Optimization of the use of fly ash and natural zeolite activated as composite for an adsorbent of lead heavy metal (Pb)

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Abstract. Coal is an alternative source of energy besides petroleum and natural gas which are widely used so they can produce a large amount of waste such as fly ash. Natural zeolite is a natural material that is widely spread in the territory of Indonesia. Fly ash and natural zeolite contain a SiO2 and Al2O3 that can be used as an adsorbent. This study aims to create a composite of fly ash/natural zeolite activated as adsorbent to optimize the performance of Pb heavy metal adsorption. Fly ash and natural zeolite were activated using NaOH 3M, and HCl 1M. The adsorption process was carried out with variations of composition 100:00, 75:25, 50:50, 25:75, 00:100 (w/w), variations in pH of 1, 2, 3, 4, 5, 6, and contact time variations 15, 30, 45, 60, 75, 90 min. The adsorbent characterization was performed with FTIR, XRD, SAA, and total specific acidity as well as the final measurement of Pb metal concentration determined by AAS spectrophotometer. The activation process can be shown on the FTIR spectra with the shift of wave numbers, XRD diffractogram showed the decrease of intensity in fly ash and natural zeolite, the increase of acidity value and surface area on each material shows the availability of more active groups. The adsorption of metal Pb reached the optimum condition on fly ash:natural zeolite composition 75:25 (w/w), pH condition of 5, and contact time 60 min, and adsorption capacity of 0.577 mg/g and 97% adsorption percentage following Langmuir isotherm. The adsorption result obtained is supported by characterization of adsorbent after and before adsorption using SEM EDX indicating the presence of Pb element on adsorbent after adsorption and the surface morphology became rougher due to effect of Pb metal absorption.

1. Introduction
Coal is an alternative energy source that has abundance in Indonesia so that it has a relatively cheaper price. According to the World Coal Association (2012) Indonesia ranks the 5th largest coal producing country in the world in 2011 [1]. Sumatra and Kalimantan are Indonesian regions which contain a lot of coal. Based on the National Energy Policy the use of coal in Indonesia in 2005 is equal to 15% of the total national energy needs, and will continue to experience up to 2025 reaching 34% as a form of reduction in fuel use. The amount of coal usage is also balanced with the amount of residual waste using coal such as fly ash [2]. The use of fly ash by knowing the elements and minerals in it is often used as raw material for cement production, construction materials, concrete reinforcement, and heavy metal adsorbent [3,4]. The use fly ash to remove heavy metals has two advantages, namely to protect environment of heavy metal contamination and to reduce fly ash waste in the environment [5].

Fly ash contains as much as 90% consisting of SiO2 and Al2O3[6]. Utilisation of fly ash for removal of some pollutants such as heavy metal so that fly ash can be used as an adsorbent [7] which
has low cost benefits. Natural zeolite is a hydrated mineral alumino silicate from porous structures with chemical physics such as cation exchange, molecular sifting, catalysis and adsorption. Natural zeolite is used as an adsorbent because it has a surface area large, low cost, and easy to get the material [8]. Zeolite exchangeable ions makes particularly suitable for removing heavy metal ions from industrial effluent waters [9].

Heavy metal is a metal known for its biodegradability and accumulation in the living system, which causes serious illnesses and disorders [10] and can also spurring environmental pollution both water, soil and air pollution. Expose this heavy metal is very risky for humans, which can damage human physiology and systems other biology if the level received is exceeded. Heavy metal cannot be degraded or destroyed [11]. Highly toxic heavy metal, can cause death or interference health that does not recover in a short period of time, such as lead (Pb).

This study aims to determine the performance of the manufacture of fly ash/natural zeolite adsorbents that has been given an activation treatment which is expected to increase the number of active site (-OH, -Al-OH, Si-OH) with high adsorption capacity, so it can adsorb Pb heavy metals optimally and effectively.

2. Experimental

2.1 Materials and Tools

The raw material of composite used in this study is fly ash derived from industry food at Mojosongo, Central Java, and natural zeolite from Klaten, Central Java. Fly ash and natural zeolite were initially ground to a 150 mesh screen. The initial material is washed and activated, fly ash uses NaOH 3M, natural zeolite activated uses HCl 1M . The material is neutralized pH using aquades and made variation of composite composition and a performance test was carried out using model of solution from Pb 1000 ppm. The tools used are buchner, FTIR, XRD, SEM-EDX, AAS, SAA (BET), Desiccator.

2.2 Methods

The adsorption process is carried out by determining the optimum conditions for each variation in the adsorption process of Pb 6 ppm. Variation in composite composition is carried out on comparison of fly ash:natural zeolite 100: 00, 75:25, 50:50, 25:75, 00: 100 (w/w), pH variation solution from pH 1-6, and variation of contact time at 15, 30, 45, 60, 75, 90 min, as well determine the type of adsorption isotherm on the fly ash:natural zeolite composite adsorption Pb heavy metals with various concentrations of 2, 4, 6, 8, 10, 12 ppm.

2.3 Determination of the type of adsorption isotherm

Determination of adsorption isotherms by simple linear regression with equations Langmuir and Freundlich. The adsorption isotherm and its type can be known from the R value approaching one [12,13].

2.3.1 Langmuir Isotherm

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e
\]

where Ce is equilibrium concentration (mg/L), qe is the amount adsorbed at equilibrium (mg/g), qm is the maximum adsorption capacity that corresponds to the monolayer coverage which is complete (mg/g), and KL is the Langmuir constant which is related to the adsorption energy Langmuir isotherm adsorption model.

2.3.2 Freundlich Isotherm

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]
where $K_f$ and $1/n$ are Freundlich constants associated with adsorption capacity and adsorption intensity. In the Langmuir equation a graph of $C_e$ vs $q_e$ is made and the Freundlich equation is made graph equation $lnq_e$ vs $lnC_e$.

3. Results and Discussion
3.1 Activation of Fly ash and Natural Zeolite
The activation process can dissolve impurities that are on the surface of fly ash with damaging the outer layer, removing water that is still trapped in the pores of the zeolite crystals later can increase surface area, causing loss of amorphous and impurity organic so that the acidic site which is initially covered by impurities becomes activated. This matter can be seen in FTIR spectra of fly ash and natural zeolites in Figures 1 and 2, that there are differences in wave and increase in transmittance intensity after the activation process, because of the increase intensity of the vibration energy.

The presence of minerals in the fly ash and natural zeolite can also be seen in Figures 3 and 4, where on fly ash there is hematite, quartz low, mulite, and corundum, while at natural zeolite contains mordenite and clinoptilolite. The activation process also causes the intensity of the diffraction pattern increases and decreases due to loss impurity and damage to materials due to high temperatures.
3.2 Specific Total Acidity Analysis

Determination of specific total acidity was carried out using gravimetric method, with ammonia base was used as its adsorbate. Ammonia is a strong base that has a small molecular size so that it can be adsorbed and enter the active site pore of the material. Based on Table 1, the total specific acidity value of each adsorbent material increased after activation. This activation process can remove impurities that are on the surface of the material, thus causing the acidic site which was originally covered by impurities to be opened and appear. The large number of acid sites shows that the material has a cluster active which will bind more metal ions.

Table 1. Results of acidity analysis

| No | Sample               | Acidity (mmol/g) |
|----|----------------------|------------------|
| 1  | Fly ash              | 0.824            |
| 2  | Fly ash active       | 1.412            |
| 3  | Natural zeolite      | 0.253            |
| 4  | Natural zeolite active | 1.056        |

3.3 Performance Test of Fly ash / Natural Zeolite Composite to Lead Metal (Pb)

Composite performance is carried out to determine the optimization adsorption process of heavy metals Pb. This optimization is carried out on variations in composition, pH of the solution, and contact time.

It can be seen in Figures 5, 6 and 7. The optimization of performance of adsorbents on heavy metals Pb is the variation composition of fly ash:natural zeolite 75:25 (w/w) with adsorption capacity 0.5433 mg/g, the optimum composite shows that the two materials stick together to the pore wall so that the material surface area increases and supports the heavy metal adsorption process of lead (Pb). PH solution is conditioned using a buffer so that the pH of the solution does not change much when the adsorption process takes place. At pH <5 there is a decrease in adsorption capacity due to the acidic condition of the solution, the surface of the adsorbent positive which is surrounded by H⁺ ion because the functional group in the adsorbent is protonated and will cause a competition with the Pb²⁺. The conditions of pH 6 decreases the adsorption capacity and made Pb metal had saturated and formed Pb(OH)₂, the optimum variation in pH of the solution at pH 5 with adsorption capacity of 0.5670 mg/g, and variation optimum contact time at 60 minutes with an adsorption capacity of 0.5770 mg/g, shows that the adsorption capacity increases with increasing contact time, this happens because the the greater the interaction between adsorbent and Pb metal, but then it will experience a decrease in adsorption capacity if it has passed the optimum contact time, which occurs because more Pb metal adsorbed will reduce the adsorbent surface area so that the adsorbent can no longer adsorb Pb metal and cause desorption or the release of Pb metal which has been bonded to the adsorbent into the solution.
3.4 SEM EDX Analysis
The SEM results in Figures 8 and 9 show that the adsorbent after adsorption shows cracks in the adsorbent which is the place where metal ions are adsorbed, other than that it can be seen that the surface of the adsorbent has an increased level of roughness. This occurs because of the effect of adsorbing metal ions on the adsorbent, because of the type of adsorbate the watery interacts with the adsorbent. Pb attached to the surface of the adsorbent is proven by EDX results as shown in Table 2.

![Figure 8. Morphology of the fly ash composite : natural zeolite 75:25 (w/w) before adsorption process](image1.png)

![Figure 9. Morphology of the fly ash composite : natural zeolite 75:25 (w/w) after adsorption process](image2.png)

| Table 2. Comparison of composite adsorbent elements before and after adsorption |
|-----------------|-----------------|-----------------|
| Adsorbent       | Si (%)          | Al (%)          | Pb (%)         |
| Fly ash/natural zeolite 75:25 (b/b) before adsorption | 59.08           | 30.88           | -              |
| Fly ash/natural zeolite 75:25 (b/b) after adsorption | 64.90           | 12.60           | 0.12           |

EDX results as shown in Table 2 show that Pb metal has been adsorbed on the adsorbent, this is shown from the shooting on the surface of a particular sample and the presence of Pb content in the composite after adsorption of 12%.

3.5 Specific Surface Area Analysis
Analysis of the surface area aims to find out how much the surface area of the adsorbent used in the adsorption process with Pb metal. The surface area can also show that the composite has been successfully formed by knowing the value of the measured surface area between the active fly ash forming material and the active natural zeolite with a new material fly ash/natural zeolite composite. The surface area of the adsorbent increases after the composting process which can be seen in Table 3, which is caused by the incorporation of the material that has been active who have many active sites and open pores.

| Table 3. Result of specific surface area analysis |
|-----------------|-----------------|-----------------|
| No              | Sample          | Specific Surface Area (m²/g) |
| 1               | Fly ash active  | 27.940          |
| 2               | Natural zeolite active | 67.264          |
| 3               | Composite       | 74.745          |

The incorporation of two active materials which has an active site that opens on the exposed surface and pores, causing fly ash particles to fill natural zeolite particles that will be interconnected each other so that it will form a space between layers that can increase the pore thickness and increase the surface area the fly ash/natural zeolite composite material so that it can be said that the composite material has been successfully formed because it has produced different characteristics from the initial
material. The larger the area the surface of the active site on the material will be more which is wide this surface will provide space in the adsorption process for Pb metal.

3.6 Determination of Adsorption Isotherms
Determination of the adsorption isotherm aims to know what type of adsorption occurs in the adsorption process between adsorbent fly ash/natural zeolite to Pb metal. The coefficient of determination ($R^2$) of each of these isotherms can explain that the type of adsorption of fly ash/natural zeolite adsorbents (75:25) on Pb metal occurs chemistry ionic bonds and physically through van der walls forces.

Table 4. Parameter of isotherm adsorption

| Adsorbent                          | Langmuir | Freundlich |
|-----------------------------------|----------|------------|
|                                   | $q_m$    | $K_L$      | $R^2$ | $K_f$  | $n$  | $R^2$ |
| fly ash/natural zeolite composite 75:25 | 0.983    | 4.053      | 0.9661 | 0.689  | 3.571 | 0.8873 |

However, adsorption tend to follow the Langmuir isotherm which has an $R^2$ value which is closer to 1 means that on the surface of the adsorbent there is an active site that is proportional to the extent surface, which can adsorb only one molecule and adsorption is limited to formation of monolayer single layer, with adsorption capacity value of 0.983 mg/g.

4. Conclusion
Activation process on fly ash material, natural zeolite can dissolve the impurities there are a material that can be shown by characterization, where the FTIR spectra is fly ash, natural zeolites after activation experience a width and depth of transmittance bands, shift in wave numbers, diffraction patterns XRD shows a decrease and increase in intensity, an increase in acidity and surface area on fly ash, natural zeolite after activation shows availability active groups of Si-OH, Al-OH, Si-O-Si, Al-O-Al, Si-O, Al-O, and more adequate surface area in Pb heavy metal adsorption process. Adsorption of Pb metal reaches optimum conditions at fly ash:natural zeolite composition 75:25 (w/w), the pH condition of the solution 5, and the contact time of 60 minutes, as well as the adsorption capacity of 0.577 mg/g and adsorption percentage 97%. Adsorption of natural fly ash/zeolite adsorbents 75:25 (w/w) on Pb metal occurs chemically through ionic bonds and physically through van der waals forces, but adsorption tends following the Langmuir isotherm with adsorption capacity of 0.983 mg/g.

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