Kinetic Study on Mercury HG (II) Removal by CNT

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***Abstract*-Kinetic of modeling data is necessary for the industrial use of adsorption. Under changed conditions, kinetic offers evidence for operational conditions for designing and optimizing effective situations for removing the pollutant. The pseudo second-order equation was used in this study in order to investigate the mechanism of adsorption of mercury by the CNTs and the potential rate-controlling steps, such as mass transport and chemical reactions. The interaction model shows how contact with different pH affects the residual concentration of the mercury at two different times. The first (contact time of 20 minutes) showcase of the removal of the mercury does not reduce much when the pH varies from pH 5 to pH 8. The second (contact time of 120 minutes) however shows that the pH affects the removal of mercury at pH 5, the residual concentration was lower compared to the residual concentration at pH 8.**

Keywords- Mercury; Pollutant Removal; CNT; Kinetic

I. INTRODUCTION

Mercury is a heavy metal and is used widely in the industry. The biggest sources of mercury release according to a report published by the United Nations are from coal-burning power plants and waste incinerators. They account for approximately 70 per cent of man-made emissions [1]. Besides that, mercury is also being used to extract gold in gold mines and this pollutes the waterways and hence will bind to have an effect towards humans and environment. Methyl mercury that is used in gold mines can accumulate in the food chain and its half-life in humans is estimated to be 70 days [2].

As a result of industrialization, various kinds of pollutants are being released into the environment daily causing great pollution to the environment. Water pollution is one of the environment essentials being polluted and drastic measures have been taken in order to conserve water. Without water, life cannot be sustained thus the balance of the ecological system is being interrupted. In Malaysia, the permissible discharge for mercury is 0.005 mg/L for standard A and 0.05 mg/L for standard B. (Federal Subsidiary Legislation Malaysia, 1979).

The presence of mercury in the water body can have serious effects towards environment and human health and the full effect of consuming mercury is still being determined. Therefore, elimination or reduction of mercury in the water body is necessary to protect both the environment and public health. One of the activities that lead to the discharge of mercury in the aquatic environment in Malaysia was the production of backlighting in liquid crystal displays (LCDs) [3].

A study conducted by [4] and [5] at the state of Johor, Malaysia stated that the sources of mercury come from burning of fossil fuels, incineration of mercury–containing pesticides, and leaching of organic mercury from antifungal outdoor paints, moreover natural origins have provided to polluted rivers water of Sedenak and Pasir Gudang area, Malaysia.

II. MATERIALS AND METHODS

The powdered activated carbon (PAC) was derived from empty fruit bunches (EFB). The activated carbon (ACs) used in this study has average diameters in the range between 8 to 12 µm [6]. The adsorption experiment is carried out by taking 50 mL of mercury solution of desire concentration (1.6 mg/L) and desired weight of adsorbent using 100 mL conical flasks. Mercury aqueous solution was used in the experiments instead of water samples as the optimization of the experimental conditions can be observed clearly. The mercury sample was prepared by dissolving the standard mercury solution (1000 ppm) at a known quantity in distilled water. The working solutions were prepared by diluting the stock solution using distilled water. Afterwards, the conical flask was agitated at desired speed using mechanical shaker. The pH condition was adjusted by using 0.1M sulphuric acid (H_2SO_4) or 0.1M sodium hydroxide (NaOH).

III. EXPERIMENTAL DESIGN

The number of runs for complete randomized experiment was determined using Design Expert 6.0.8 central composite design software. Two-Level Factorial Design was used. The parameters listed such as the adsorbent dosage, pH, contact time and the agitation speed ranges was selected to be the optimal condition in maximizing the removal of mercury as shown in Table 1.

TABLE 1 EXPERIMENT PARAMETERS AND ITS VARIATION

No.	**Parameter**	**Variation**		**Reference**
		Low (-1)	**High (1)**	
1	Dosage (mg)	10	30	Yusuf, 2009 [10]
2	pH	5	8	Rezaee *et al.*, 2005 [12]
3	Time Contact (min)	20	120	Touaibia & Benayada, 2005
4	Agitation speed (rpm)	50	150	Yahya, 2007 [13]
5	Concentration of mercury (mg/L)	1.6	1.6	Canstein *et al.*, 1999 [5]

IV. EXPERIMENTAL RESULTS

The experimental result from Table 2 showed that the minimum residual occurred at pH 6.5, agitation speed of 100 rpm, contact time of 70 minutes and AC dosage of 20 mg. At these conditions, the final concentration of mercury was 0.0075 mg/L where it managed to remove the mercury up to 99%. Furthermore, it showed that the AC had successfully removed the mercury and met the requirement of the DOE Malaysia regulations.

TABLE 2 RESULT OF THE EXPERIMENT

Run	A:pH	B:Ag. speed	C:Contact time	D:Dosage	Hg(II)	Average	Removal
		rpm	min	mg	mg/L	mg/L	%
1	5	50	20	10	0.704		
2	5	50	20	10	0.669	0.6865	57.09
10	5	50	120	30	0.119	0.1115	93.03
6	5	150	20	30	0.211	0.2765	82.72
14	5	150	120	10	0.071	0.0720	95.50
17	6.5	100	70	20	0.004		
18	6.5	100	70	20	0.011	0.0075	99.53
3	8	50	20	30	0.470		
4	8	50	20	30	0.560	0.5150	67.81
12	8	50	120	10	0.508	0.5120	68.00

A. Interaction between pH (A) and Contact Time (C)

In the ANOVA analysis in Table 3, the only interaction model among pH, A, agitation speed B, time C, dosage D (AB, AC, AD, BC, BD and CD), model AC demonstrated to have significant effects toward the model. Model AC is the interaction between pH and the contact time and this is showed at the Fig. 1 below.

TABLE 3 ANOVA ANALYSIS FOR ACTIVATED CARBON

Source	**Squares**	**Mean Square**	**Prob > F**	**Remark**
Model	0.84	0.12	<0.0001	Significant
A	0.045	0.045	0.0007	Significant
B	0.22	0.22	<0.0001	Significant
C	0.38	0.38	<0.0001	Significant
D	0.17	0.17	<0.0001	Significant
AB	3.063×10^{-6}	3.063×10^{-6}	0.9674	Not Significant
AC	0.031	0.031	0.0022	Significant
AD	6.126×10^{-4}	6.126×10^{-4}	0.5673	Not Significant
BC	0.000	-	-	-
BD	0.000	-	-	-
CD	0.000	-	-	-
Curvature	0.20	0.20	<0.0001	Significant

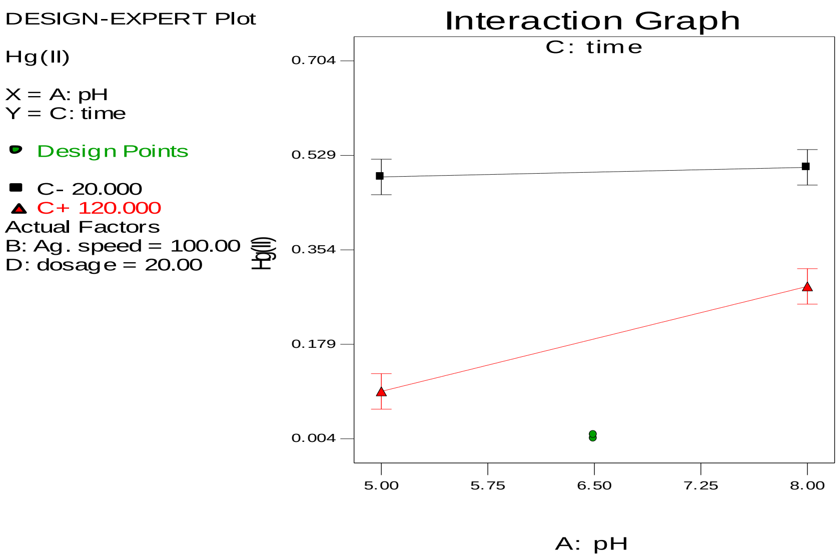


Fig. 1 Interaction between pH (A) and contact time (C)

The interaction model AC shows how, at two different times, contact with different pH affects the residual concentration of the mercury. The first line (contact time of 20 minutes) showcases that the removal of the mercury does not reduce much when the pH varies from pH 5 to pH 8. The second line (contact time of 120 minutes) however shows that the pH affects the removal of mercury. At pH 5, the residual concentration was lower compared to the residual concentration at pH 8. This may due to the fact that acidity influences the hydrolysis of the metal. Hydration is followed by hydrolysis, according to the following two-ray reversible reaction, giving acidic properties to heavy metal solutions. At lower acidity, the above equilibrium is shifted to the left causing more highly charged metal complexes to form [7].

V. KINETICS OF ADSORPTION

Kinetic data is major for the industrial use of adsorption. Kinetic gives evidence for evaluation among different biomaterials under different operational conditions for designing and optimizing operational conditions for pollutant removal from wastewater systems [8].

The equilibrium adsorption is mainly in the design of adsorption schemes since it specifies the size of the adsorbent during the adsorption course. The equilibrium curve was modeled in Fig. 2 at pH condition of pH 5. The equilibrium concentration (C_e) based on Fig. 2 was found to be 0.0605 mg/L. The Adsorption Capacity (Q_e) was calculated and the Q_e was found to be 0.002566 mg/g.

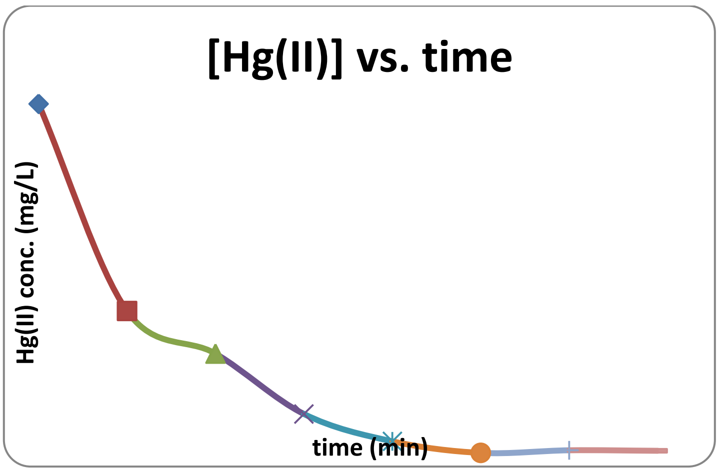


Fig. 2 Mercury concentration vs. time

In Jianlong’s study [9], the pseudo first-order kinetic equation was not used in his study since it is not applicable to all the results. Consequently, the pseudo second-order equation was used to explore the mechanism of adsorption of mercury by the CNTs and the potential rate-controlling steps, such as mass transport and chemical reactions [9].

The plot $\frac{t}{qt}$ versus time (Fig. 3) yields high correlation coefficients (R^2=0.9938). This has proven that the adsorption kinetic adsorbent followed the pseudo second-order equation. It indicates that the amount governing steps in the adsorption procedure are chemisorptions which imply that there were interactions involving sharing or exchanging electrons between adsorbate and adsorbent. It simply showed that there were strong interactions between AC and mercury (Hg).

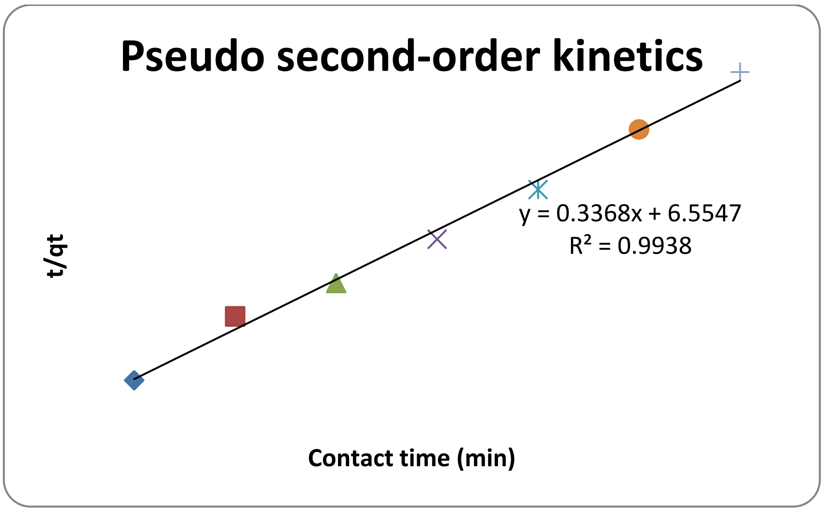
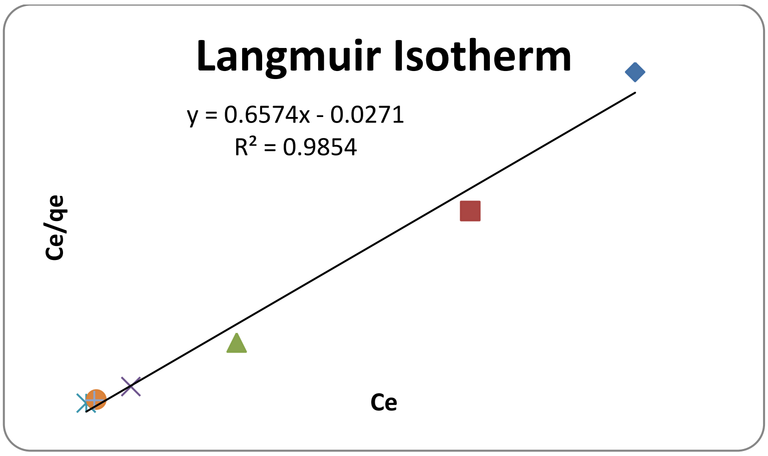


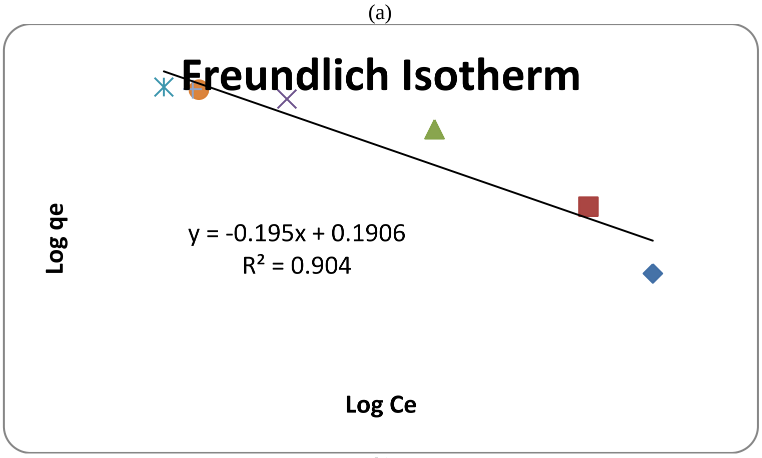
Fig. 3 Pseudo second-order kinetics of Hg(ll)

VI. ADSORPTION ISOTHERM

The Langmuir and Freundlich equations were used to define the data resulting from the adsorption of Hg(Il) by ACs over the whole parameters variety studied. Based on Fig. 4, the adsorption capacity (x_m) was firm from the slope the graph.



(a)



(b)

Fig. 4 Adsorption isotherm model for (a) Langmuir and (b) Freundlich Model

Then, the equation obtained was used to calculate the constant n in Freundlich isotherm and x_m in Langmuir isotherm. Based on the assessment of the two models, it is experimental that Langmuir isotherm model displays a better fitting with the experimental data in which it found higher correlation coefficient (R^2=0.9854) related to Freundlich Isotherm (R^2=0.904). This directs the applicability of monolayer coverage of Hg(Il) ions on the consistent surface of the adsorbent. A simply acceptable connection coefficient of Langmuir isotherm also directs that Hg(Il) ions adsorbed to the surface of ACs. Therefore, it is proved that ACs has the possibility of being a decent adsorbent for the elimination of Hg(Il) ions in water treatment.

B. Modelling for the Removal of Hg(II) using ACs

The correctness of the model was considered using the analysis of variance (ANOVA). The regression equation comprising all the explanatory variables for CNTs analysis was constructed as follows:

$$\mathbf{Hg(II) = 0.34 + 0.053*A - 0.12*B - 0.15*C - 0.1*D - (4.375 \times 10^{-4})*A*B + 0.044*A*C - (6.18 \times 10^{-3})*A*D}$$

By referring to the Design-Expert 6.0.8, "F value" and "Prob>F" of the output indicates the test statistics and significant P values respectively. Therefore, significance of the parameters indicated can be identified. The F-values and the consistent significant p-values provide the proof of a slope and the meaning of the explanatory variables to the reply variables. While the R^2 value provides the evidence of the difference in the Y variable that is clarified by the differences in the independent factors.

In Table 2, the Model F-value of 69.40 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" of this large could occur due to noise. The values of "Prob>F" less than 0.0500 indicates that the model terms are significant. For this model A, B, C, D and AC are significant model terms. If the "Prob>F" values are greater than 0.1000, it indicates that the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), the model reduction may improve the model. The "Curvature F-value" is a value measured by the change between the average of the center points and the average of the factorial points. The "Curvature F-value" of 115.46 implies there is significant curvature in the design space. The "Adj. R-Squared" takes into account the factors that can contribute to the inflating the results. The "R-Squared" of 0.941 is in reasonable agreement with the "Adj. R-Squared" of 0.9677. In the ANOVA analysis, the "Adeq Precision" measures the indication to noise ratio. A ratio greater than 4 is desirable. According to the ANOVA analysis, the "Adeq Precision" of 23.545 shows a satisfactory indication specifies that the model can be used to direct the design space. The value of R^2 that was attained from this study is 0.9818 which means 98.918% of the difference in adsorption capacity can be described by the pH, ACs dosage, and agitation speed and contact time. The adjusted R^2 achieved from this study is 96.77% of the difference in the adsorption capacity. This adjusted R^2 is necessary when relating two or more regression models that forecast the same dependent variable but have different number of explanatory variables. By using this adjusted R^2, the best model can be identified. It can be concluded from this study that the most influential factors that contribute to the lowest residual mercury concentration are pH, ACs dosage and agitation speed in which the interactions of these factors contribute to the highest F-value and lowest P-value.

VII. COMPARATIVE ANALYSIS OF VARIOUS ADSORBENTS

Previously, there are many types of adsorbent that have been used to remove Hg(Il) from aqueous water. This shows that there have been great concerns on the removal of toxic metals from water due to its adverse effects on human being. Table 4 was constructed to explain the types of adsorbent that were used to remove Hg (Il) ions and its percentage uptake of Hg(Il).

Grounded on Table 4, displays that there are various studies on the elimination of Hg (II) using several types of adsorbent, the main reason for comparison is to find the best parameters and the the highest percentage of removal. However, the percentage elimination for each adsorbent is diverse due to the difference in the working factors (pH, agitation speed, dosage, temperature and many more).

TABLE 4 COMPARISON BETWEEN ADSORBENTS TO REMOVE MERCURY

Adsorbent	**Condition**				**% Removal**	**Reference**
	pH	**Contact Time (min)**	**Dosage (mg)**	**Agitation Speed (rpm)**		
Sago waste	5	105	20	120	70	Kadirvelu *et al.*, 2004
Acetobacter xylinum	5	10	10	-	78	Rezaee *et al.*, 2005
Pseudomonas putida	6-6.5	10 days	10g	-	98	Canstein *et al.*,1999 [11]
Empty Fruit Bunch	6.5	70	20	100	99	This study

Therefore, this reasonable study was conducted to further comprehend the mechanism of adsorption and associate the types of adsorbents that were previously used to eliminate Hg(1I). It can be seen in Table 4 that *Pseudomonas putida* gives the highest percentage among the three adsorbents that were being compared with removal percentage of 98. However, considering the contact time of 10 days to achieve the highest removal, it may not be suitable for scale up purposes. However, the contributing factors that contribute to the highest percentage removal are surface functional groups that can be oxidized by acids (nitric acid) and adsorbent dosage. The identical essentials of these adsorbents are that it requires acidic condition for the optimal removal of Hg(Il) ions from aqueous solution. Thus, in order to achieve optimal removal of Hg (Il) ions, the pH of the solution must be maintained in a slightly acidic conditions for the complete removal of Hg(ll).

VIII. CONCLUSION

The experimental results were analyzed using Langmuir and Freundlich equations. Correlation coefficients (R^2) showed that the Langmuir model was used as it best described the model. Results from this study were described by the Langmuir Isotherm in which the highest adsorption capacity obtained from this analysis was 1.521 mg/g. Comparative study was conducted at the end of this project in order to differentiate the effectiveness of different type of adsorbents to remove mercury. Based on the analysis, it was found that the ACs used in this was as reliable as other ACs and had the highest percentage removal. This means that there is a potential to use and further develop the Activated Carbon from empty fruit bunch (EFB) from palm fruit. Waste generated in the palm oil industry can be converted to AC to remove heavy metals such as mercury and the operational costs for adsorption of heavy metals can be reduced compared to using CNT as adsorbent. Activated carbon derived from EFB is one of the best materials as it can reduce the risk to human health and provide alternative metal-removing method. It is demonstrated that ACs can be used as an adsorbent for the removal of Hg(Il) ions in wastewater treatment. However, further study must be done to further validate the effectiveness of this method in terms of costs and large scale treatment of Hg(Il) in the real industry.

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