Research Article

Adsorption Kinetics of Fe and Mn with Using Fly Ash from PT Semen Baturaja in Acid Mine Drainage

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ABSTRACT

One used method to reduce heavy metal ions in acid mine drainage is to adsorb them by coal fly ash. This research aimed to study the isotherms equilibrium and the adsorpstion kinetics that fit with decreasing metals ion. Acid mine draigane and fly ash were charge into batch coloumn adsorption with specified comparison. Variables investigated were dactivated and activated fly ash, adsorption times (0, 20, 30, 40,50, and 60 minutes), adsorben weights (10, 20, 30, 40, 50, and 60 gram), and pH (1, 3, 5, 7, and 9). The results showed that fly ash can be used to reduce the levels of heavy metal ions Fe and Mn. Coal fly ash adsorption model of acid mine drainagefits to Freundlich adsorption isotherm in all condition. First order pseudo kinetics model is suitable for Fe and Mn adsorption processes. The value of adsorption rate constants of Fe and Mn (deactivated fly ash) were 0.2388 min^{-1} with R^2 = 0.4455 and 0.4173 min^{-1} with R^2 = 0.9781, Fe and Mn (activated fly ash) 0.5043 min^{-1} with R^2= 1 and 0.2027 min^{-1} with R^2= 0.8803.

Keywords: sintetics adsorption, acid mine drainage, fly ash, Langmuir isotherm, Freundlich isotherm

1. INTRODUCTION

Increased coal demand has fueled increased coal exploration [1]. Coal Exploration by mining will produce mine wastewater. Mine wastewater consists mainly of acid mine drainage and mud. The coal mine wastewater contains residues, causes acidity, and ions metal which if disposed directly into the environment will cause environmental damage. In addition, coal is also one of the mining materials used for steam power plants. The process of burning coal to generate steam power will produce residual combustion called fly ash and bottom ash which if not utilized properly, will interfere with human health and the environment. The components in fly ash vary depending on the coal source being burned, but all fly ash contain silicon dioxide (SiO_2) and calcium oxide (CaO) [2].

The various uses of fly ash are as raw materials for cement production and construction materials [3]. As an adsorbent, fly ash has advantages of being economical, good for gas or liquid waste treatment [4], and capable of absorbing heavy metals in wastewater [5]. The condition of silica and alumina in fly ash is large enough to allow fly ash to be used as a potential adsorbent. These mean many active centers of solid surface that can interact with adsorbate. Adsorbent from fly ash has been widely used, such as fly ash is used as an adsorbent of CO gas emissions in motor vehicles by varying the activation temperature of fly ash [6]. Moreover, there was also the research about adsorption NO_2 gas by fly ash. The results showed that fly ash can absorb NO_2 gas with optimum within 5 minutes [7].

Therefore, this research aimed to study fly ash that can be utilized as an adsorber of acid mine drainage, the happening phenomenon by determining the adsorption equilibrium, and its adsorption kinetics model.

1.1. Adsorption isotherm

Adsorption is a phenomenon in which a quantity of gas or solution is settled on a surface. For example contact between gas and solution in a metal. The interaction that occurs will cause the metal surface properties to change. The gas or the attracted solution is called adsorbate while the metal surface is called the adsorbent [8]. There are commonly two kinds of isotherm adsorption models are Langmuir isotherms and Freundlich isotherms.

1.2.Adsorption of Langmuir isotherms

The following model of Langmuir equation :

$$qc = (Qb\ Ce)/(1+bCe) \qquad (1)$$

The linear form of the equation is expressed in

$$Ce/qe = 1/Qb + Ce/Q \qquad (2)$$

Where qe is the amount of adsorbate that adsorbed per unit of adsorbent weight (mg g^{-1}), Ce is the concentration of adsorbate in equilibrium (mgL^{-1}), whereas q and b are Langmuir constants.

1.3. Adsorption of Freundlich isotherms

The following model of Freundlich equation :

$$qe = KF\ C1/n \qquad (3)$$

The linear form of the equation follow in the following equation:

$$\log qe = \log KF + 1/n \log Ce \qquad (4)$$

K_F and n are the adsorption capacity and the adsorption intensity.

Table 1. Fe and Mn metal content in acid mine drainage before treatment

Metals	Concentration (mg/L)
Fe	17.12
Mn	8.68

Table 2. Concentration decreasing of Fe and Mn on adsorption times

Adsorption times (minutes)	deactivated		activated	
	Fe (mg/L)	Mn (mg/L)	Fe (mg/L)	Mn (mg/L)
10	0.18	0.07	0.19	0.007
20	0.13	0.01	0.08	0.007
30	0.17	0.007	0.12	0.04
40	0.09	0.007	0.15	0.03
50	0.11	0.007	0.16	0.01
60	0.19	0.007	0.27	0.007

Table 3 . Concentration decreasing of Fe and Mn on adsorbent weights

Adsorbent weights (gram)	deactivated		activated	
	Fe (mgw/L)	Mn (mg/L)	Fe (mg/L)	Mn (mg/L)
10	0.1	0.02	0.09	0.04
20	0.19	0.007	0.14	0.007
30	0.54	0.11	0.13	0.02
40	0.19	0.007	0.27	0.007
50	0.106	0.007	0.25	0.03

Table 4. Concentration decreasing of Fe and Mn on pH

pH	deactivated		activated	
	Fe (mg/L)	Mn (mg/L)	Fe (mg/L)	Mn (mg/L)
1	0.18	0.007	0.13	0.01
3	0.16	0.007	0.18	0.007
5	0.09	0.007	0.18	0.007
7	0.19	0.007	0.27	0.007
9	0.13	0.007	0.2	0.007

The K_F and n values are derived from the intercept and slope of the graph plot between the log qe versus log Ce.

1.4. Kinetics Adsorption Models

1.4.1. Adsorption kinetics first order pseudo

$$dQ/dt = k (Q_e - Q) \qquad (5)$$

where Q and Qe are the amount of adsorbed substance per unit of adsorbent mass (mmol g^{-1}) at time t and at equilibrium, k is the first order adsorption kinetics constant (min^{-1}).

1.4.2. Adsorption kinetics second order pseudo

$$\frac{dQ}{dt} = k(Q_e - Q)^2 \qquad (6)$$

where k is the second order adsorption kinetics constant.

2. EXPERIMENTAL SECTION

2.1. Materials

Acid mine drainage obtained from PT Bukit Asam which is acidic water contained iron (Fe) and Mangan (Mn) solution. Adsorbent used is fly ash from PT Semen Baturaja measuring 212 μm which is not activated and activated with NaOH.

2.2. Methods

Acid mine drainage and fly ash (not activated and activated) are charged into adsorbtion column, the adsorption process is carried out in batch (with various observations variables). After sendimentation, samples were taken and analized with AAS spectrophotometer

3. RESULTS AND DISCUSSION

The decreasing concentrations of Fe and Mn in various conditions are listed in Table 1-4.

3.1. Langmuir and Freundlich isotherms adsorption

3.1.1. Langmuir and Freundlich isotherms on adsorption times

Langmuir and Freundlich isotherm parameters obtained as the effect of adsorption time are shown in Table 5 and Figure 1 and 2. From Figure1 we got the linearity relation to calculate the Langmuir constant and the greatest determination coefficient (R^2) [9]. The constant Langmuir value for Fe (deactivated), Fe (activated), Mn (deactivated), and Mn (activated) on adsorption times are -0.0010 L/mg, -0.001 L/mg, -0.00005 L/mg, and -0.00003 L/mg while the best coefficient of determination is 0.9647 so that the Langmuir Isotherm model for time variation can be said that Fe (deactivated) is suitable using Langmuir Isotherm model compared to others.

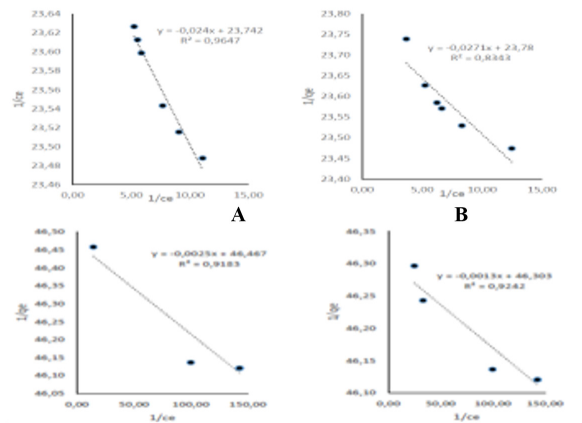The adsorption isotherm model appropriate for the data can be

Figure 1. Langmuir isotherms modwe on adsorption times for: (a) Fe (deactivated fly ash), (b) Fe (activated fly ash), (c) Mn (deactivated fly ash), and (d) Mn (activated fly ash)
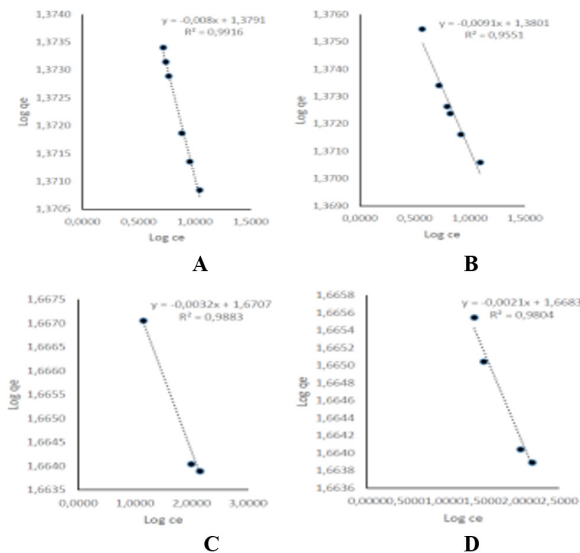
Figure 2. Freundlich isotherms model on adsorption times for:
(a) Fe (deactivated fly ash), (b) Fe (activated fly ash), (c) Mn (deactivated fly ash), (d) Mn (activated fly ash)

determined by looking at the largest determinant coefficient (R^2), but the research data has no correspondence with the Langmuir model. It can be seen in Table 1, the Langmuir constant value in Fe (activated) and Fe (deactivated) and the Mn constant value (deactivated) and Mn (activated) on the Langmuir isotherms are negative. The decrease of Fe and Mn metal content over time has the best level of conformity with Freundlich Isotherms model.

3.1.2. Langmuir and Freundlich isotherms on adsorbent weights

Langmuir and Freundlich isotherm parameters obtained as the effect of adsorption time are shown in Table 6.

From Table 6, Fe (activated) is better than Fe (deactivated) because it has a coefficient of determination (R^2)> 0.6 it indicates that Fe (activated) is suitable using the Langmuir equation while for Mn (deactivated) and Mn (activated) the value of coefficient of determination (R^2) less than 0.6 so that linear line is not significant at this weight variation. This may happen because the adsorbent is not able to absorb Mn metal inside the adsorbate.

For isotherms Fereundlich model, Fe (deactivated) has a constant value smaller than Fe (activated) so that Freundlich Isotherm model approach more to coefficient of determination (R^2) where in this case Fe (activated) has a coefficient of determination greater than 0.6 is 0, 8261 and it can be said that Fe metals are absorbed by more adsorbents. Fe (deactivated) was possible during the study weights variation was not uniformly the same with volume of adsorbate so that when absorption by iron adsorbents in the adsorbate was saturated and impacted data obtained.

While in Mn (deactivated) has a coefficient of determination (R^2) 0.0375 and on metal Mn (activated) has a coefficient of determination (R^2) 0.0752, from the determination coefficient can be known that Mn (deactivated) or Mn (activated) is not linear because the determinant coefficient is less than 0.6. This may occur because the variation in the weight of the amount of adsorbent is not able to absorb Mn metal, other factors can also occur during the study such as the solution is too long contact with the adsorbent, imperfect filtration, there is still adsorbent deposits when it gets the results to be analyzed so that with too many adsorbent contacts with adsorbate result in the metal contained in the adsorbate already in saturation or equilibrium state. However, in this weight variation the most suitable isotherm model is Freundlich Isotherm.

Tabel 5. Langmuir and Freundlich isotherms parameters on adsorption times.

Parameter	Langmuir			Freundlich		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_f (mg/g)	n	R^2
Fe (deactivated)	-0.001	0.042	0,9647	23.94	-125	0.992
Fe (activated)	-0.001	0.042	0,8343	23.99	-109.8	0.955
Mn (deactivated)	-0.000	0.022	0,9183	46.84	-312.5	0.988
Mn (activated)	-0.000	0.022	0,9242	46.59	-476.1	0.980

Table 6. Langmuir and Freundlich isotherms on adsorbent weights

Parameters	Langmuir			Freundlich		
	K_L (L/mg)	Q_m (mg/gr)	R^2	K_F (mg/gr)	n	R^2
Fe (deactivated)	-0.042	0.565	0.122	15.89	-59.52	0.001
Fe (activated)	-0.077	0.027	0.847	150.07	-0.8	0.826
Mn deactivated)	0.006	0.045	0.205	19.61	9.78	0.038
Mn (activated)	0.000	0.030	0.002	12.48	4.67	0.075

Table 7. Langmuir and Freundlich isotherms adsorption of pH

Parameters	Langmuir			Freundlich		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F (mg/g)	n	R^2
Fe (deactivated)	-0.001	0.042	0.959	23.93	-128.2	0.989
Fe (activated)	-0.002	0.042	0.928	24.08	-88.49	0.982
Mn (deactivated)	-	-	-	-	-	-
Mn(activated)	-0.000	0.022	1	46.34	-1000	1

Table 8. Kinetics adsorption constant in pseudo first order and pseudo second order

Parameters	k_1 (min^{-1})	R^2	k_2 (g.mmol^{-1}.min^{-1})	R^2
Fe (deactivated)	0.239	0.446	15721	0.33
Fe (activated)	0.504	1	55868	1
Mn (deactivated)	0.417	0.978	733080	0.995
Mn (activated)	0.203	0.880	111711	0.548

3.1.3. Langmuir and Freundlich isotherms on pH solutions

Langmuir and Freundlich isotherm parameters obtained as the effect of adsorption time are shown in Table 7.

Table 7 showed that Fe (activated) has a coefficient of determination of 0.9276 greater than 0.6 with a Langmuir constant of -0.0019 L/mg. From the difference of both can be seen that Fe (deactivated) was better than Fe (activated). Mn (activated) has a determination coefficient of 1 with Langmuir constant of -0.000009 L/mg. For the Langmuir equation model the most suitable variation of pH is Mn (activated) because Mn in acid mine drainage in perfectly adsorption by activated fly ash.

Freundlich isotherms are often used in adsorption of liquids. The assumption of this isotherm is based that there is a heterogeneous surface with some type of active adsorption center. Freundlich isotherm also explains that the surface adsorption process is heterogeneous where not all of the adsorbent surfaces have adsorption power. This is evident from the results in Table 7, where the resulting R^2 for each parameter is almost 1. In the pH variation, the Freundlich isotherms are considered the most suitable to describe the occuring adsorption.

3.2. Kinetics adsorption

The kinetic adsoprtion constant of pseudo order are listed in Table 8. From Table 8 that is known the largest value of k_1 in Fe (activated fly ash) is 0.5043 min^{-1}that in the pseudo first order kinetics model. In the pseudo-second-order kinetics model, the largest k_2 values were 737080 $g.mmol^{-1} min^{-1}$ in Mn (deactivated), and 111711 $g.mmol^{-1}.min^{-1}$ in Mn (activated). The adsorption kinetics satisfies the pseudo first order adsorption kinetics because it was seen in R^2 value because in the second order kinetics obtained for Fe (deactivated) and Mn (activated) tends to be smaller when compared to the first order adsorption kinetics model [10]

4. CONCLUSION

Based on experimental results, fly ash can be used to reduce the levels of heavy metal ions Fe and Mn. Coal fly ash adsorption model of acid mine drainage fits to Freundlich adsorption isotherm in all condition. First order pseudo model kinetics is suitable for Fe and Mn adsorption processes. The value of adsorpsi rate constants vary around : Fe and Mn (deactivated fly ash) 0.2388 min^{-1} with R^2 = 0.4455 and 0.4173 min^{-1} with R^2 = 0.9781, Fe and Mn (activated fly ash) 0.5043 min^{-1} with R^2= 1 and 0.2027 min^{-1} with R^2= 0.8803.

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