

# Adsorption of mercury from aqueous solutions using palm oil fuel ash as an adsorbent - batch studies

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**Abstract.** Palm oil fuel ash (POFA) is one of the most abundantly produced waste materials. POFA is widely used by the oil palm industry which was collected as ash from the burning of empty fruit bunches fiber (EFB) and palm oil kernel shells (POKS) in the boiler as fuel to generate electricity. Mercury adsorption was conducted in a batch process to study the effects of contact time, initial Hg(II) ion concentration, and temperature. In this study, POFA was prepared and used for the removal of mercury(II) ion from the aqueous phase. The effects of various parameters such as contact time (0- 360 min), temperature (15 – 45 °C) and initial Hg(II) ion concentration (1 – 5 mg/L) for the removal of Hg(II) ion were studied in a batch process. The surface characterization was examined by scanning electron microscopy (SEM) and particle size distribution analysis. From this study, it was found that the highest Hg(II) ion removal was 99.60 % at pH 7, contact time of 4 h, initial Hg(II) ion concentration of 1 mg/L, adsorbent dosage 0.25 g and agitation speed of 100 rpm. The results implied that POFA has the potential as a low-cost and environmental friendly adsorbent for the removal of mercury from aqueous solution.

## 1. Introduction

Malaysia produces about 47% of the world's palm oil supply and can be considered as one of the world's largest producers and exporters of palm oil. Due to the intensive planting and milling operations, Malaysia generates huge quantity of oil palm biomass including oil palm fibres, oil palm kernel shells, empty fruit bunches (EFB) as residues from harvesting and processing activities. POFA is a waste material generated in boiler due to the burning of palm oil industry waste as fuel to generate electricity [1]. The conventional method to discard these wastes is by incineration in the boiler as fuels for steam production in the oil palm mill [2]. However, the issue regarding palm oil wastes management has led to concerns. This is because, after processing and extraction of oil, solid residues and liquid wastes will be generated from the fresh fruit bunches and resulted in varying by-products including empty fruit bunches fibre, shell, and effluent. As a result, air, river, sea, and groundwater pollutions have increased in recent years due to the large amount of waste produced [3]. Therefore, prevention should be taken to manage the agriculture by-products for sustainable future. To avoid environmental pollution, the by-products can be reused and recycled for other purposes. Thus, the study of POFA as a low cost adsorbent has been done to tackle the waste disposal problem.

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One of the major environmental concerns is the pollution of water bodies by heavy metals [4]. The World Health Organization (WHO) considers mercury as one of the top ten chemicals or groups of chemicals of major public health concern. Mercury is one of the most harmful environmental contaminants, which is harmful even at low concentrations. The main sources of mercury emissions besides its natural origins are ore mining, the burning of fossil fuels, and the industrial production processes [5]. The Hg(II) ions can cause respiratory failure, kidney injury, chronic diseases, central nervous system disorders, brain damage and severe environmental pollution [6].

Many conventional techniques have been utilized to reduce Hg(II) ion concentrations in water, including solvent extraction, precipitation, ion-exchange, reverse osmosis, membrane separation, coagulation and adsorption [7]. Among the various water treatment techniques described, adsorption is generally viewed as the most reliable wastewater treatment containing Hg(II) ion due to its convenient operation, low cost, and high efficiency. Several adsorbents have been used for mercury removal from wastewater such as coal fly ash [5], coconut pith [8], eucalyptus wood [9] and fir wood sawdust [10]. Among these adsorbents, activated carbon has become the most popular and widely used adsorbents for wastewater treatment. Activated carbon is a form of porous carbon with a high surface area, used extensively as an adsorbent in the removal of organic and inorganic pollutants [10]. Ash materials are significant sources for activated carbon preparation as they contain appropriate carbon fractions [5]. Ash is a good candidate to produce activated carbon, because it is often used as an adsorbent to remove Hg(II) ion, for example, [11] investigated the different fly ash samples on mercury speciation in simulated flue gas. Also, [12] prepared activated carbon from palm ash as an adsorbent to remove dyes from aqueous solution. As a result, Hg(II) ion removal from water using adsorption techniques proved to be the most applicable on an industrial scale [4].

The objective of this study is to evaluate the adsorption of Hg(II) ions by POFA from aqueous solutions in batch process. The effects of operating variables namely temperature, contact time and initial Hg(II) ion concentration were investigated under batch experimental conditions. Experimental results indicated that POFA has higher adsorption rate for the removal of mercury (Hg(II) ion) in an aqueous solution.

## **2. Experimental procedure and methodology**

### *2.1. Materials*

POFA was obtained from Kilang Lepar Sawit in Kuantan, Pahang. It was cleaned with distilled water several times to remove dust and impurities and dried in an oven at 110 °C for 24 hr to remove any surface moisture. 50 g of POFA was activated with 0.5 M H<sub>2</sub>SO<sub>4</sub> for 24 hr. It was sieved through 100 µm and stored in an airtight container.

### *2.2. Adsorbate*

Analytical grade mercury standard solution obtained from Merck was used to prepare the stock solutions containing 1,000 mg/L of mercury metal ions which were further diluted with deionized water to obtain the required concentrations. The prepared solution was used for batch adsorption experiments.

### *2.3. Characterizations of POFA*

Particle sizes distributions of POFA was analysed using Mastersizer 2000 (Malvern Instruments Ltd, UK). Mastersizer EVO 50 SEM (Carl Zeiss, Germany) instrument was used to study the morphology of the POFA. POFA sample was sprinkled on double-sided carbon tape mounted on a SEM stub and the images of 1000X magnifications were captured.

### *2.4. Batch experiments*

The batch adsorption experiment was done by using 50 ml of initial Hg(II) ion concentration of solution in a conical flask for each experimental run. The pH of the solution was adjusted using 0.1 M

sodium hydroxide (NaOH) and 0.1 M hydrochloric acid (HCl) as required. The adsorbent was added as specified in the experimental design and specified time accordingly. The mercury removal process was analysed using the effect of initial Hg(II) ion concentration, contact time and temperature. In the first set of experiment, the contact time was varied in the range of 0 - 360 min at a fixed pH (pH 7). The influence of initial Hg(II) ion concentration on the removal efficiency was studied in the range 1 - 5 mg/L. The effect of temperature was studied in the range of 15 - 45 °C using an incubator shaker for 4 hr. The temperature was controlled using temperature-controlled incubator shaker operated at 100 rpm. Equations (1) was used to obtain the removal efficiency.

$$R (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $R$  is the percentage of the removal of mercury,  $C_0$  and  $C_e$  are the initial and residual Hg(II) ion concentrations (mg/L), respectively. The adsorption capacity ( $q_e$ ) was calculated according to the following equation (2):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where  $m$  is the mass of adsorbent used (g),  $V$  is the total volume of Hg(II) ion solution (ml),  $C_0$  is the initial Hg(II) ion concentration (mg/L), and  $C_e$  is the residual Hg(II) ion concentration (mg/L).

### 2.5 Analysis of the metal

Samples of solutions were filtered through vacuum filter and the filtrates were analysed using the direct mercury analyser RA-3310 (Nippon Instrument Corporation, Japan).

## 3. Results and discussion

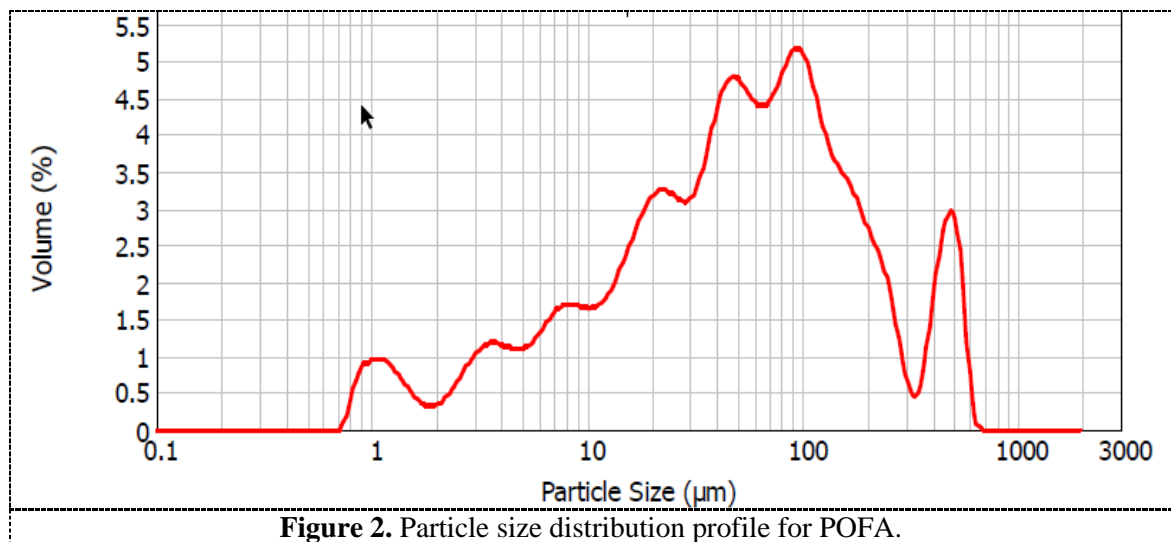
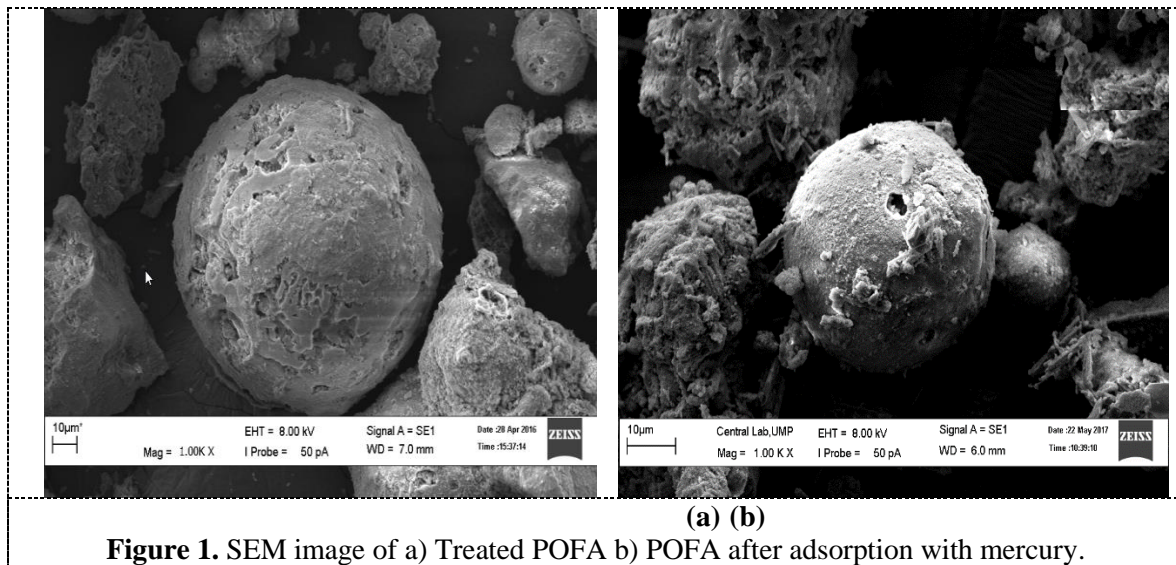
### 3.1. Characterization of the adsorbent

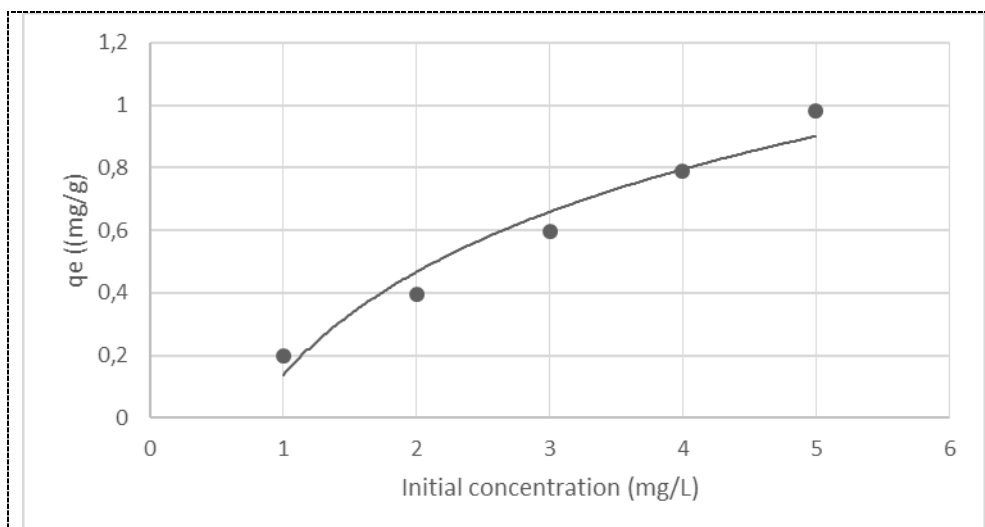
Figure 1(a)(b) shows the characteristic morphology of the treated POFA and POFA after adsorption with mercury. Figure 2(a) illustrated that treated POFA possessed regular spherical shape and has a porous surface. Previous studies reported by [13] stated that ash consists of a series of spherical clear particles of different sizes. Figure 2(b) showed that the shape of the particles to be regular spherical shapes to completely irregular shapes. This is because POFA surface are covered with smaller particles and irregular deposits. Similar conclusions were made by [14] while studying the characterization of fly ash from coal combustion and found that the morphological features of the smallest fraction of fly ash are irregular in shape. This is evidence that porous structures with several smaller particles are covering the porous surface.

Figure 2 shows the particle size distribution of POFA. The bell-shaped curve for the particle size distribution were obtained. The graphical representation shows that there is a growing trend from 1 µm up to 100 µm and the highest peak of the function is observed in the area of 100 µm. The maxima occur at a relatively smaller range (90 - 100 µm) of particle diameters with the volume percentage of the particles is 5.2 %. It can be stated that between the range of 1 µm and 100 µm, have the largest volume percentage of the POFA and quantitatively negligible when it reached 600 µm.

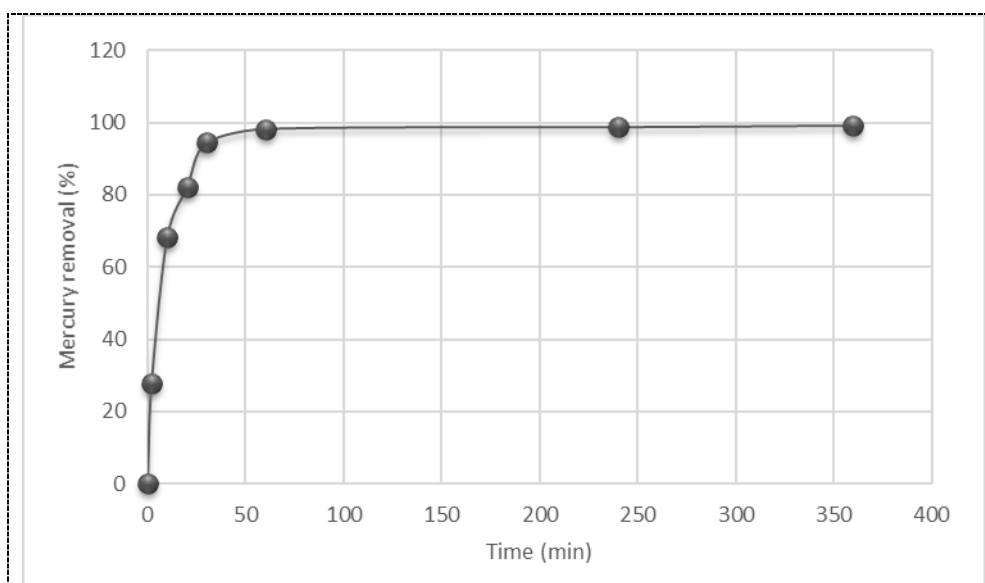
### 3.2. Effect of initial Hg(II) ion concentration

Figure 3 presented the impact of initial Hg(II) ion concentration in the range of 1 - 5 mg/L. It is clear that the adsorption capacity of mercury gradually increased with the increase of initial Hg(II) ion concentration. In this experiment, the highest adsorption capacity of Hg(II) ions was 0.98 mg/g at the initial Hg(II) ion concentration of 5 mg/L. When all the active sites are involved in the adsorption process, the saturation and the maximum adsorbent capacity is achieved. Similar trend has been reported by [15] where the adsorption capacity of clay increased with the increase of initial metal ion concentration before attaining a plateau profile.

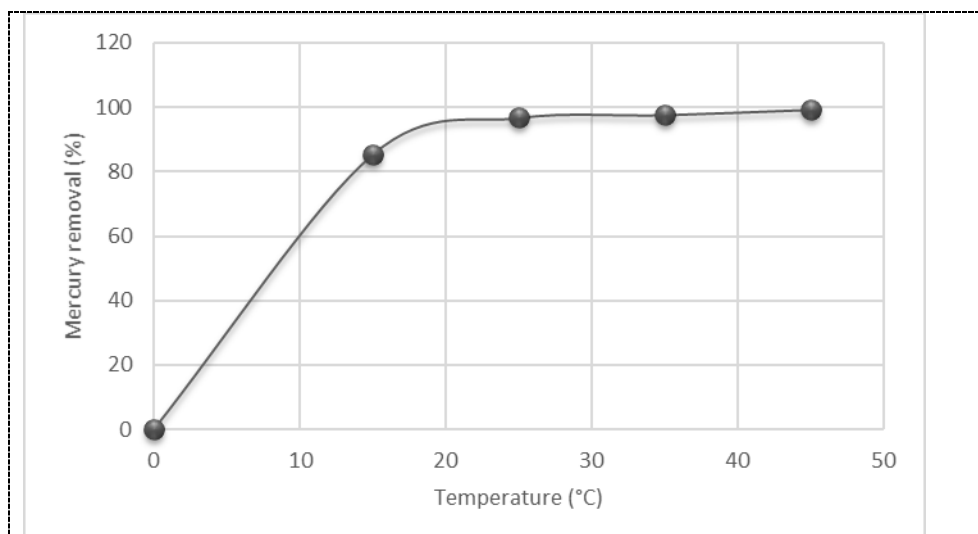




**Figure 3.** Effect of initial Hg(II) ion concentration on the adsorption of mercury by POFA. Conditions: time = 4 h; temp. = 25 °C; agitation rate = 100 rpm; pH 7; adsorbent dosages = 0.25 g.



**Figure 4.** Effect of contact time on the adsorption of mercury by POFA. Conditions:  $C_0 = 5$  mg/L; temp. = 25 °C; agitation rate = 100 rpm; pH 7; adsorbent dosages = 0.25 g.



**Figure 5.** Effect of temperature on the adsorption of mercury by POFA. Conditions: time = 4 h;  $C_0$  = 5 mg/L; agitation rate = 100 rpm; pH 7; adsorbent dosages = 0.25 g.

### 3.3. Effect of contact time

The effect of contact time on the adsorption of Hg(II) ion are shown in Figure 4. It can be observed that the adsorption of Hg(II) ion removal increased significantly with time from 0 to 60 min. The contact time needed for Hg(II) ion solutions to reach equilibrium was 60 min and reached a plateau at 60 - 240 min with 98 % of Hg(II) ion is adsorbed. According to [6] the binding of Hg(II) ions is high due to the existence of a greater number of functional sites available for Hg(II) ions adsorption in the initial stage. Then, when the available functional sites decreased, the adsorption efficiency slowed down due to the formation of repulsive forces between the Hg(II) ions on the POFA surface.

In fact, [10] reported that the adsorption of mercury using fir wood sawdust shows the same general trend when the adsorption of Hg(II) ion removal increased noticeably over a short period of contact time, then decreased gradually while approaching the equilibrium.

### 3.4. Effect of temperature

The effects of temperature are one of the most important factors for the adsorption of mercury. The effect of temperature on the mercury removal was studied in the range of 15 - 45 °C with an initial Hg(II) ion concentration 5 mg/L, pH 7, adsorbent dosages of 0.25 g and agitation rate 100 rpm. The result is shown in Figure 5. The mercury removal increased significantly to 97 % as the operating temperature was raised to 25 °C. When the temperature rises, the pores enlarge and more surface will be available for the adsorption of Hg(II) ions. Hence, there is an increase in the removal of Hg(II) ion. The mercury removal increased with the increase in temperature due to the endothermic nature of this process [15]. By increasing the temperature of Hg(II) ion solution, the attractive forces in the aqueous phase is weakened and consequently, more Hg(II) ions become free and reach the solid surface. Similar conclusions were made by [16] while studying the effect of temperature on the mercury adsorption using eucalyptus bark and found that a decrease in Gibbs free energy,  $\Delta G$ , as well as a positive enthalpy value,  $\Delta H$ , by raising the temperature revealed that the adsorption process is endothermic. Additionally, the increase of temperature can enhance the rate of intraparticle diffusion and the adsorption increases accordingly. [17] reported a similar result for the adsorption of Hg(II) ion removal by MnO<sub>2</sub>/CNTs nanocomposite adsorbent. They also showed that the intraparticle diffusion plays an important role in the adsorption of Hg(II) ion removal.



#### 4. Conclusion

In this study, the removal of Hg(II) ion from aqueous solutions using POFA was examined using various parameters namely the initial Hg(II) ion concentration, temperature, and contact time. The highest mercury removal was 99.60 % when the parameters were at 100 rpm of agitation speed, 4 hr of contact time, initial Hg(II) ion concentration of 1 mg/L, adsorbent dosage 0.25 g of adsorbent dosage and pH 7. Overall, it can be concluded that POFA has the potential to be used as a suitable adsorbent for the removal of mercury from aqueous solution as it can be obtained at low cost.

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