Activation And Characterization Of Andisol Soil And Fly Ash Composite In Adsorption Of Lead (II) Metal Ion

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Abstract
This study was aimed to determine of lead(II) metal ion adsorption ability by using adsorbents from the composite of andisol soil and fly ash. Andisol soil and fly ash were activated with NaOH 3M. The adsorbent characterization was performed by Fourier Transform Infrared Analyzer (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Surface Area Analyzer (SAA). The adsorption of lead (II) metal ion performed on solution pH of 1, 2, 3, 4, 5, and 6, variation of composition andisol soil and fly ash composite of 100:0, 25:75, 50:50, 75:25 and 0:100 (w/w), and contact time of 30, 60, 90, and 120 minutes with the batch system. Measurement of final concentration at the time of equilibrium was done using AAS. The optimum condition of lead (II) metal ion adsorption was obtained at pH of solution 5, activated andisol soil and fly ash composition 50:50 (w/w), contact time 60 minutes. The result of adsorption followed Freundlich isotherm with adsorption capacity of 0.435 mg/g. The percentage of lead(II) metal ion removed is 97.11%.

Keyword: andisol soil, fly ash, lead, adsorption

1. INTRODUCTION
Increasement human activity has caused a variety of adverse effects on human life and the environment. The impact of these activities is waste containing hazardous chemicals such as heavy metals which are polluting the environment. One of the heavy metals that can be found in wastewater which has high toxicity is lead (Pb). Lead metal is produced from the battery industry, petroleum combustion, smelting, pesticides, mining and waste waste including household waste [1]. If an environment has been contaminated with heavy metals, the cleaning process will also be difficult [1]. Therefore, the presence of heavy metals needs to be minimized or even eliminated because of the dangers to human health and the environment.

Some methods that have been used to remove heavy metals include ion exchange, precipitation, neutralization, biosorption and adsorption. The most developed adsorption method at this time because this method is a simple preparation process, the cost is relatively cheap, efficient and can be done at low concentrations so that it is easier to apply than other methods.

Andisol soil is a volcanic ash soil that is found at an altitude of around (700-1500) m above sea level [2]. Based on previous research, andisol soils can be used as adsorbers for some heavy metals because andisol soil surface has properties such as cation and anion exchange, absorption of organic and inorganic compounds, and acidity derived from silanol (Si-OH) functional groups and aluminols (Al- OH and AlOH₂; -OH and -OH₂ are single /
monodental coordinate) [3]. Andisol of Mount Lawu is capable of absorbing metal Cd of 0.30 mg/g [4].

Fly ash is a solid waste produced from burning coal which is usually released without special treatment [5]. The chemical composition of fly ash shows that most of it is composed of metal oxides, especially SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> which have active groups so that fly ash can be used as heavy metal adsorbents. Afrianita et al. [6] conducted a study on the determination of the effectiveness and absorption capacity of fly ash as an adsorbent of lead (Pb) metal in industrial wastewater. The value of lead (Pb) adsorption efficiency at 1.3 mg/L concentration reached 79.23% with an absorption capacity of 0.103 mg of lead metal (Pb)/g of fly ash powder. However, an adsorbent without pre-treatment if applied as an adsorbent gives less optimal results. This is due to impurity. Its activity can be increased by activation both physically and chemically.

Physical activation aims to evaporate the water trapped in the adsorbent pore so that the specific surface area increases. Increased adsorption capacity of andisol soil chemically can be done by acid or base treatment. Chemical activation can dissolve impurities so that the pores will be more open. The decrease in impurities causes the surface of the adsorbent to be clean, the surface area and acidity to increase, so that the adsorption ability becomes better.

In this study, in addition to activation, addition of fly ash into andisol soils will be made so that andisol and fly ash composites will be formed which are used as adsorbents for Pb (II) metal ions. The addition of fly ash which has a mineral content similar to andisol soil is expected to increase the percentage of adsorption of Pb (II) metal ions in solution.

2. METHOD
2.1 Andisol Soil Activation
50 grams of andisol soil were mixed with 250 mL of 3 M NaOH solution with the temperature of 70 °C for 5 hours then cooled, filtered and washed with distilled water until the pH was neutral. Furthermore, activated andisol soil was dried in an oven at a temperature of 105 oC for 4 hours. Then analyzed with FTIR, XRD.

2.2 Fly Ash Activation
50 grams of fly ash are mixed with 300 mL 3M NaOH with a temperature of 85-90°C for 4 hours is then cooled, filtered and washed with distilled water until the pH is neutral. The activated fly ash is then dried in an oven at 105 ° C for 4 hours. Then analyzed with FTIR, XRD.

2.3 Making and Optimizing Composite Composition of Andisol and Fly Ash Soil Composites
Variations adsorbent composition between andisol and fly ash are 100:0, 25:75, 50:50, 75:25, and 0: 100 (w/w). Each variation of the composition of the adsorbent was mixed by stirring using a stirrer and then beated for 1 hour. The mixture was filtered and dried in an oven at a temperature of 105°C for 4 hours. Andisol soil composites and dry fly ash are then crushed and sieved to pass the 150 mesh sieve. Composite was mixed with 10 mL of 6 ppm Pb solution. Composites are filtered with Whatman filter paper 42. Filtrate is measured by AAS.

2.4 Optimization of pH The Solution
0.1 grams of andisol and fly ash soil composites in the optimal composition were mixed with 10 mL of 6 ppm Pb solution using a variation of pH buffers 1, 2, 3, 4, 5, and 6. The solution was stirred for 60 minutes at constant speed at room temperature. Composites are filtered with Whatmanfilter paper 42. Filtrate is measured by AAS.
2.5 Optimization of Contact Time
The same preparation used in the variations of contact time 30, 60, 90 and 120 minutes on the optimum composition and pH.

2.6 Determination of Adsorption Isotherms
The same preparation was carried out using initial concentrations: 2, 4, 6, 8, 10 and 12 ppm at optimum pH and contact time

3. RESULT AND DISCUSSION

3.1 Activation of Andisol Soil and Fly Ash
Activation of andisol soil and fly ash are done to improve physical and chemical properties. In general, the physical activation process aims to remove water molecules in the pore while chemical activation can dissolve impurities so that the pores will be more open. The loss of the impurities causes the surface of the adsorbent to be clean, the surface area and acidity to increase, so that the adsorption ability becomes better. Andisol soil is chemically activated by using strong NaOH solution. The impurity contained in andisol soil is humus acid. Activation is carried out with NaOH because humus acid easily dissolves in alkaline conditions compared to acidic conditions. In addition, NaOH because Na⁺ ions from the NaOH base play an important role in dissolving Si to form sodium silicate so that the andisol soil structure becomes more negative. The more negatively charged andisol soil surface can maximize the work of andisol soil in adsorbing Pb (II) metal ions.

The process of activating fly ash with NaOH generally aims to remove unburned carbon in the form of a very tight and stable glassy layer on the fly ash surface. The glassy chain has high Si and Al active sites. Therefore, this surface layer of glassy fly ash must be destroyed so that the porous and amorphous active sites inside it fly to the fly ash surface. A strong base of NaOH plays an important role in dissolving Si and a little Al to form sodium silicate and sodium aluminate. The effect of andisol and fly ash soil activation can be observed through FTIR spectra shown in Figure 1 and Figure 2.

Based on FTIR spectra in Figure 1 and Figure 2 andisol and fly ash soils after experiencing activation showed OH stretch absorption with peak dilation. The absorption peaks of Si-O-Si or Al-O-Al on active andisol soils and active fly ash show an increase in absorption intensity which looks sharper. This shows that activation has dissolved the impurities resulting in a stronger vibration.
3.2 Specific Total Acidity Analysis
Specific total acidity analysis was carried out using the gravimetric method using ammonia bases. The acidity value obtained will show the presence of active groups on the surface of the adsorbent. The results of the acidity analysis of each adsorbent before and after activation can be seen in Table 1.

| No. | Sample                  | Acidity (mmol/g) |
|-----|-------------------------|------------------|
| 1.  | Andisol Soil            | 3.05             |
| 2.  | Active Andisol Soil     | 5.17             |
| 3.  | Fly Ash                 | 0.83             |
| 4.  | Active Fly Ash          | 1.41             |

Based on Table 1 shows that the total specific acidity value of each adsorbent increases after activation. The activation process is possible to cause the impurities found on the surface of the adsorbent to dissolve, so that the acidic site that was originally hidden will become open or bring up an acid site that was previously covered by impurities. The increasing number of acid sites shows that andisol and activated fly ash are able to provide more active sites, where the active site will interact with Pb (II) metal ions in the adsorption process.

3.3 Performance Test of Adsorbent in Lead(II) Metal Ion Solution
3.3.1 Optimization of Adsorbent Composition
Composition optimization was carried out at pH 5 with contact time 60 with a ratio of andisol / fly ash 100:0; 75:25; 50:50; 25:75; 0:100 (w/w). The results of testing the effect of adsorbent composition on the adsorption capacity of Pb (II) ions are shown in Figure 3.

![Figure 3](image-url)

**Figure 3.** Graph of Effect of Composition on Adsorption Capacity of Composite of Andisol and Fly Ash

Based on Figure 3 it can be seen that the optimum conditions of adsorbent for the absorption of Pb (II) metal ions are the composition of andisol and fly ash composites 50:50 (b / b) with adsorption capacity of 0.567 mg / g and absorption percentage of 91.62%. The
test results show that each component in the adsorbent mixture, namely andisol and fly ash, is in existence supporting each other in absorbing Pb (II) metal ions.

3.3.2 Optimization pH of Solution Optimization of pH conditions was carried out at pH 1-6 for 60 minutes with a ratio of soil composite composition andisol: fly ash which was optimum 50:50 (w/w). The test results of the effect of pH on Pb solution on adsorption capacity are presented in Figure 4.

![Figure 4. Graph of Effect of pH Variations on Adsorption Capacity Lead(II) Metal Ion in Composite Andisol Soil:Fly Ash 50:50 (w/w)](image)

Based on Figure 4 it can be seen that the higher the pH, the greater the adsorption capacity. However, at pH 6 conditions decreased adsorption capacity showed that Pb(II) solution began to precipitate. The initial concentration at pH 6 is much smaller than the others. At pH 6 the adsorption capacity decreases because Pb metal will form Pb(OH)₂ so that the adsorption process is difficult. Based on the constant price of the yield of 1.43 × 10⁻²⁰ (Ksp) Pb (OH)₂, the precipitation will occur at pH 6. Therefore, the optimum condition of the Pb (II) ion solution is pH 5.

3.3.3 Optimization Contact Time of Solution Optimization of contact time was carried out on the ratio of soil composite composition andisol: fly ash 50:50 (w/w) with contact time variations of 30, 60, 90 and 120 minutes. The test results of the effect of contact time on the adsorption capacity of the solution can be seen in Figure 5.

![Figure 5. Graph Effect of Contact Time Variation on Adsorption Capacity of Pb (II) Metal Ions on Composite Andisol Soil: Fly Ash 50:50 (w/w)](image)

Based on Figure 5 it can be seen that the longer the contact time between the adsorbent and the Pb solution, the greater the adsorption capacity until the optimum conditions are obtained. The optimum contact time achieved was 60 minutes which showed that at this time adsorption equilibrium had occurred between the adsorbate concentration absorbed and the concentration of the adsorbate remaining in the solution. Furthermore, at 90 minutes contact
time, there was a decrease in adsorption ability which indicated that the surface of the adsorbent was saturated with the metal solution so that it experienced desorption or the metal being released into solution because on the surface of the adsorbent there was no active site capable of binding to Pb (II) metal ions.

3.4 Surface Area Analysis

The greater the surface area of the adsorbent, the more adsorption capability will increase. Test results of specific surface area of andisol active soil, active fly ash and soil composite andisol: fly ash 50:50 (w/w) are shown in Table 2.

| No. | Sample                             | Surface Area (m²/g) |
|-----|------------------------------------|---------------------|
| 1.  | Active Andisol Soil                | 24.8                |
| 2.  | Active Fly Ash                     | 54.3                |
| 3.  | Composite Andisol Soil and Fly Ash 50:50 (w/w) | 74.7                |

Based on the data in Table 2, it can be seen that after the active andisol and fly ash are composited, the surface area increases compared to the surface area of each component. Increasing the surface area of the soil composite andisol: fly ash (50:50) (w/w) indicates that the adsorbent can have a better adsorption capacity because the higher the surface area, the adsorption ability will increase.

3.5 Determination of Adsorption Isotherm

The appropriate isotherm type is determined based on the correlation coefficient ($R^2$) shown in the graph of the linear equation of each isothermic curve. Linear equation with $R^2$ value close to or equal to 1 (one), it can be concluded that the type of adsorption isotherm follows the equation. Langmuir and Freundlich isotherm curves for Pb (II) metal ions can be seen in Figure 6 and Figure 7.

Based on the results of linear regression on the isotherm curve, the $R^2$ value for Langmuir isotherm is 0.723 with the adsorption capacity of 0.17 mg/g while the Freundlich isotherm has a $R^2$ value of 0.964 whose adsorption capacity is 0.4355 mg/ g. The adsorption process has a tendency to follow the Freundlich isotherm model compared to the Langmuir isotherm because the $R^2$ value is closer to 1, so it can be concluded that the adsorption occurs in physics through van der Waals forces which means that the adsorbent has a heterogeneous
surface and each molecule has different adsorption potential Pb metal with a multilayer adsorption process (more than one absorption layer).

4. CONCLUSION
Composite of andisol soil adsorbent: fly ash can adsorb metal ion lead(II) with andisol soil composition:fly ash 50:50 (w/w), the best conditions at pH 5, contact time for 60 minutes with adsorption capacity of 0.525 mg/g and adsorption percentage of 97.2%. The best type of adsorption adsorption isotherm for Pb(II) metal ions follows Freundlich isotherm with adsorption capacity of 0.435 mg/g.

5. REFERENCES
[1] Nordberg, J. F.; Parizek, J., Pershagen, G., and Gerhardsson, L., 1986, Factor Influencing Effect and Dose-Respons Relationships of Metals, In Handbook on the Toxicology of Metals, Elsevier, New York.
[2] Munir, M., 2008, Pemanfaatan Abu Batubara (Fly ash) untuk Hollow Block Yang Bermutu Dan Aman Bagi Lingkungan. Tesis, Universitas Diponegoro: Semarang.
[3] Afrianita, R., Dewilda, Y., and Monica R., 2014, Jurnal Teknik Lingkungan UNAND 11: 67-73.
[4] Kusumastuti, I., 2014, Pemanfaatan Tanah Andisol aktif-asam humat untuk pembuatan adsorben terhadap ion logam besi (Fe), Skripsi, Universitas Sebelas Maret, Surakarta.
[5] Lasryza, A. and Dyah Sawitri., 2012, Jurnal Teknik Pomits 1 (1): 1-6.
[6] Afrianita, R., Dewilda, Y., and Fitri R., 2013, Jurnal Teknik Lingkungan 10: 1-10.