TMP). The transmembrane pressure is the driving force for sample to go through the membrane. The increasing or decreasing of flux will depend on the Hg as the Hg will stuck at the membrane pores and membrane cleaning need to be done with NaCl.

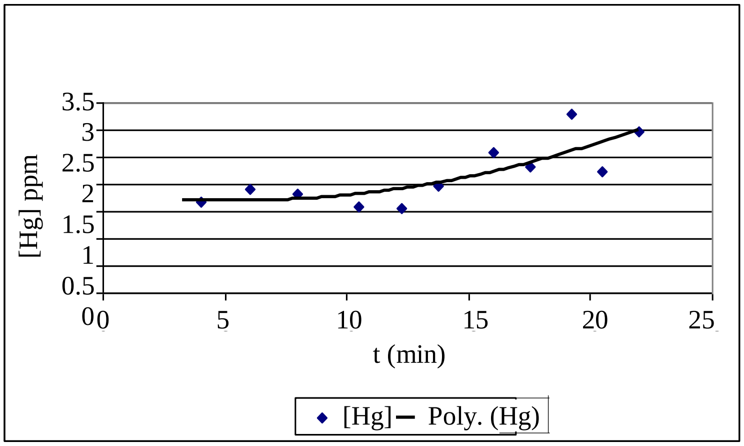

Figure 8: Effect of Membrane Pressure on Hg concentration

The best pressure to get the lowest value of Hg concentration was around 10-15 psi (Figure 8). 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 since it is the Ultra Filtration Membrane (10^{-6} m) the ion will be filtered only in a small amount.

The effect of flux on Hg concentration can be observed in Figure 9. It showed that increasing the flux will increase Hg concentration in permeate sample. When the flux was increased, the pressure and transmembrane pressure also increased. Hence, the force on the Hg ion also increased.

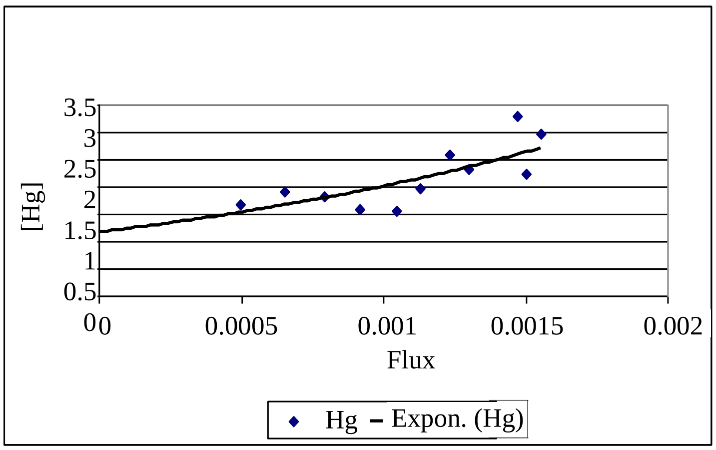

Figure 9: Flux against Hg concentration

3.3 Effect of pH on Membrane

Adjusting the pH value will cause the mercury to precipitate. From previous study, the pH range is around 5-7 [10]. It is assumed that 70% of mercury will be removed.

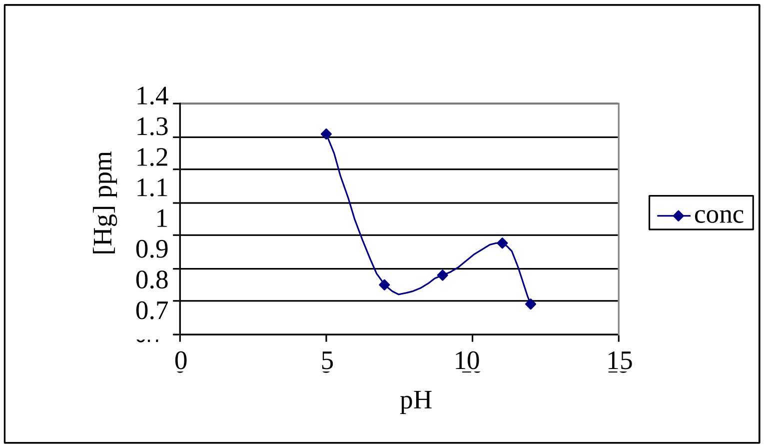

Figure 10: Effect of pH on Membrane without Pretreatment

Figure 10 shows the effect of pH on membrane without pretreatment. The Hg concentration decreased sharply as the pH increased. From literature review, increasing the pH will increase the thickness of the membrane and the pores become smaller. This concentration remains low until pH 9. At this level, it is believed that NaCl starts to clean the membrane. So, between pH 7-9, it will increase the membrane thickness and between pH 9-14 NaCl will react as cleaning reagent for membrane.

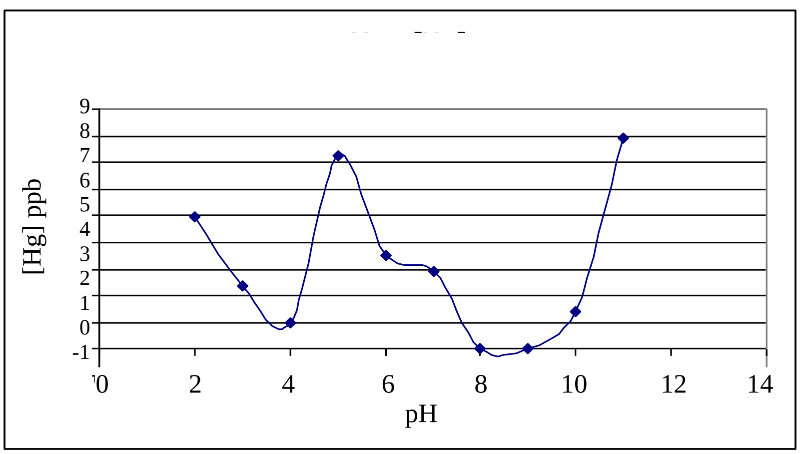

Figure 11: Effect of pH on Membrane Separation with Pretreatment

The best pH for membrane separation with pretreatment was between pH 8-9 (Figure 11). This is because when in base condition, the membrane pores thicken and blocked the Hg ion from penetrating the membrane. For pH beyond the pH 9, the attraction between base and membrane were losing and hence the Hg concentration increased. On the other hand, Hg accumulated at a low concentration in pH 4. Hg ion can accumulate in protein cell (*P.Putida*) and was filtrated together, causing the lower concentration. The accumulation is around pH 4 and decreasing the pH caused Hg concentration to increase.

4. CONCLUSIONS

The usage of membrane in filtrating mercury from wastewater gives a high impact because of its ability to filtrate by manipulating the pH level with the existence of pretreatment. Hence, mercury can be removed using Ultra-filtration Membrane by adjusting the pH even though there is difference of pores size in large scale. Starting with the pretreatment stage is advisable to increase the ability.

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