EFFECT OF MERCURY CONCENTRATION AND OPERATING PARAMETERS ON MERCURY REMOVAL USING PORTABLE MERCURY REMOVAL RIG FOR PETROCHEMICAL WASTEWATER

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ABSTRACT

Mercury is a type of heavy metal that naturally occurs in the earth's crust, which can be found in soil, rocks and sea. Mercury is released to the environment through natural processes such as rock erosion, soil decomposition or volcanic eruptions and also released through human activities, petrochemical industrial processes and chlor-alkali industries. Mercury is widely used in the thermometer, thermostat, barometer, bulbs, dental amalgams and switches. Other than that, mercury is one of the hazardous chemical elements that exist on the earth that can attack the human central nervous system, kidney, lungs and other body systems. Portable Mercury Removal Rig (PMRR) was used in mercury removal process under room temperature with different operating pressure; 5, 10 and 23 psig, different inlet concentration; 2, 4, 6 and 8 ppm, different pH and by using different absorbent; extruded activated carbon (EAC), granular activated carbon (GAC) and ion exchange (IE) resins. Extruded Activated Carbon (EAC) was the best absorbent with pH sample range from 2 to 4 in using the PMRR. It was also found that 5 psig was the best operating pressure and concentration from 2 to 4 ppm was the most suitable concentration to be used. This study shows that EAC can be used as an efficient absorbent in removing mercury in wastewater as it give about 99.8 % of mercury removal.

KEYWORDS: *Mercury removal; petrochemical wastewater; activated carbon*

1.0 INTRODUCTION

Mercury has been widely used thoroughly in the industries such as in the thermometer, manometer, barometer, laboratory chemicals, fixatives and cleaning supplies (Kaur et al., 2014). Mercury amalgams are commonly used in dentistry by applying it on the teeth. This type of amalgams become a dental restorative material choice because of its low in cost, easy application, high strength and durability.

Mercury is also used in batteries, normal fluorescent bulb and switch, but due to its carcinogenic effect, wide variety of choices and enhancement of technologies, nowadays their popularity has decreased. Manohar, Krishnan and Anirudhan (2002) stated that wastewater from industries such as chlor-alkali manufacturing, oil refinery, paint, pharmaceutical and battery manufacturing industries contain mercury. Out of all

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industries that have been stated, chlor-alkali manufacturing industries have been the main contributor for mercury contamination in the environment (Mohan et al., 2001). In fact, chlor-alkali industries serve a threat to aquatic life as well as for drinking water (Shafeeq et al., 2012). The problem of mercury in the wastewater not only is the concern of the company, but also Department of Environment (DOE) Malaysia. Mercury exists in several forms that are elemental mercury, organic mercury and lastly inorganic mercury. These different types can cause different types of illness or hazards (Bernhoft, 2012). Generally, when mercury enters the human body, it will attack the central nervous system and liver. Mercury can cause blindness, mental and emotional deterioration, involuntary immobilization and other. Mercury has mutagenic, teratogenic, carcinogenic criteria and promotes tyrosinemia. This could bring to the toxicological effects such as paralysis, neurological damage, chromosome breakage, impairment of pulmonary, chest pain, kidney malfunction and etc.

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 (Karthika and Sekar, 2012). While in common wastewater from petrochemical industries, it is about 0.1- 9.0 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 example of the disaster that is caused by mercury in the past is in the late 1950s when more than hundreds of people are killed and disabled through the intake of fish and shellfish. This disaster happened in Minamata, Japan (Rani et al., 2012).

Many technologies have been identified to be capable of removing mercury from wastewater. They include several physical and chemical separation processes such as solvent-extraction, ion-exchange, 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 a large scale application. The other techniques required either high energy or big amount of chemicals. Furthermore, current technologies used require a large space in plant or oil rig, but by applying Portable Mercury Removal Rig (PMRR), this problem can be solved. Besides, it requires fewer workers to operate the rig. Thus the company can save space and cost that can be used for other purposes.

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

2.0 MATERIALS AND METHODS

2.1 Experimental Procedures

There are three procedures included which are before, during and after the experiment. At an early stage, 1000 ppm of mercury stock solution was prepared by using mercury (II) chloride and distilled water, to be used in the experiment. Then, activated carbon filter for extruded activated carbon (EAC) was prepared. To avoid the filter from being flushed due to high pressure, a sponge was used at the top of the activated carbon and

the filter was installed in the PMRR. After an experiment using EAC was completed, the filter was substituted by using granular activated carbon (GAC) and ion exchange (IE) resins. The Figure 1 shows the schematic diagram of Portable Mercury Removal Rig (PMRR).

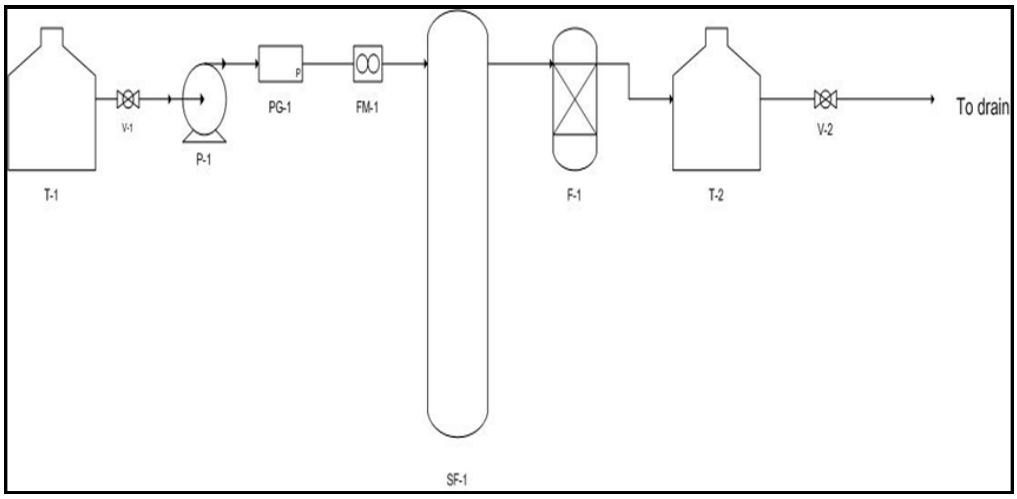

Figure 1. Schematic Diagram for Portable Mercury Removal Rig (PMRR)

Figure 2. Portable Mercury Removal Rig (PMRR)

During the experiment, a sample of 40 L of synthetic mercury wastewater was prepared at different mercury concentrations of 2, 4, 6, and 8 ppm. Then, the wastewater being treated using PMRR. Both inlet and outlet sample parameters were taken for analysis. After the experiment, PMRR was cleaned and the next experiment was operated by using different types of absorbent filter. Figure 2 shows the picture of Portable Mercury Removal Rig that have been used in this research study.

2.2 Analysis of Mercury removal

All the data that were obtained from the experiment were analyzed to measure the mercury concentration before and after the treatment. Mercury concentration was detected by using DMA-80 mercury analyzer. After the initial concentration of mercury (C_i) and after treatment mercury concentration (C_o) was detected, the percentage removal of mercury was calculated using Equation (1).

$$\left(\frac{C_i - C_o}{C_i}\right) x\ 100\ \% \quad (1)$$

2.3 Analysis of pH and conductivity

Value of pH was determined by using pH meter. Calibration was done to avoid from the deviation of value. The probe of the pH meter was inserted into the sample. After the reading was constant, the pH indicator symbol (√A) was shown. So, the reading can be recorded. For conductivity, it was measured by using CW 6120 conductivity meter. The probe of the conductivity meter was inserted into the sample and it need to be stirred. After the reading was constant, the value is recorded.

3.0 RESULTS AND DISCUSSION

3.1 Effect of synthetic mercury wastewater temperature on mercury removal

Temperature of samples before and after treated was recorded and it shows that all the temperature for influent wastewater was about 29 ˚C to 30˚C. This is due to room temperature where the experiment was run and temperature of deionized 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 treatment of wastewater. It is found that adsorption of mercuric ions increases with decreased in temperature of the influent wastewater due to increase mobility of ions and a decrease in retarding forces acting on the diffusing ion.

3.2 Effect of influent concentration on percentage of mercury removal

The effect of wastewater initial concentration on mercury removal is shown in the graph below. Figure 3 below shows the conductivity value of wastewater using granule activated carbon (GAC) as the absorbent at the inlet and outlet of PMRR. Concentration is one of the factors that affect the conductivity of the solution. From Figure 3, it shows that the inlet conductivity also much higher than the outlet after being treated using GAC and the conductivity corresponds to the concentration of mercury in wastewater. As the concentration decreased, the conductivity also decreased.

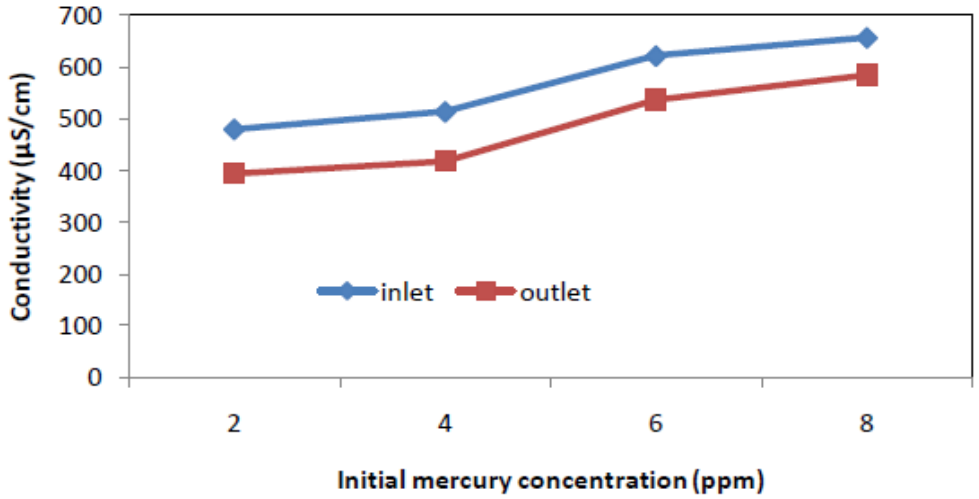

Figure 3. Graph of conductivity vs. initial mercury concentration

Figure 4 below shows the percentage of mercury removal vs. initial mercury concentration. As the influent concentration increased, the percentage of mercury removal decreased. The highest percentage mercury removed was at the inlet concentration of 4 ppm followed by 2 ppm, 6 ppm and 8 ppm. If the concentration is high, so the ion of mercury is high in the solution thus the absorbent may not have enough active sites for adsorption to treat the wastewater. As the consequence, mercury ions are not completely adsorbed from the solution due to the saturation of the binding sites (Ismaiel et al., 2013). Lloyd- Jones, Range-Mendez and Streat (2004), state that the mechanisms of mercury sorption by the sorbents are strongly dependent on the solution parameter such as the concentration of the solution. Besides, (Kadirvelu, Kavipriya, Karthika, Vennilamani & Pattabhi, 2004) also state that the adsorption was dependent on the initial Hg (II) concentration. Meanwhile Goyal, Bhagat and Dhawan (2009) said that the breakthrough time of Hg (II) ions of granular activated carbon and activated carbon cloth decrease on increasing feed concentration. So, it is justified that the initial mercury concentration at the inlet played a very important role in the percentage of mercury removal from the wastewater during the treatment.

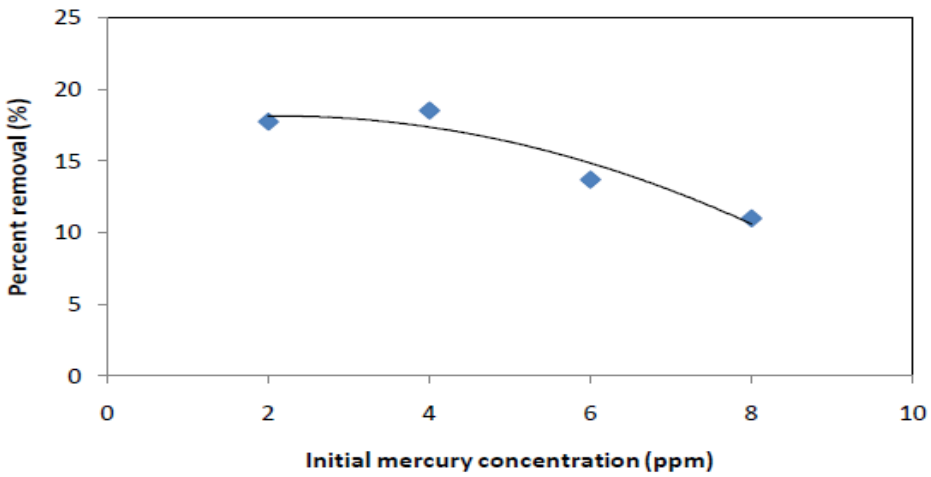

Figure 4. Graph of percentage removal of mercury vs. initial mercury concentration

3.3 Effect of Initial pH value on mercury removal

The pH values of the influent wastewater vs. the initial mercury concentration using different absorbent were shown in Figure 5. Theoretically 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. However, there is some inconsistency in the reading of EAC influent pH value. This might be due to an error during analysis. Meanwhile, Figure 6 shows the pH of effluent wastewater vs. initial mercury concentration for different absorbent. If compared the inlet and outlet pH value, the pH value at the outlet is much lower. This is because of the lower mercury concentration at the outlet. Value of pH is directly proportional to the concentration of mercury in wastewater.

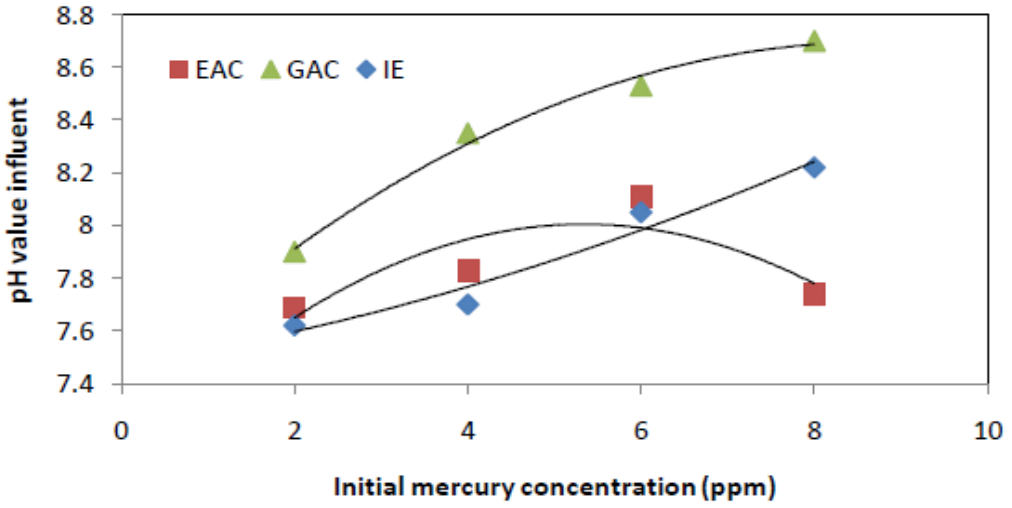

Figure 5. Graph of pH value at the influent vs. initial mercury concentration

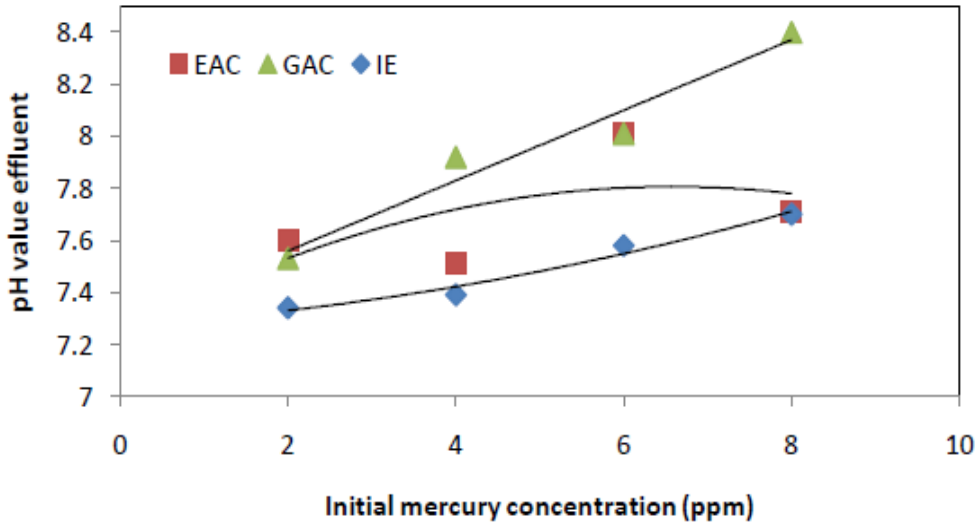

Figure 6. Graph of pH value at the effluent vs. initial mercury concentration

According to Figure 7, it shows the percentage of removal vs. initial mercury concentration. Based on the figure, the percentage removal of mercury for GAC adsorbent decreased as the initial influent mercury concentration increased. For GAC, the highest removal occurs at 4 ppm, meanwhile for IE at 8 ppm. For GAC and EAC, the removal percentage is reduced with the increasing mercury concentration. For IE as the adsorbent, the percentage of mercury removals were quite promising. This show the effectiveness of ion exchange resins are as the absorbent for high concentration of mercury in this PMRR system.

The removal percentage using GAC and EAC absorbent decreased because the pH value of the inlet mercury wastewater increased. The degree of removal strongly dependent on the initial pH of the solution and it decreased as the increased and high mercury concentration (Sulaymon & Swadi, 2014; Chiarle et al., 2000; Barron-Zambrano et al., 2002; Rengaraj & Moon, 2002; Chojnacki et al., 2004; Rangel-Mendez & Streat, 2002; and Kadirvelu et al., 2004). The researchers agreed that the removal of mercury from aqueous solution or wastewater is strongly influenced by the initial pH. Mercury removal using activated carbon increased at a pH value greater than pH 4 (Yardim et al., 2003). The mercury uptake increased when pH increased from 4 to 6 (Llyod-Jones et al., 2004).

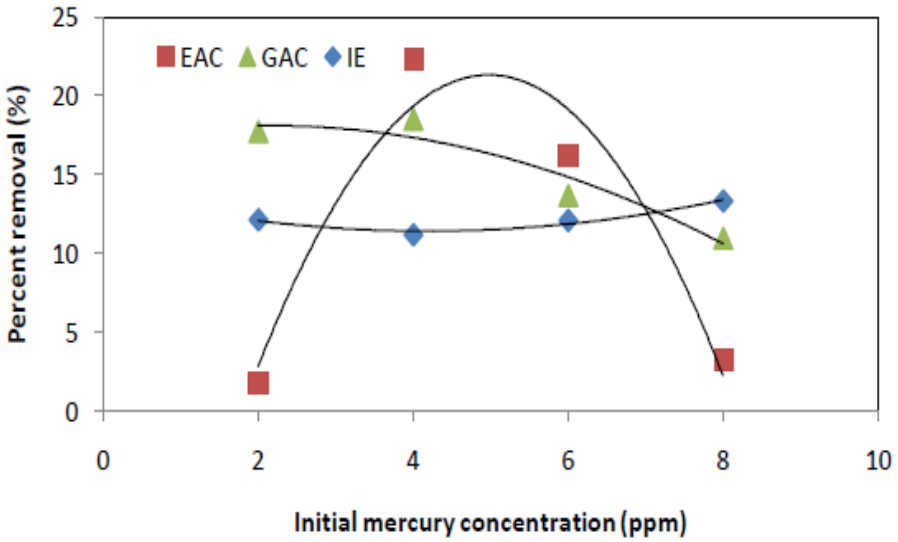

Figure 7. Graph of removal of mercury vs. initial mercury concentration

3.4 Effect of inlet pressure percentage on mercury removal

In Figure 8, it can be observed that the highest percentage of mercury removal from the wastewater is about 15% at 5 psi operating pressure for all three types of adsorbent. Ion exchange resin has the most promising effectiveness because of pressure gauge of about 23 psi, it managed to remove mercury at 6.49% which is higher than EAC and GAC. EAC and GAC only manage to achieve about 3.23% and 3.29% mercury removed at 23 psig. Overall mercury removals were relatively low due to less contact time between the adsorbent and the wastewater. Thus the amount of mercury removed was quite low. Goyal et al., (2009) in their research said that the breakthrough time of Hg (II) ions of activated carbon increased with the decreased of an 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 and the treated water. Other than that, adsorption will increase up to a certain extent till saturation level is achieved. Even after this saturation level, no more adsorption will take place even higher pressure is applied. Thus, it can said that the inlet pressure has a significant influenced on the percentage of mercury removal using PMRR.

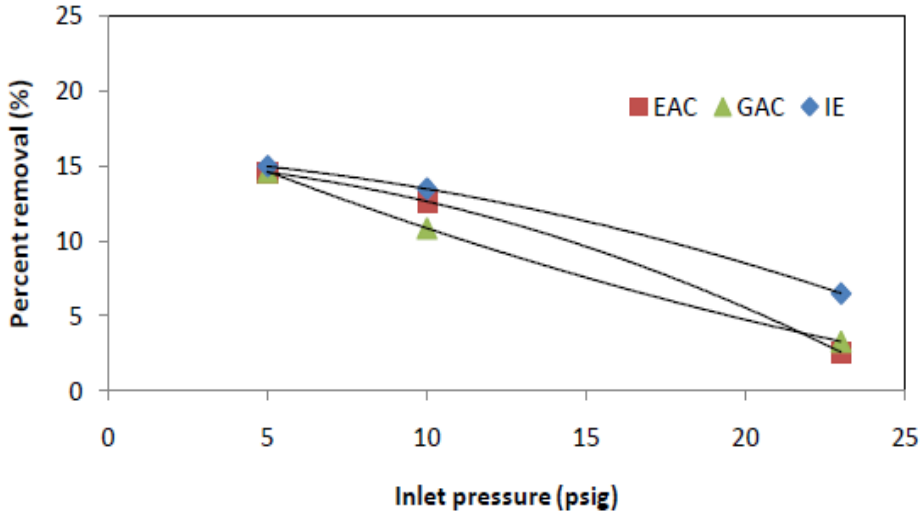

Figure 8. Graph of percentage of mercury removal vs. inlet pressure

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

In order to determine the exact amount of mercury in samples, several scaled up samples were tested using the direct mercury analyzer. Initial inlet concentration was similar for all samples which is 14 ppm with 10 psig as inlet pressure. Based on the data recorded in Table 1, EAC has the highest efficiency in removing mercury in wastewater which is 99.88 %, followed by GAC and IE. The concentration of mercury in treating sample was 0.0074 ppm, 0.0197 ppm and 0.0247 ppm respectively. EAC is effective because the amount of carbon on their surface and its high surface area and micro pore volume (Zhang et al., 2005). 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 (Lloyd-Jones et al., 2004).

Table 1. Mercury outlet concentration of different types of absorbent

Absorbent	Outlet concentration (ppm)	Percentage removal (%)
Ion Exchange	0.0247	99.82
Extruded activated carbon	0.0174	99.88
Granular activated carbon	0.0197	99.86

4.0 CONCLUSION

The efficiency of mercury removal in wastewater was affected by the pH value of wastewater source, initial concentration of mercury, operating pressure and type of adsorbent used. When the pH of the water increased, the percentage removal of mercury from the wastewater decreased. The optimum initial concentration of mercury that gives highest percentage removal is 2-4 ppm, while 8 ppm is the most unsuitable inlet mercury concentration to be treated by PMRR. The recommended operating pressure is 5 psig, while 23 psig is the most unsuitable operating pressure. For the initial pH, the range of pH from 2 to 4 is the best. Meanwhile, for the adsorbent, EAC is the best adsorbent because of its highest removal of mercury followed by followed by GAC and IE.

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