Kinetics of Hg and Pb Removal in Aqueous Solution Using Coal Fly Ash Adsorbent

Eko Prasetyo Kuncoro[1] and Mochammad Zakki Fahmi [2]

Abstract—***The objective of this research was to investigate the kinetics aspect of Hg and Pb adsorption using coal fly ash. A series of a Hg and Pb adsorption experiment using coal fly ash with contact time variation was carried out. The results were plotted to pseudo first order kinetic, pseudo second order kinetic and intra-particle diffusion model. High values of R2 were obtained from the plots of kinetics model for both heavy metals investigated, these values exceeded 0,8. The conclusion obtained was that Hg adsorption kinetics followed pseudo second order kinetic model while Pb adsorption kinetics followed intra-particle diffusion.***

Keywords—Hg, Pb, coal fly ash, adsorption, kinetics.

I. Introduction

Many production activities had ameliorated the condition of human life. These activities produced products, services, and wastes. Heavy metals wastes are the wastes that menace human life. They are toxic and tend to accumulate in the organism tissues. Many researches focused on Hg and Pb. Hg and Pb are found as waste in the industrial activities. The effect of Hg exposure to the environment can be found in Minamata tragedy documentation where Hg was considered as pollutant that caused birth defect and neural problem. An investigation showed that Hg had correlation with cardiovascular disease [1]. The effects of Pb exposure to organism are neurogical disorders, birth defects, and growth retardation [2].

There are many methods adapted to reduce heavy metals toxicity [3,4,5]. Chemical precipitation is the most used technique to remove heavy metals. This technique is useful to handle high concentration of heavy metals but it produces sludge problem to the environment. Membrane filtration is an emerging technique used to remove heavy metals. Laboratory researches showed that this technique could remove low concentration of heavy metals but it has disadvantage for its high cost of membrane. Adsorption becomes the most used technique beside precipitation to remove heavy metals. It is easy for operation and high separation can be obtained for low concentration of heavy metals.

The progress of adsorption is the use of waste materials as adsorbents. There are wastes from agricultural and industrial wastes. These types of wastes are found in high quantity as solid wastes. Further treatments to handle these wastes are needed. Combustion and landfill are usually practiced but these methods have limitations so the use of wastes as adsorbents is considered as a good choice. One of the industrial wastes is coal fly ash. It can be found from thermal power plant using coal as fuel for combustion. The capability of coal fly ash to remove various heavy metals had been reported [6]. Kinetics aspect of adsorption is important for the design of adsorption system. It provides important information of adsorbate rate removal. There are many kinetic models of adsorption. Among these models, pseudo first order, pseudo second order and intra-particle diffusion are widely used. Pseudo first order model indicates that adsorption rate is proportional to the free sites on the surface adsorbent while pseudo second order model indicates that adsorption rate is proportional to the square of the free sites [7]. Intra-particle diffusion model indicates that adsorption rate influenced by diffusion mechanism [8].

The objective of this study was to evaluate kinetics aspect of Hg and Pb adsorption onto coal fly ash.

II. Materials and Methods

A. Preparation of adsorbent

Coal fly ash used in this research was obtained from a thermal power plant in Paiton, East Java province. Preparation of adsorbent was followed procedures in the previous work [9]. Several treatments were given to the coal fly ash. Coal fly ash was heated at 1200 C for 24 hours in the oven then it was sieved to get the particle size of 149-250 µm. Fifteen gram of coal fly ash was mixed with 100 mL solution of 0.1 M CH3COOH, then the solution was stirred for one hour and it was stabilized for 16 hours. The solution then filtered by Buchner filter. The sample of coal fly ash obtained was heated at 1200C for 24 hours in the oven.

B. Preparation of metals solution

The metals solutions were prepared by dissolving metals salts ($Hg(NO_3)_2$ and $Pb(NO_3)_2$) in to demineralized water. The concentration of Hg and Pb solutions used for kinetic experiments was 100 mg/L.

C. Batch kinetics study

To study adsorption kinetic aspect of Hg and Pb onto coal fly ash, a set of kinetic experiments was carried out: 100 mL solutions containing 100 mg/L of Hg were mixed with 15 g of coal fly ash and the solutions were shaken for appropriate contact times (60, 120,180, 240, 300, 360 minutes). The solutions were filtered and analyzed by AAS (Shimidzu, Japan) to determine the residual concentration of Hg. The same procedure was used for Pb solution. The results of kinetic experiments were plotted to pseudo first order, pseudo second order, and intra-particle diffusion kinetic model.

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D. Pseudo first order kinetic model

The pseudo first order kinetic model is given by the following equation [10]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

where q_e is the amount of heavy metal adsorbed at equilibrium, q_t is the amount of heavy metal adsorbed at time t, k_1 is the pseudo first order rate constant.

E. Pseudo second order kinetic model

The pseudo second order kinetic model is given by the following equation [11]:

$$(t/q_t) = 1/(k_2 q_e^2) + (1/q_e)$$

where k_2 is the pseudo second order rate constant.

F. Intra-particle diffusion kinetic model

The intra particle diffusion kinetic model is given by the following equation [12]:

$$q_t = k_{id} (t)^{1/2}$$

where k_{id} is the intra-particle diffusion coefficient.

III. Result and Discussion

Figure 1 and 2 present the results of Hg and Pb adsorption kinetic experiments. The equilibrium condition was obtained after 350 minutes of contact time for both Hg and Pb adsorption by coal fly ash. In the beginning of adsorption until 200 minutes of contact time, the Hg removal was 80% while the Pb removal was 60%. The metal uptake by adsorbent depends on the metals type. The use of coal fly ash in this study was interesting for Hg removal until 200 minutes because it provided relatively faster Hg removal than Pb removal. After 300 minutes of contact time, the value of Hg and Pb removal was around 80%. In general the adsorption of metals increases as a function of time.

To determine the best-fitting kinetic model, linear regression was used. The best kinetic model could be used as reference to know rate-controlling step in the metals adsorption. The plot of t versus ln $((q_e-q_t)/q_e)$, t versus t/q_t, $t^{1/2}$ versus q_t was used to investigate pseudo first order, pseudo second order, and intra-particle diffusion kinetic model respectively. Figure 3, 4, and 5 present pseudo first order, pseudo second order, and intra-particle diffusion kinetic model plot respectively for Hg adsorption by coal fly ash. The value of linear regression coefficient (R^2) of Hg data was 0.9629 for pseudo first order kinetic model plot. The higher value of linear regression coefficient obtained from pseudo second order and intra-particle diffusion kinetic model plot: 0.9906 and 0.9891 respectively. This result suggested that Hg adsorption by coal fly ash followed pseudo second order kinetic model. In this model, the mechanism involved was chemical reaction mechanism [13]. In this case, there was a chemical bond that was formed at adsorbent surface. Pseudo second order kinetic model was also successfully applied to the kinetic adsorption of Hg by adulsa leaf powder, bamboo leaf powder and sulfurized adsorbent from agricultural waste [14,15,16]. Table 1 presents the comparison of the linear regression coefficient of Hg adsorption kinetic model using various adsorbents.

Figure 3, 4, and 5 also present the plot of kinetic model investigated for Pb adsorption by coal fly ash. Linear regression coefficient of pseudo first order kinetic model was 0.9555 while linear regression coefficient of pseudo second order and intra-particle diffusion kinetic model was 0.871 and 0.9739 respectively. This result was different from the result obtained in the case of Hg adsorption. The highest value of linear regression coefficient was obtained for intra-particle diffusion kinetic model. This result suggested that the mechanism involved was surface adsorption [17]. However the pseudo second order kinetic model could be applied for this case, the value of linear regression coefficient was relatively high. Pseudo second order kinetic model was also successfully applied to the kinetic adsorption of Pb by *Solanum melongena* and *Cinnamomum camphora* leaf powder [18,19]. Using *Solanum melongena* leaf powder, the linear regression coefficient of pseudo first order, pseudo second order, and intra-particle diffusion kinetic model was 0.958, 0.999, dan 0.976. Table 2 shows the comparison of the linear regression coefficient of Pb adsorption kinetic model using various adsorbents.

VI. Conclusion

The kinetic aspect of Hg and Pb adsorption by coal fly ash was investigated. Pseudo first order, pseudo second order, and intra-particle diffusion kinetic model was used. Hg adsorption kinetics followed pseudo second order kinetic model while Pb adsorption kinetics followed intra-particle diffusion.

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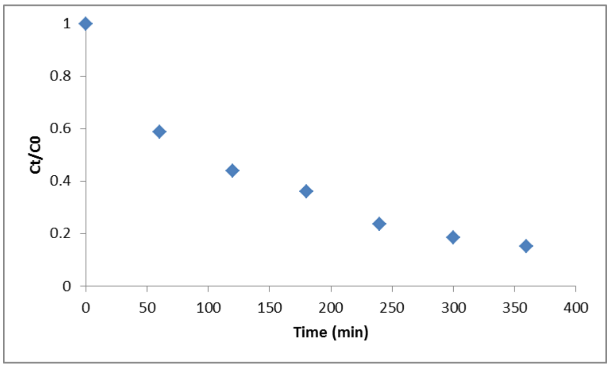

Figure 1. Kinetic of Hg adsorption by coal fly ash

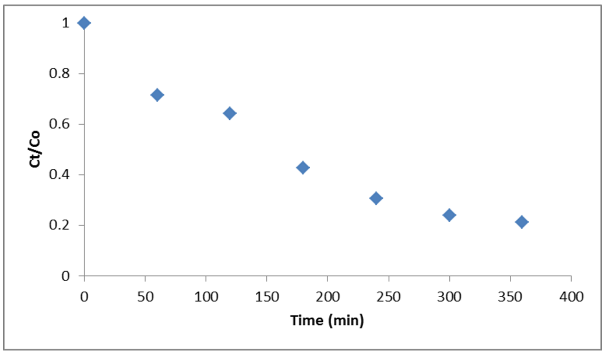

Figure 2. Kinetic of Pb adsorption by coal fly ash

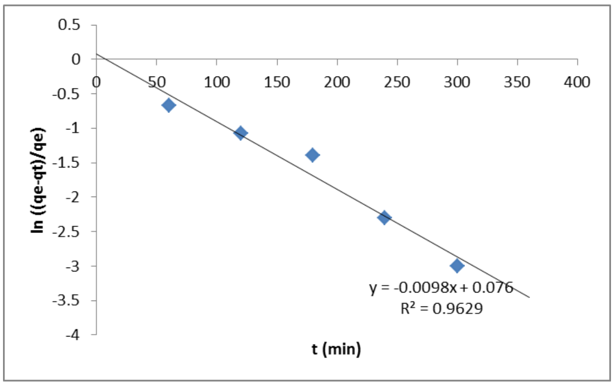

Figure 3. Pseudo first order kinetic plot of Hg adsorption by coal fly ash

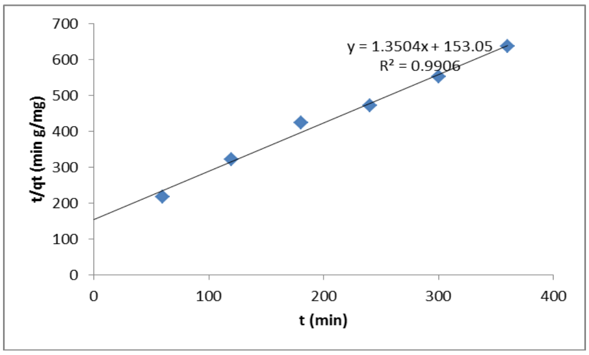

Figure 4. Pseudo second order kinetic plot of Hg adsorption by coal fly ash

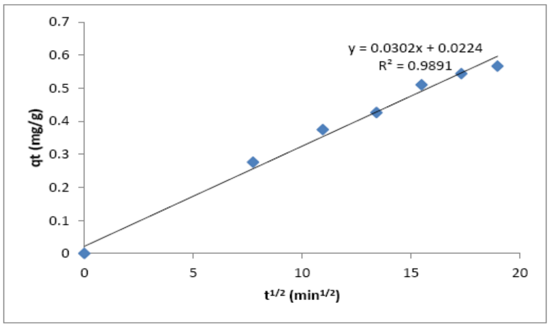

Figure 5. Intra-particle diffusion kinetic plot of Hg adsorption by coal fly ash

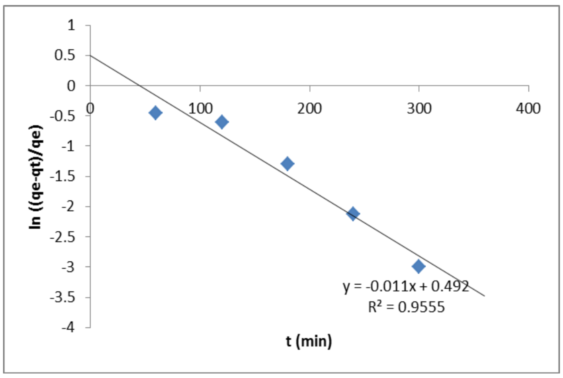

Figure 6. Pseudo first order kinetic plot of Pb adsorption by coal fly ash

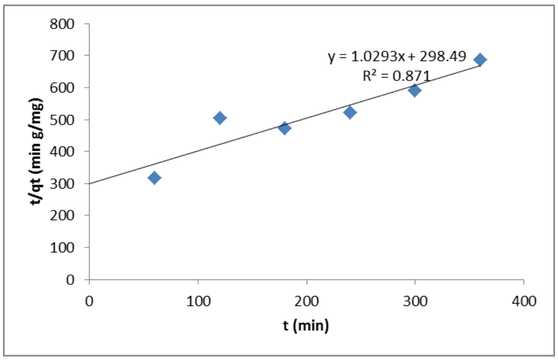

Figure 7. Pseudo second order kinetic plot of Pb adsorption by coal fly ash

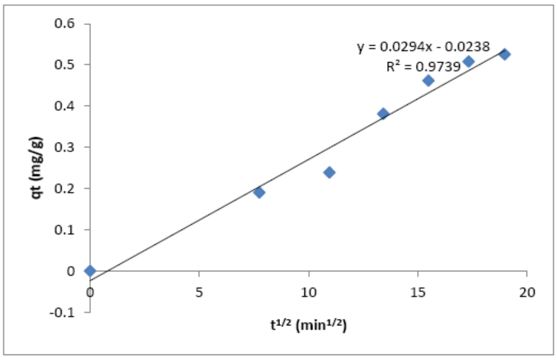

Figure 8. Intra-particle diffusion kinetic plot of Pb adsorption by coal fly ash

TABLE 1.
COMPARISON OF THE LINEAR REGRESSION COEFFICIENT OF HG ADSORPTION KINETIC MODEL

Adsorbate	Adsorbent	R^2 (pseudo first order)	R^2 (pseudo second order)	R^2 (intra-particle diffusion)	Reference
Hg	Adulsa leaf powder	0.9830	0.9980	0.9152	[16]
Hg	Bamboo leaf powder	0.9700	0.9900	-	[17]
Hg	Coal fly ash treated by CH_3COOH	0.9629	0.9906	0.9810	This study
Hg	Sulfurized adsorbent from agricultural waste	0.8460	1.0000	-	[18]

TABLE 2.
COMPARISON OF THE LINEAR REGRESSION COEFFICIENT OF PB ADSORPTION KINETIC MODEL

Adsorbate	Adsorbent	R^2 (pseudo first order)	R^2 (pseudo second order)	R^2 (intra-particle diffusion)	Reference
Pb	Coal fly ash treated by NaOH	0.83300	1.00000	0.40700	[13]
Pb	Coal fly ash treated by CH_3COOH	0.95550	0.87100	0.97390	This study
Pb	*Solanum melongena* leaf powder	0.95800	0.99900	0.97600	[20]
Pb	*Cinnamomum camphora* leaf powder	0.92027	0.99996	0.59452	[21]