

A Factorial Analysis Study on Removal of Mercury by Palm Oil Fuel Ash Adsorbent

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Mercury is an extremely toxic pollutant that currently being emitted and distributed globally. The exposure of the mercury will mainly cause health effect and the exposure can be in term of dose, age of person exposed and duration of exposed. One of the adsorbent can remove mercury is an activated carbon from palm oil fuel ash (POFA). POFA was used as a low cost adsorbent. An adsorbent prepared from POFA was successfully synthesised and used to remove mercury (Hg^{2+}) from mercury model solution in a batch process. The effects of pH [A], contact time [B], initial concentration of the Hg^{2+} solution [C], adsorbent doses [D] and agitation speed [E] were screened by using response surface methodology (RSM). A half fraction two-level factorial analysis with five factors was selected for the experimental design to determine the best adsorption conditions for mercury removal. From this study, it was found the highest mercury removal was 98.03 % at adsorbent capacity 0.10 mg of Hg^{2+} /g of the adsorbent with conditions of pH 2, contact time 4 h, initial Hg^{2+} concentration of 5 mg/L, adsorbent doses 0.25 g and agitation speed 200 rpm. The most important factor which gives the highest percentage contribution for mercury removal efficiency is contact time [B] with 22.76 % followed by initial mercury ion concentration [C] of 5.50 %. The model obtained in this present study is significant and had a maximum point which is likely to be the optimum point and possible for the optimisation process later. These results suggest that POFA has a potential used as an effective, low cost, and eco-friendly green adsorbent for the removal of mercury from waste water.

1. Introduction

The presence of heavy metal ions in natural or industrial waste water and their hazardous impact has generated considerable concern in many years (Chowdhury et al., 2011). In Malaysia, waste water is contaminated by various substances and one of them is heavy metals which are hazardous to the environment. Mercury is one of the most toxic metals present in the environment. Mercury has attracted wide attention due to its high toxicity to human and other organisms (Zhang et al., 2016). An effective way should be developed for the selective monitoring and effective removal of mercury contamination in water or wastewater generated by both natural processes and human activities.

According to Sharma et al. (2015) the removal of these heavy toxic metals by conventional methods generate a huge quantity of toxic chemical sludge and are not economical both in terms of operating and capital costs. Several researchers have developed a new alternative and low cost removal technique at laboratory scales which may have great potential for commercial applications. The commonly used methods for the removal of heavy metal ions from the wastewater include precipitation, coagulation or flocculation, ion exchange, reverse osmosis and electrochemical operation (Khoramzadeh et al., 2013). Among various mercury removal method currently in study, the adsorption process which offers as an effective and economic method for wastewater treatment (Sharma et al., 2015). In the adsorption process, a numerous number of adsorbents have been investigated to remove mercury. These include coconut pith char (Johari et al. 2016), silica (Samana et al., 2014), chitosan (Nasirimoghaddam and Sabbaghi, 2015) and palm shell (Ismail and Yusoff, 2013). This study aimed to find the best condition in the mercury removal efficiency. A half fraction two-level factorial

analysis with five factors was studied for their effect to the mercury removal efficiency. This work is crucial for the optimisation stage later because each main effect had the tendency to affect one another.

2. Experimental procedures

2.1 Material preparation

The palm oil fuel ash (POFA) was collected from palm oil mill boiler at Kilang Sawit Lepar, Kuantan. It was washed with deionized water for several times to remove foreign particles and oven dried overnight at 110 °C to remove moisture. It was sieved through 100 µm and stored in airtight container. Mercury stock solution was prepared at 1,000 mg/L. This stock solution was then diluted to 1 mg/L and 5 mg/L using deionised water. All the adsorption experiment was carried out at room temperature. The required quantity of Hg²⁺ solution was dissolved in ultrapure water. Then, a small amount of HNO₃ was added to preserve the solution. The pH of the solution was adjusted using 0.1 M of HCl and 0.1 M NaOH. The mixture of the sample is shaken by using incubator shaker at the constant room temperature. The suspension is filtered using a vacuum pump and the filtrates are analysed using the direct mercury analyser Milestone DMA-80 (ATS Scientific, USA).

2.2 Adsorbent characterisation

Characterisation of POFA was done by EVO 50 SEM (Carl Zeiss, Germany) for raw POFA and after mercury sorption. Next, FTIR of raw POFA and after mercury sorption were recorded on a Spectrum 100 FTIR spectrometer (Perkin Elmer, USA). The thermal stability was determined using TGA with a TA Instruments model Q-500 (USA) on POFA.

2.3 Two-level factorial analysis experimental setup

The experimental design for factorial analysis was performed using Design Expert 7.0.0 (Stat-Ease Inc., USA) software. The effects of five independent variables as shown in Table 1 were screened by using response surface methodology (RSM). The condition ranges chosen were based on the other researcher's previous work (Rio and Delebarre, 2003) and from (Chowdhury et al., 2010). The factors were constructed in factorial designs of 2⁵⁻¹ to screen their effect on the response of mercury removal efficiency. All experiments consist of 16 run listed in Table 2.

Table 1: Low and high values for each parameter

Factor	Units	Low value (-1)	High value (+1)
A: pH		2	6
B: Contact time	h	1	4
C: Initial concentration of the Hg ²⁺ solution	mg/L	1	5
D: Adsorbent doses	g	0.10	0.25
E: Agitation speed	rpm	100	200

Several factors were tested earlier and obtained from literature study. To identify the factors that affects the mercury adsorption. Five independent variables which are pH [A], adsorption time [B], initial concentration of the Hg²⁺ solution [C], agitation speed [D] and adsorbent doses [E] were selected for factorial designs of 2⁵⁻¹ in order to screen their effect on the response of mercury removal efficiency. Factorial design was applied to screen the mercury removal from mercury model solution. The ranges of the individual factors were chosen from the preliminary test. Statistical analysis was performed using Design Expert software (Stat-Ease, Inc.). Mercury removal efficiency was calculated using the following Eq(1).

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

where R is the percent removal of mercury, C_0 and C_e are the initial and residual concentration (mg/L) of mercury ion. The amount of mercury adsorbed by POFA was calculated from the difference between the initial Hg²⁺ concentration (C_0) and the equilibrium concentration (C_e) was calculated and used to determine the adsorptive capacity (q_e) as follows in Eq. (2).

$$q_e = (C_0 - C_e)V/M \quad (2)$$

where V is the total volume of mercury (II) solution (mL), M is the mass of adsorbent used (g), C_0 is the initial concentration of mercury ion solution (mg/L), and C_e is the residual Hg²⁺ concentration (mg/L).

3. Results and discussions

3.1 Material preparation

The Fourier Transform Infrared Spectroscopy (FTIR) technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of aromatic compounds (Daffalla et al., 2010). The change in intensity or shift in peak position gives information about interaction adsorbate and adsorbent. As shown in Figure 1, the adsorption peak at $3,356\text{ cm}^{-1}$ indicates the existence of phenolic and aliphatic OH group and the broad band was attributed to the presence in POFA after sorption with mercury similar to Kuncoro and Fahmi, (2013). After contacting with Hg, there is a change in intensity of spectral, then transmittance intensity is lower. The small band at $1,630\text{ cm}^{-1}$ indicates the presence of alkenes and primary amines group. The peaks at $1,020\text{ cm}^{-1}$ for the POFA after sorption with mercury assigned for Si-O-Si asymmetric stretching vibration of SO_4^{2-} group. POFA sample at this band has highest SiO_2 content (Kipcak, et al., 2012). After adsorption of Hg^{2+} , the interaction between the POFA surface and Hg^{2+} was evidenced by a shift in the O-H and N-H bands from $3,356.40\text{ cm}^{-1}$ and $1,081.65\text{ cm}^{-1}$ to $3,312.56\text{ cm}^{-1}$ and $1,019.75\text{ cm}^{-1}$. These results provide strong evidence for the adsorption of Hg^{2+} onto the POFA surface. According to Esmaeili et al. (2012), the presence of carboxylic acid and sulphate groups can act as binding sites for metals.

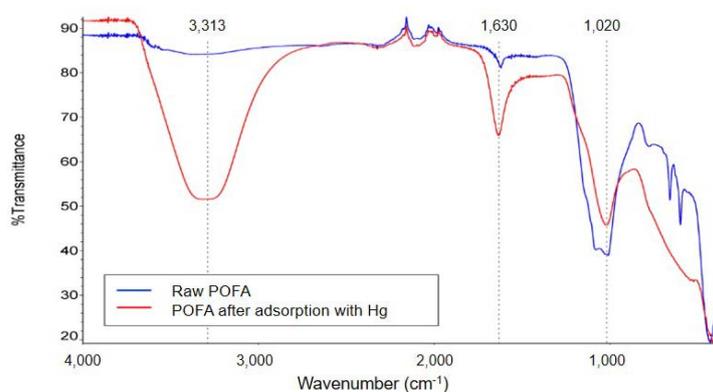


Figure 1: FT-IR spectra of the raw POFA and after adsorption with mercury

In this thermal gravimetric analysis (TGA) test, the mass loss was measured while the specimens were gradually exposed to increasing temperatures. The thermal stability of the POFA form was studied by thermal TGA in the conditions conducted at $24.58\text{ }^{\circ}\text{C}$ which is almost at room temperature up to $895.53\text{ }^{\circ}\text{C}$ for the process to complete. The results for POFA are displayed in Figure 2 below. It can be observed that there were three main areas of weight loss. The first was showed sharp decrease weight before $250\text{ }^{\circ}\text{C}$ as recorded in TGA thermogram is attributed to the loss of evaporable water in the POFA as observed in Bakri et al. (2012). The weight loss which marked the major decomposition of the POFA took place between $200\text{ }^{\circ}\text{C}$ and $650\text{ }^{\circ}\text{C}$, which saw a 2.53% weight lost, caused by the decomposition of CaCO_3 and the burning of residual coal of the ash (Santos, et al., 2014). The third weight loss, little change occurred in the percentage of weight remaining beyond $650\text{ }^{\circ}\text{C}$. Above $900\text{ }^{\circ}\text{C}$, the ash had thermogravimetric stability and the average total percentage of weight remaining was 95.07% . Similar results reported by Santos et al. (2014) where the small weight loss is associated with high ash content found in POFA.

Scanning electron microscope (SEM) presented in Figure 3 indicates the surface morphology of POFA. The image was captured at $1,000\times$ magnification. From the SEM image, it can be seen that the POFA mainly consists of alumina silicate spherical particles with smooth outer surfaces, also known as cenospheres (Nyale et al., 2013). It has been seen clearly that the adsorbents are highly porous in nature which is a desirable characteristic of any adsorbent.

3.2 Factors affecting mercury removal efficiency

The highest percentage of mercury removal was obtained at 98.03% with the adsorption conditions at 100 rpm , $\text{pH } 2$, 4 h , 5 mg/L of initial concentration of the Hg^{2+} solution, and 0.25 g of adsorbent dosage as shown in Table 2. The relative size of effects was visually demonstrated by Pareto chart in Figure 4, where the bar length is proportional to the absolute value of estimated effect. For main effects, an effect is said to be positive when an increase to its high level will cause an increase in the response while the negative effect is when an increase in its high level will result in a decrease in the response. For interactions, the positive effect is when

both factors were a chance to the same level (low or high), the response will increase. The negative effect is when both factors were change to the opposite level (one at its low and the other at its high), the response will increase (Martendal et al., 2007). Effects of t-value limit (black line) are considered statistically significant at 95 % confidence level while effects below t-value limit are not likely to be significant. Effect above Bonferroni's corrected t-value limit (red line) is almost certainly significant (Anderson et al., 2009). A quick analysis was performed on the selected effects using Pareto chart to statistically check for significance of the selected effects at 95 % confidence level. All the selected effects (A, B, C, D, E, AC, AE, BE, CD, CE, and DE) shown to be significant at both t-value limit and Bonferroni's corrected t-value limit. The fitted model for the factorial analysis in coded form was shown in Eq(3).

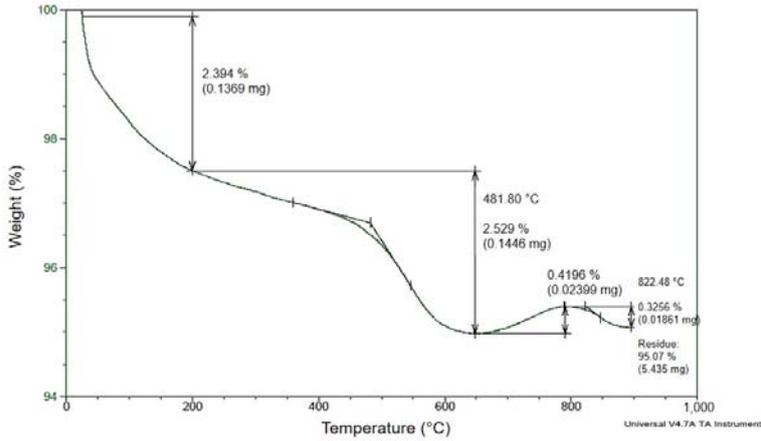


Figure 2: TGA results on POFA

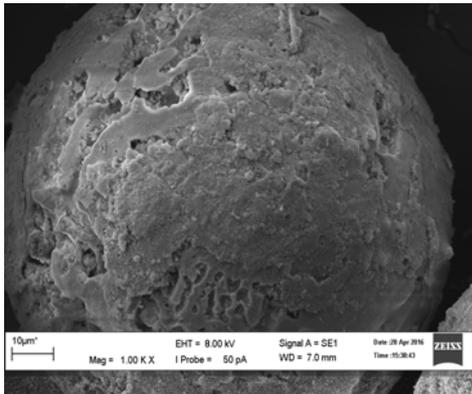


Figure 3: SEM image of POFA

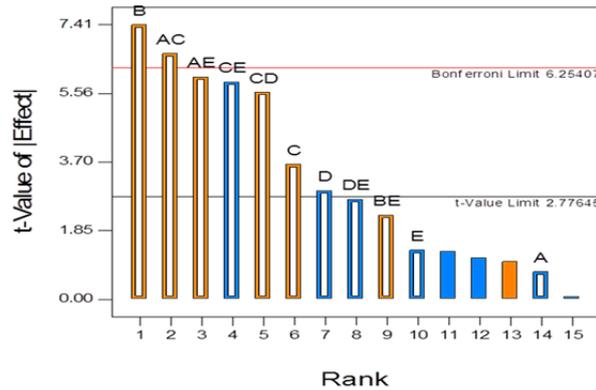


Figure 4: Pareto chart

$$\text{Mercury removal efficiency} = 71.62 - 0.97*A + 9.69*B + 4.76*C - 3.83*D - 1.73*E + 8.67*A*C + 7.85*A*E + 2.97*B*E + 7.31*C*D - 7.67*C*E - 3.53*D*E \quad (3)$$

Based on the coded factors, the coefficients of A to E are small compared to the interception. This gives an indicator of the existent of the design plateau as the other coefficient for the factors are lower than the interception at 71.62. This plateau showed that the design had a maximum point which is likely to be the optimum point.

3.3 ANOVA

The analysis of variance (ANOVA) test results are as shown in Table 3. As can be seen, the model obtained was significant with p-value 0.0047. Coefficient of determination (R^2), adjusted R^2 and predicted R^2 values were used to evaluate the fitness of the model. Adjusted R^2 is a modification of R^2 , which adjusts for the number of explanatory terms in a model relative to the number of data points (Anderson and Whitcomb., 2005). The R^2 value of 0.9834 ($R^2_{adj} = 0.9378$) indicates that the predicted values obtained from the model is a good fit of the experimental data (Dong and Sartaj, 2016).

Table 2: Experimental design of factor screening process using 2^{5-1} factorial design with their response

Std. Order	Factors					Response
	pH	Contact time (h)	Initial concentration of the Hg ²⁺ solution (mg/L)	Adsorbent doses (g)	Agitation speed (rpm)	Mercury removal efficiency (%)
1	2	1	1	0.10	200	74.67
2	6	1	1	0.10	100	42.67
3	2	4	1	0.10	100	97.33
4	6	4	1	0.10	200	97.33
5	2	1	5	0.10	100	73.67
6	6	1	5	0.10	200	71.67
7	2	4	5	0.10	200	65.33
8	6	4	5	0.10	100	80.93
9	2	1	1	0.25	100	59.67
10	6	1	1	0.25	200	44.87
11	2	4	1	0.25	200	74.33
12	6	4	1	0.25	100	44.00
13	2	1	5	0.25	200	37.73
14	6	1	5	0.25	100	90.53
15	2	4	5	0.25	100	98.03
16	6	4	5	0.25	200	93.20

Table 3: Analysis of variance (ANOVA)

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	p-value	
Model	6,486.72	11	589.70	21.55	0.0047	significant
A-pH	15.07	1	15.07	0.55	0.4991	
B-Contact time	1,500.98	1	1,500.98	54.86	0.0018	
C-Initial Hg ion concentration	362.81	1	362.81	13.26	0.0219	
D-Adsorbent doses	234.63	1	234.63	8.58	0.0429	
E-Agitation speed	47.85	1	47.85	1.75	0.2565	
AC	1,202.88	1	1,202.88	43.97	0.0027	
AE	985.18	1	985.18	36.01	0.0039	
BE	141.19	1	141.19	5.16	0.0856	
CD	855.42	1	855.42	31.27	0.0050	
CE	941.42	1	941.42	34.41	0.0042	
DE	199.30	1	199.30	7.29	0.0541	
Residual	109.43	4	27.36			
Cor Total	6,596.15	15				

C.V. = 7.30 %; $R^2 = 0.9834$; Adjusted $R^2 = 0.9378$; Adeq. Precision = 13.450.

In percentage of contribution, the most important factor which gives the highest percentage contribution for mercury removal efficiency is contact time [B] with 22.76 % followed by initial mercury ion concentration [C] of 5.50 %. pH [A] shows the lowest contribution which is 0.23 %. Other variables that less contributed to the effect of the mercury removal efficiency were agitation speed [E] and adsorbent doses [D] by having a value of 0.73 % and 3.56 %.

4. Conclusion

The best condition for the mercury removal efficiency using POFA was obtained at agitation speed 200 rpm, pH 2, 4 h, initial Hg²⁺ concentration of 5 mg/L, and adsorbent doses of 0.25 g with 98.03 % mercury removal. The most important factor which gave the highest percentage contribution for mercury removal efficiency is contact time [B] with 22.76 % followed by initial mercury ion concentration [C] of 5.50 %. The model obtained in this present study is significant and had a maximum point which is likely to be the optimum point and

possible for the optimisation process later. POFA was performed excellently well as adsorbent in mercury removal at high contact time (4 h) and initial concentration of the Hg^{2+} solution (5 mg/L). It can be concluded that POFA can potentially be a suitable adsorbent for mercury removal from waste water as it can be obtained at low-cost.

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