Comparative Phosphorus Removal Efficiency from Municipal Wastewater Using Acid Mine Drainage Sludge and Its H₂O₂ Activated form As Adsorbents

Irene Yulianto¹, Setyo Sarwanto Moersidik¹* and Nova Amanda¹

¹ Environmental Engineering Study Program, Civil Engineering Department, University of Indonesia, Depok - Indonesia
Email: ssarwanto@eng.ui.ac.id

Abstract. Acid mine drainage (AMD) sludge is by-product from AMD treatment that formed by iron deposition. This sludge has a potential to be used as an active adsorbent to remove phosphate from domestic wastewater. The adsorbent that was used in this research is AMD sludge from PT Bukit Asam Tbk., Tanjung Enim that majorly composed of Si, Fe and Al compound (determined by the XRD test). Phosphate adsorption was done by AMD sludge and MD sludge that was activated by hydrogen peroxide. Activation process by hydrogen peroxide affected the chemical and physic characteristic of sludge and it showed from the results that the concentration of Si, Fe and Al were shifted by 7.33%, 7.03%, and 1.49%, respectively. Meanwhile for the physical characteristic; specific surface area, pore volume, and pore size were shifted by 19.51 m²/g, 0.0635 cm³/g, and 142.694 nm, respectively. Phosphate removal by AMD sludge has a greater result than activated sludge. Adsorption capacity of AMD sludge was well described by Freundlich isotherm model, which is equal to 6.358 mg P/g. Meanwhile, adsorption capacity of activated sludge was well described by Langmuir isotherm model, which is equal to 0.48 mg P/g. Results in this study indicated that the activation process with hydrogen peroxide affects the ability of phosphate adsorption that was showed by the difference of removal percentage.

1. Introduction

Mining is one of the sectors that used by the government in national development activities. However in the practice, apart from increasing the country’s prosperity, mining also has an impact to the environment [1]. One of the impacts is the contamination of surface water and ground water from mining activities. The pollution is caused by acid mine drainage.

Acid mine drainage treatment can be carried out in two ways; passive treatment technology and active treatment technology. In passive treatment technology, acid mine drainage goes through chemical and biological processes that occur in nature, without being given any chemical additives. Whereas in active processing technology, there are some processes that can be used to treat the acid mine drainage, such as neutralization, aeration and deposition.

Acid mine drainage sludge comes from deposits that formed by chemicals that was used as agents to neutralize acid mine drainage [2,3]. Sludge with high amount of iron hydroxide is produced along with acid mine drainage treatment which progressively develops over time, so a disposal site is needed [4]. It was also stated that the discharge of acid mine drainage sludge is a serious problem due to the characteristics of the sludge itself and also the limited land for disposal. Acid mine drainage sludge that is dumped in landfill has the potential to contaminate the underground layer [5,6]. Generally, the heavy metal content in acid mine drainage sludge makes it hard to be reused [7]. However, there are several options in reusing acid mine drainage sludge, such as production of building materials, agricultural land applications, metal adsorbents in wastewater management, carbon dioxide
sequestration and other uses. Acid mine drainage sludge has a high iron and aluminium content because it has gone through a neutralization process through the addition of alkaline lime. Therefore, it has the potential to be used as an adsorbent for water contaminant content [5]. One of the water contaminants that can be adsorbed by acid mine drainage sludge is phosphate that contained in domestic wastewater. Excess phosphate in waters can caused eutrophication that detonate algae growth [8]. Phosphate removal water can be carried out through an adsorption process using sludge [9, 16]. The mechanism that occurs in the adsorption process is the exchange of ligands and the complexation of phosphorus with ions of iron, aluminium, and calcium.

There are several factors that influence the adsorption process, which are surface area of adsorbent, physical and chemical properties of the adsorbate, acidity of the solution, temperature, adsorbent porosity, and chemical characteristics of the adsorbent surface [10]. Neutral or acidic condition can increase the ability of phosphate adsorption [11]. It was also stated that the adsorption of phosphate by acid mine drainage sludge is endothermic, so that the increase in temperature is also able to increase the adsorption ability. In addition, preparation and activation processes are also carried out prior to adsorption testing. Acid mine drainage sludge was activated using hydrogen peroxide (H$_2$O$_2$) and ammonia as agents in research [11]. Therefore, this research was conducted to determine the effect of the preparation and activation processes on the phosphate adsorption ability of acid mine drainage sludge. The results of adsorption will be compared with the one from sludge that was not activated.

2. Material and Method

2.1. Adsorbent

The adsorbents that was used in this study are AMD sludge and activated sludge. AMD sludge was collected from acid mine drainage treatment site called PIT-3 Barat, Banko Barat site, PT Bukit Asam Tbk., Tanjung Enim. AMD sludge on that treatment site was treated with limestone. The sludge was sieved through a fine screen (100 mesh) after it was dried at 105°C temperature and crushed [12]. For activated sludge, the AMD sludge was actively treated with hydrogen peroxide [11,13].

2.2. Adsorbate

The adsorbate that was used in this study is synthetic wastewater. Synthetic wastewater was prepared by adding 20 mg of KH$_2$PO$_4$ to one litre aquadest with volumetric flask [11].

2.3. Batch adsorption

Batch adsorption studies were performed in this study to find out the adsorbent’s performance on phosphate adsorption. Batch adsorption was done by agitating 100 ml of synthetic wastewater with certain amount of adsorbent and certain periods of time using orbital shaker at 150 rpm. Later samples were filtered and phosphorus concentration was analyzed. For adsorption isotherm study, various dosage of adsorbent (AMD sludge and activated sludge) ranging from 2 to 10 g/L were added to 100 ml of synthetic wastewater and agitated for 2 h at room temperature and pH 7±0.1. Whereas for adsorption kinetic study, 10 g of adsorbent (AMD sludge and activated sludge) were added to 100 ml of synthetic wastewater and agitated at various periods of time ranging from 5 to 180 min at room temperature and pH 7±0.1.

2.4. Phosphorus analyses

Phosphorus concentration was analyzed with UV-Vis Spectrophotometry HACH DR/2000 type. Sample of 50 ml were added by 1 ml of amino acid reagent (Cat. 193432) and molybdate reagent (Cat. 223632), respectively. The phosphate concentration was read from UV-Vis Spectrophotometer at 530 nm wavelength.

2.5. Characteristics analyses

Characterizations for AMD sludge and activated sludge were done by X-Ray Diffractometer (XRD) and BET method. For chemical characteristic, 1 to 2 g of sludge was analyzed with PANalytical
X’Pert Pro MPD. X-rays worked by using Cu K (α) 1.54 Å filtered radiation at a voltage of 40 kV and a current of 30 mA. Step scans run continuously in a 10-90° 2θ, with a stepping size of 0.02°. The result then was interpreted by HighScore Plus by PANalytical B.V 2012. For physical characteristic, sludge was analyzed using a surface area analyzer instrument with nitrogen (N₂) isotherm adsorption at 77°K operating conditions and 120°C degassing temperature.

3. Results and discussion

3.1. Characteristics of adsorbent
The chemical characteristics of AMD sludge and activated sludge presented in Table 1. Results showed that the major constituents of both sludge are Si, Fe and Al. The concentration of S, K, Ca and Ti are between 1.4 to 5.6%. Other elements are all in trace amounts below 1%, respectively. Some of trace elements were subsided after the sludge gone through activation process. Iron and aluminium are both dissolved metals from neutralization process of AMD drainage. Meanwhile, the high content of silica probably comes from the sediment due to inadvertent contamination [14].

The physical characteristics of AMD sludge and activated sludge presented in Table 2. The specific surface area, pore volume, and pore size of AMD sludge were identified by BET method. The result showed that specific surface area, pore volume and size are increased after the sludge was activated. The enhancement showed that activation process with hydrogen peroxide affected the physical characteristic of AMD sludge.

| Element | Concentration (%) | Element | Concentration (%) | Element | Concentration (%) |
|---------|------------------|---------|------------------|---------|------------------|
|         | Activated sludge | AMD sludge |         | Activated sludge | AMD sludge |         | Activated sludge | AMD sludge |
| Al      | 14.22            | 12.73    | Mn               | 0.17    | 0.24             | Nii    | -                | 0.04     |
| Si      | 47.1             | 39.77    | Fe               | 26.07   | 33.1             | V      | -                | 0.07     |
| P       | 0.71             | 0.66     | Cu               | -       | 0.03             | Cr     | -                | 0.04     |
| Si      | 1.63             | 1.66     | Zn               | -       | 0.11             | Eu     | -                | 0.2      |
| Cl      | 1.03             | 0.74     | Rb               | -       | 0.08             | Yb     | -                | 0.03     |
| K       | 5.28             | 5.59     | Sr               | -       | 0.09             | Pb     | -                | 0.03     |
| Ca      | 1.44             | 1.96     | Y                | -       | 0.03             |        |                  |          |
| Ti      | 2.36             | 2.53     | Zr               | -       | 0.22             |        |                  |          |

Table 1. Composition of AMD sludge and activated sludge.

| Characteristic       | Activated Sludge | AMD Sludge |
|----------------------|------------------|------------|
| Specific surface area | 42.11 m²/g     | 22.60 m²/g |
| Pore volume          | 0.124 cm³/g     | 0.0605 cm³/g |
| Pore size            | 153.4 nm        | 10.706 nm   |

Table 2. Physic characteristics of AMD sludge and activated sludge.

3.2. Sludge dose and contact time on adsorption
The effect of sludge dose on phosphate removal can be seen in Figure 1. Both phosphate removal by AMD sludge and activated sludge increased as the sludge dosage increased from 2 g/L to 10 g/L. With the dosage of 10 g/L, 90.62% P removal by AMD sludge and 55.52% P removal by activated sludge were achieved. However, removal percentage by activated sludge is lower than AMD sludge. It happened because the enhancement only occurred to the surface area and not to the concentration of phosphate binder. The relationship between contact time and phosphate removal is presented in Figure 2. Phosphate removal by AMD sludge increased as the contact time increased from 5 to 120 min and
then decreased at 180 min. Meanwhile, the removal by activated sludge increased when the contact time increased from 5 to 60 min and then decreased at 120 min. The degradation happened due to the slow diffusion process of ions into the adsorbents [15]. In previous research, it showed that after the agitation process for 60 min, the phosphate adsorption process in AMD sludge noticeably insignificant, indicating that the phosphate adsorption equilibrium had been reached [11].

![Figure 1. Effect of adsorbent dosage on phosphate removal.](image1)

![Figure 2. Effect of contact time on phosphate removal.](image2)

3.3. Adsorption isotherms
Two isotherm models have been used to evaluate the performance of phosphate adsorption, which are Freundlich model and Langmuir model. The results can be seen in Table 3. It was shown that the phosphate adsorption by AMD sludge was well described using Freundlich model (Equation (1)) due to its $R^2$ value is greater than the Langmuir model.

$$q_e = K_F C_e^{1/n_f}$$  \hspace{1cm} (1)

$C_e$ (mg/L) and $q_e$ (mg/g) are the concentration of the liquid and solid phase of the adsorbate at equilibrium. While $K_F$ is the adsorption capacity (mg/g)(L/mg)$^{1/n}$ and $1/n_f$ represent the adsorption intensity. As showed in Figure 3, the linear relationship between $q_e$ and $C_e$ is 0.965. The $K_F$ and $1/n_f$ from the equation were 0.971 and 0.699, respectively. Then from the Equation (1), the adsorption capacity ($q_m$) was 6.358 mg P/g.

Meanwhile, the phosphate adsorption by activated sludge was well described using Langmuir isotherm model (Equation (2)).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$  \hspace{1cm} (2)

As showed in Figure 4, the linear relationship between $q_e$ and $C_e$ is 0.965. The $K_L$ from the equation was 0.106. Then from the Equation (2), the adsorption capacity ($q_m$) was 0.48 mg P/g. Adsorption capacity for the adsorption process by AMD sludge has a greater value than the value by activated sludge. This corresponds to the ratio of the results of phosphate removal where the removal percentage by AMD sludge is greater than the removal percentage by activated sludge.
Table 3. Results from Freundlich and Langmuir models

| Adsorbent        | Freundlich model | Langmuir model |
|------------------|------------------|----------------|
|                  | $R^2$           | $K_F$ [(mg/g)(L/mg)^{1/n}] | $q_m$ (mg P/g) | $R^2$ | $K_L$ (L/mg) | $q_m$ (mg P/g) |
| AMD sludge       | 0.9646          | 0.971          | 6.358          | 0.737 | 0.099        | 9.345          |
| Activated sludge | 0.907           | 0.0004         | 28.22          | 0.9439 | 0.106 | 0.48          |

Figure 3. Freundlich isotherm of phosphorus adsorption by AMD sludge.

Figure 4. Langmuir isotherm of phosphorus adsorption by activated sludge.

4. Conclusion

The AMD sludge from PT Bukit Asam Tbk., Tanjung Enim is majorly composed of Si, Fe and Al compound and it determined by the XRD test. Activation process by hydrogen peroxide affected the chemical and physic characteristic of sludge and it showed from the results that the concentration of Si, Fe and Al were shifted by 7.33%, 7.03%, and 1.49%, respectively. Meanwhile for the physical characteristic; specific surface area, pore volume, and pore size were shifted by 19.51 m$^2$/g, 0.0635 cm$^3$/g, and 142.694 nm, respectively. Phosphate adsorption by AMD sludge has a greater adsorption capacity than the adsorption by activated sludge. Adsorption capacity of AMD sludge is well described by Freundlich isotherm model, which is equal to 6.358 mg P/g. Meanwhile, adsorption capacity of activated sludge is well described by Langmuir isotherm model, which is equal to 0.48 mg P/g. The activation process with hydrogen peroxide in this study affects the ability of phosphate adsorption that was indicated by the difference of removal percentage. However, pilot studies are necessary in order to develop the efficiency of activation process and to specify the best activation agent for AMD sludge.

5. References

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