Phosphate Adsorption using KOH Activated Coal Bottom Ash

Fatimah Agussalim, Alfikri Ramadhan, Budi Pratama Tarigan

Chemical Engineering Department, Engineering Faculty, Universitas Sumatera Utara, Medan, Indonesia, 20155

Abstract: Research on phosphate adsorption using activated KOH coal bottom ash has been carried out. This study aims to assess the utilization of bottom ash as an adsorbent to adsorb phosphate ions from water bodies. Research starts from the activation process for 5 hours with 3 M NaOH solution. Then the pre-activated and post-activated bottom ash are characterized using Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS). Based on the results of the characterization with SEM-EDS, the surface of pre-activated bottom ash surfaces seems smooth because they are still covered by impurity metals such as Fe, Ti and Mg. After activation, bottom ash surfaces become rough because impurities such as Fe, Ti, and Mg are lost and thus the pores are opened. The bottom ash then was applied to absorb phosphate ions with variations of particle size (50-70 mesh, 70-110 mesh, and 110-140 mesh) and dosage of adsorbent (1, 2, and 3 g) and were contacted for 60 minutes to 1000 ml phosphate solute of concentration 10 mg/l. Remaining phosphate ions concentration in solute after adsorption are analyzed using UV-vis spectrophotometer. Best adsorption of phosphate ions with 74.8% efficiency was obtained at particle size of 110-140 mesh and dosage adsorbent of 3 g. The highest adsorption capacity (7.02 mg / g) was obtained with dosage of 1 g adsorbent. Freundlich and Langmuir's models were used to describe the phosphate ion adsorption by KOH activated bottom ash isotherm. Based on the data obtained, the suitable model for this study is Freundlich model with a value of R^2 = 0.9721.

1 INTRODUCTION

Phosphate is a nutrient that is very important for life. Phosphate is a key component added in making fertilizers to produce food (Ashley et al, 2011; Cordell et al, 2009). However, the presence of phosphate with a range of more than 0.01-0.1 mg/L in a body of water can trigger a eutrophication process which will reduce the penetration of sunlight into the body of water during the day so that photosynthesis that will produce oxygen is also reduced (Kumar et al, 2019).

The phenomenon of eutrophication can trigger the growth of algae and microorganisms so that the waters become green, turbid, odourless and reduce oxygen levels (Ajmal et al, 2018). There are several ways that have been successful in reducing phosphate levels in the body of water, namely biological treatment (Peng el al, 2016), chemical precipitation (Van der Houwen et al, 2001), struvite formation (Muhmood et al, 2018), membrane processing (Peleka, 2006), and adsorption (Ghaneian et al, 2014;

Usman et al, 2018). The adsorption method has several advantages compared to other methods, which are simple, inexpensive, and high efficiency (Seftel et al, 2018).

Bottom ash from burning coal PT. SOCIMAS was used as an adsorbent in this study. Bottom ash has a high particle size, surface area and porosity making it a good choice for use as an adsorbent (Gorme et al, 2010). Bottom ash has a large Si and Al content that makes bottom ash can be used as zeolite or adsorbent (Bertolini et al, 2013). Some previous studies have used bottom ash as an adsorbent and its absorption efficiency is quite high (Gorme et al, 2010; Bertolini et al, 2013; Gandhimathi et al, 2013; Mittal et al, 2013., Dincer et al, 2007; Saleh et al, 2012)

This study aims to examine the potential of bottom ash which has been activated with KOH as an adsorbent by looking at the effect of particle size and dosage of adsorbent usage. The Langmuir and Freundlich isotherm models were used to model the isotherm data for their applicability.

2 RESEARCH METHOD

The activation of bottom ash using KOH solute has been held with the following procedures: dissolve 30 gr of bottom ash in 250 ml KOH solute of 3 M, stir with stirring rate of 200 rpm for 5 hours at temperature of 85-95°C. The mixture then washed, filtered, and dried in oven at temperature of 105°C. The structure and composition of pre-activated and activated bottom ash was analyzed using SEM-EDS.

A batch experiment was performed by taking a specified amount of adsorbent and combining it with 1000 ml phosphate solution at concentration of 10 mg/l. After adsorption, the concentration of phosphate was determined using a spectrophotometer UV-Vis with SNI 06-6989.31-2005 method.

In order to investigate the effect of particle size on phosphate adsorption, three different sizes of adsorbent (between 50 and 70 mesh, between 70 and 110 mesh, and between 110 and 140 mesh) and constant adsorbent dosage (1 g) was used. To observe the effect of adsorbent dosage on phosphate removal and adsorption capacity, three different adsorbent dosage (1, 2, and 3 g) were used. In order to determine the fitting isotherm model, the initial concentrations of adsorbate was varied accordingly (2, 4, 6, 8, and 10 mg/l).

3 RESULTS AND DISCUSSION

3.1 Effect of Activation

The effect of activation is shown in Fig. 1 and 2. As shows in Fig. 1, bottom ash before activation doesn't have pores because covers by impurities and Fig. 2, bottom ash after activation have more much pores because bottom ash after activation have fewer impurities than bottom ash before activation. This can make bottom ash has bigger adsorption capacity (Bronislaw, 2016).

Similar result was observed in a study of overview on the effect of activation on the performance of graphene based adsorbent by Jie, et al. (Ma, 2017). According to cited authors, adsorbent with more much pores increase the amount of adsorbate which could adsorbed.

The activation process also change the chemical composition of bottom ash. Activation process can eliminate impurities in the bottom ash. In Table 1, it can be seen elements such as Fe, Mg, and Ti are lost after the activation process. The lost elements can provide additional pores for adsorption process.

Table 1: Chemical composition of bottom ash before and after activation

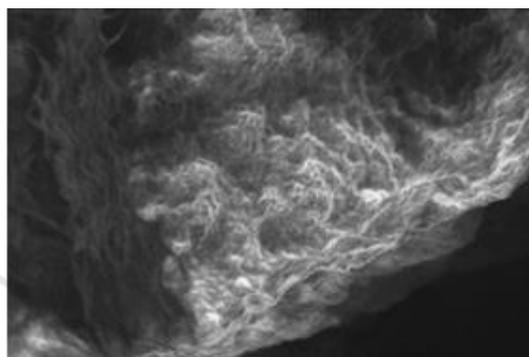| Element	Percentage	
	Before activation	After activation
O	47.67	48.79
Si	19.59	13.92
Al	8.58	12.69
Br	15.13	16.44
K	0.61	6.25
Ca	1.49	1.18
Na	2.07	0.73
Fe	3.08	-
Mg	1.08	-
Ti	0.70	-

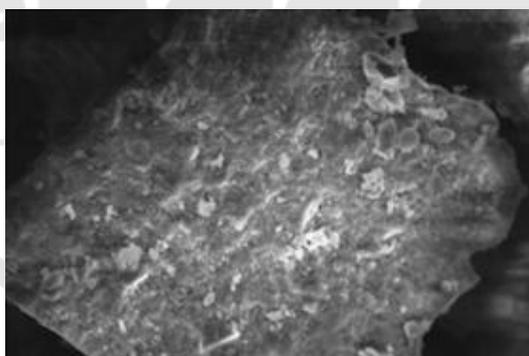Figure 1: SEM bottom ash result before activation

Figure 2: SEM bottom ash result after activation

3.2 Effect of Particle Size

The effect of particle size is shown in Fig. 1. As shown in Fig. 1, the phosphate removal percentage increase as the particle size was decreased. The highest phosphate percentage removal (70.2 %) was achieved by the adsorbent of particle size between 110 and 140 mesh.

Similar result was observed in a study of overview on the effect of particle size on the performace of wood-based adsorbent by Ikenyiri and Ukpaka (Ikenyiri, 2016). According to cited authors, adsorbent with smaller particle size has higher surface

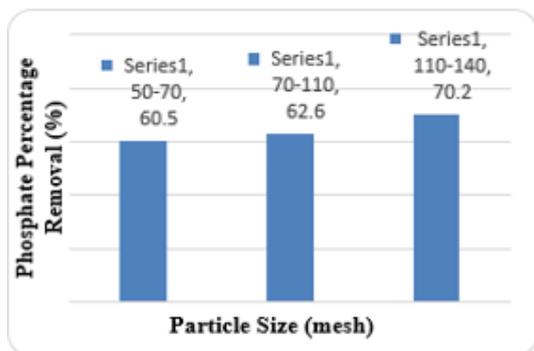area, thus increase the amount of adsorbate which could adsorbed.

Figure 3: Phosphate percentage removal at three different particle size

3.3 Effect of Adsorbent Dosage

The effect of adsorbent dosage on phosphate adsorption is shown in Fig. 2 and 3. It was observed that phosphate percentage removal increase with an increase of adsorbant dosage. In contrast, adsorption capacity decrease with an increase of adsorbent dosage. The highest adsorption capacity (7,02 mg/g) was achieved with adsorbent dosage of 1 gr. The similar trend was reported by Hasfalina, et al (Hasfalina et al, 2012). Futher increment of adsorbent dosage above 1 g/L resulted in a decline in adsorption capacity.

Charles and Odoemelam had stated in their study that an increase in adsorbent dosage will provide greater availability of the exchangeable sites or surface area (Charles et al, 2010). Hence, the percentage of phosphate removal in this study increases as the adsorbent dosage increases (Fig. 2). However, the increase is not significant and higher adsorbent dosage does not provide higher adsorption capacity (Fig. 3). The trend where phosphate adsorption capacity descreases as adsorbent dosage increases in this study might be due to the adsorptive capacity of bottom ash that was available was not fully utilized at higher adsorbent dosage in comparison to lower adsorbent dosage.
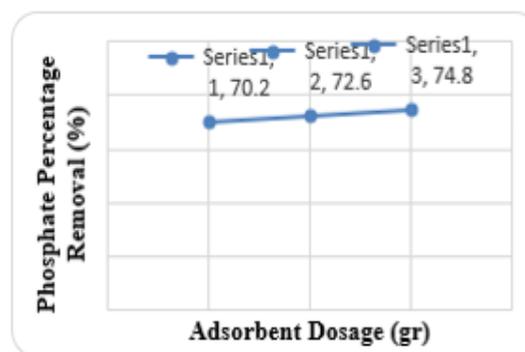

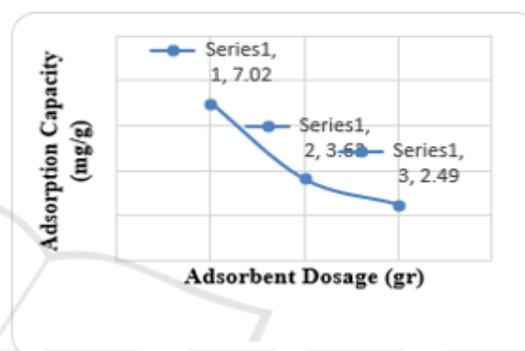Figure 4: Phosphate percentage removal at different adsorbent dosage

Figure 5: Phosphate adsorption capacity at different adsorbent dosage

According to Waseem et al, high adsorbent dosage does not always gives optimum result and higher adsorption capacity compared to lower dosage (Waseem et al, 2012). This is possibly because of at higher adsorbent dosage, lumps was formed and thus decrease overall surface area of adsorbent.

3.4 Adsorption Isotherm Model

The Freudlich and Langmuir adsorption models were used to determine the fitting model for phosphate adsorption using KOH activated bottom ash. The Freudlich and Langmuir isotherm are given in Eq. 1 and 2, respectively (Ahmed et al, 2010).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{1}$$

Where qe is the amount of phosphate adsorbed per mass adsorbent used (mg/g), Ce is equilibrium concentrate of solution (mg/l), Kf is Freudlich constants and 1/n is adsorption intensity.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \tag{2}$$

Where q_{max} is adsorption capacity at monolayer, b is Langmuir constants, q_e is the amount of phosphate adsorbed per mass adsorbent used (mg/g), and C_e is equilibrium concentrate of solution (mg/l).

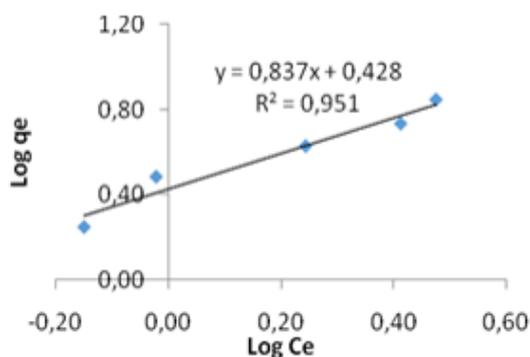The experimental data was applied to the isotherm models, and corresponding plots are given in Fig. 4 and 5.
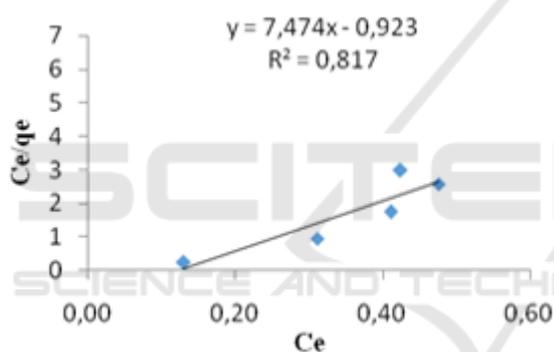

Figure 6: Freudich plot for phosphate removal

Figure 7: Langmuir plot for phosphate removal

Based on Fig. 6 and 7, a summary table was made and shown in Table 2.

Table 2: Freudlich and Langmuir Constants

Parameter	Freudlich	Langmuir
R^2	0.9512	0.8171
Q_{max}	-	9.149
K	2.671	0.662
n	1.194	-

In Table 2, the values of R2 were compared. The R^2 value of Freudlich model (0.9512) is well fitted compared to the R^2 value of Langmuir model (0.8171). This is indicating that the mechanism of phosphate adsorption using KOH activated bottom ash obeyed the Freudlich isotherms. The good fit of the Freudlich isotherm to an adsorption system assumes tha there is a multilayer adsorption and reversible adsorption which considers the interaction between adsorbate molucules (Freundlich, 1906).

4 CONCLUSIONS

In general, it can be concluded that the parameters such as particle size and adsorbent dosage did affect the adsorption of phosphate removal using KOH activated bottom ash. The highest percentage removal value of 70.2 % was achieved by using adsorbent with particle size between 110 and 140 mesh. Higher adsorbent dosage gives a decrease in adsorption capacity, with the highest value of adsorption capacity was achieved by using adsorbent dosage of 1 gr. Equilibrium data by the Freudlich isotherms (R^2 = 0.9512) was found to be well fitted in describing adsorption isotherm of KOH activated bottom ash for phosphate removal.

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