Synthesis of Zeolite from Lapindo Mud Using the Hydrothermal Method as a Lead Heavy Metal (Pb) Adsorbent in Industrial Waste

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Abstract

Environmental problems are one of the main problems for developing countries like Indonesia, especially the problem of lead waste (Pb) from industry. If the dangerous heavy metal Pb is discharged into the environment, it can cause various problems in the environment and certainly can threaten human life. If the lead is released into the water around the industry it will certainly be able to flow into the river, even to the sea. Bioaccumulation of Pb in water can cause the formation of toxic organometallic compounds in the body of marine fish, which can allow these compounds to enter the food chain, and can disturb both the environment and human health. Meanwhile, on the other hand there is an event that has long happened that until now and is considered a disaster, namely the Lapindo mudflow. The purpose of this study is to find out how to reduce the content of heavy metals Pb produced from industrial waste by adding synthetic zeolites made from Lapindo mud. Zeolite is a substance that can function as an adsorbent for various types of waste, one of which is heavy metal. In this study, qualitative and quantitative tests were carried out on the influence of the mass of zeolite based on Lapindo mud to the binding of Pb heavy metal ions. Qualitative data analysis is done by describing the results of observations of the presence of white deposits that are formed as the final results of qualitative tests. Quantitative data analysis is performed by weighing the mass of white deposits that are formed. Based on the results of the study, obtained a relationship that is the greater the mass of zeolite, the greater the decrease in levels of heavy metal Pb in liquid waste. According to the results obtained in this study. In this study, the best zeolite mass used in adsorbing Pb metal ions was 2 grams. In the treatment with 2 grams of zeolite mass it has the best ability to absorb heavy metal Pb up to 90.15%.

Keywords
adsorbtion, zeolite, lapindo mud, and lead(Pb).

1. Introduction

The development rate of the industry in Indonesia certainly affects the quality of the surrounding environment. The increasing number of industries will cause an increase in pollution of water sources originating from industrial waste discharged into the waters without prior processing (Agustina, et. Al., 2014). One negative impact of an industry is that it produces wastewater. Industrial wastewater usually contains many toxic and hazardous chemical compounds and also contains heavy metals. The presence of heavy metals can damage the ecosystem in the environment and disrupt human health whose risks are very dangerous.

One of the most common heavy metal wastes produced by almost all industries is lead heavy metal (Pb). Heavy metal Pb is a pollutant that has a harmful effect because of its nature which cannot be deciphered biologically and is stable. Heavy metal elements can be spread on the surface of the water. Generally, the path of waste from industrial waste material that uses Pb will damage the environmental environment of the water that it enters (Palar, 2004). Lead / Pb is one of the heavy metals that are harmful to humans. The maximum lead level in waters recommended by WHO is less than 0.01 ppm (Ensafi and Shiraz, 2008). Wastewater containing Pb compounds that pollute water bodies with high concentrations can cause death in aquatic biota. Pb concentrations reaching 188 mg / l can kill fish in waters, if living aquatic biota in water bodies containing Pb compounds at a concentration of 2.75-49 mg / l and exposed for 245 hours will cause death in crustaceans while in Pb concentrations that dissolved of 3.5-64 mg / l exposed for 168-336 hours will cause Insecta death (Ensafi and Shiraz 2008). In addition to the danger for Pb heavy metal aquatic biota, it is also a danger for human survival, Pb metal accumulation in the body can cause chronic poisoning. As for its effects on human health, it can cause brain damage, spasms, and death. Its toxicity is in small doses and takes place continuously in children can cause neurotoxic (nerve poison) and behavioral abnormalities. Lead is a poisonous substance in the form of elements, compounds or ions. Therefore, it is necessary to handle waste that contains mercury species. So far, waste containing lead can be handled generally through the adsorption method using activated carbon However, the handling of mercury using the adsorption method using activated carbon still has weaknesses, the adsorbent material is still dependent on natural materials, one of which is wood. Currently the demand for wood for the furniture and paper industry is very high. If wood is continuously used, it will certainly cause environmental balance to be disturbed. If plants continue to decrease, CO_2 pollution will increase, because plant photosynthesis will occur even less. Therefore it is necessary to have an alternative adosorbent material that can be used to absorb lead from industrial waste.

Meanwhile, on the other hand there is an event that has long happened that until now and is considered a disaster, namely the Lapindo mudflow. According to Trimayanto, et. al. (2019) Lapindo mud is a natural gas drilling event that occurred in Sidoarjo Regency, East Java, which resulted in adverse impacts on the community on their lives. Lapindo mud is indeed a mudflow disaster which until now has not been able to be stopped, but it would be nice for academics from students to conduct research to explore the potential of Lapindo mud to be something that is beneficial to the community. So far it has never been thought that Lapindo mud has a lot of potential to be utilized as something useful. Lapindo mud is a natural resource (SDA) which is rich in valuable minerals, which can be used as raw material for making zeolites. Zeolite is one material that can be useful as an adsorbent for heavy metals, one of which is Lead (Pb).

According to Mustopa (2013), Lapindo mud contains various silica minerals and polysilicate salts which are compounds of raw material for making zeolites. Zeolite is a crystalline silicate material with a highly ordered structure and high porosity. The general formula for zeolites is $M_{x/n}(Al_2O)_x(SiO_2)_y.zH_2O$ (M: cations with a validation n outside the interchangeable framework). The advantages of zeolite as an adsorbent are having large and uniform pores, large absorption capacity, and can be applied over a wide temperature range. If zeolite is put into a waste containing heavy metals, the M cation is a metal cation that can be exchanged with heavy metals such as Pb. This chemical adsorption occurs which causes a decrease in heavy metal content in the waste. Therefore, it is necessary to conduct research related to the synthesis of zeolites with very economical and abundant raw materials such as Lapindo mud.

Moving on from these various problems and potentials, in this scientific work research was conducted on the synthesis of zeolites from Lapindo mud as an adsorbent of heavy metal lead (Pb). It is expected that the synthetic zeolite from Lapindo mud that will be developed can help in the handling of lead heavy metal waste which mainly comes from industrial waste such as the agrochemical industry, the paint industry, the ceramic industry and others. In this study, testing on samples containing Pb heavy metal ions at certain concentrations. Zeolite that has been made previously is used to absorb the remaining active ingredient of heavy metal Pb in samples with various zeolite mass variations.

2. Materials and Methods Used

2.1 Tools and Materials

The tools used in this study were 500 ml beakers, autoclaves, ovens, AAS spectrophotometers, analytical scales, 100 ml measuring cups, pestle mortars, spatulas, while the materials used in this study were Lapindo mud, aquades, HCl 2M, 7M NaOH, solid Al_2O_3, $PbNO_3$ solution with a concentration of 25 g/L.

2.2 Methods of Making Silica

Lapindo mud that has been dried, crushed and sieved 100 mesh and then weighed as much as 100 grams, then washed using 2 M HCl solution at a ratio of 1: 2 (w/v) for 1 hour. The results are filtered using filter paper filter paper and the sediment is washed using aquademineral until neutral. The results were reacted with 7 M NaOH solution in a ratio of 1: 2 (w/v) and stirred using a magnetic stirrer for 4 hours at 40ºC. After sodium silicate is formed then the precipitate is separated with filtrate using filter paper and the filtrate is heated at 40ºC for 10 minutes, then titrated with 3M HCl solution until the pH approaches 7 and white silica precipitate is formed. The resulting silica precipitate is then filtered using filter paper. The precipitate was washed using aquademineral aimed at removing impurities, and the SiO_2 precipitate was dried at 100ºC for 2 hours.

2.3 Method of Making Zeolite

The zeolite synthesis method from Lapindo mud uses the hydrothermal method. Lapindo mud is washed with distilled water for 1 hour and the mud is dried in the oven to dry. After drying, the mud is crushed and sieved using a 150 mesh sieve. then the mud is soaked using 2 M HCl in a ratio of 1: 2 for 3 hours. Then rinsed with neutral aquades (pH = 7) then dried at 100-110°C until dry. Then filtered and taken the precipitate. Then the precipitate was reacted with 7 M NaOH at a temperature of 90°C in a ratio of 1: 2 and stirred for 4 hours to form a sodium silicate solution. Then added Al_2O_3 and distilled water and stirred for 30 minutes until homogeneously mixed. Then the mixture was incubated for 24 hours and then put in an autoclave and heated in the oven for 48 hours at 90°C. then the solids are then washed with distilled water and crystallized with a hydrothermal reactor at a temperature of 100°C-110°C for 48 hours. The formed crystals are washed with distilled water to pH = 7-8, then dried at 100°C for 24 hours.

2.4 Zeolite Adsorption Power Test Against Pb(II) Ions

To find out the binding of Pb metal waste in the sample can be done through a qualitative test method with the following stages:

a. zeolites that have been made are placed in 5 chemical beakers with zeolite mass variations of 0 each; 0.5; 1; 1,5; 2 grams.
b. 10 mL of $PbNO_3$ solution was added with a concentration of 25 g / L in each beaker.
c. Leave for 60 minutes while stirring occasionally so that the zeolite can bind the active ingredients of the sample and than separating the filtrate.
d. The filtrate from each treatment was put into 4 test tubes for a qualitative test.
e. Each filtrate added 3-5 drops of hydrochloric acid.
f. If after the addition of hydrochloric acid does not form a white precipitate, then the adsorption test is qualitatively declared successful.

To find out the adsorption of Pb metal waste in the sample can be done through quantitative test methods with the following stages:

a. The sediment from the qualitative test process is filtered using filter paper (which has weighed its mass).
b. Sediment in filter paper is roasted to a temperature of 100ºC until its mass is constant.
c. Sediment and filter paper are weighed.
d. To find out the mass of the sediment, the mass from the results of the process is reduced by the mass of the initial filter paper.

3. Results and Discussion

3.1 Silica extraction from Lapindo Mudflow

Lapindo mud used is mud taken at a distance of ± 1 km from the center of the blast. Lapindo mud that has been dried, crushed, and sieved 100 mesh and then weighed as much as 100 grams, then washed using 2 M HCl solution with a ratio of 1: 2 (w/v) for 1 hour aims to remove impurities that are solution in acid, then filtered using filter paper filter paper to separate the filtrate and its sediment. The precipitate was washed using aquademineral until neutral aimed at removing residual chlorine, then reacted with a 7 M NaOH solution in a ratio of 1: 2 (w/v) aimed to form sodium silicate compounds, stirring using a magnetic stirrer for 4 hours at 40ºC in order to homogenize , and heating aims to decompose NaOH compounds into Na^+ and OH^-. The Na^+ ion formed then binds to $[SiO_3]^{2-}$.

In the SiO_2 extraction process, the high electronegativity of the O atom causes Si to be more electropositive, resulting in an intermediate $[SiO_2OH]^-$ which is unstable. Dehydrogenation will occur here and the hydroxyl ion will bind with hydrogen to form a water molecule, two Na^+ ions will balance the negative charge that is formed and interact with the SiO_3^{2-} ion, to form sodium silicate. The reaction mechanism for the formation of sodium silicate is written in figure 1. The results of the sodium silicate obtained are then separated from the black Lapindo silt precipitate using filter paper obtained by sodium silica which is clear brown and thick in color.

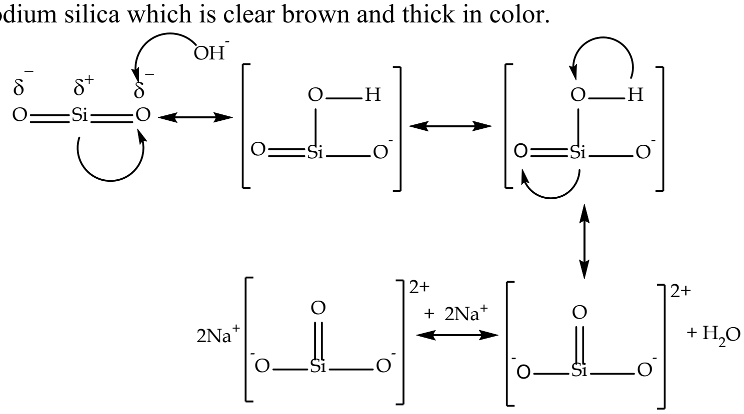

Figure 1. Mechanisms for the reaction of sodium silicate formation.

After sodium silicate is formed then the precipitate is separated from the filtrate using filter paper to separate the precipitate and the filtrate. The filtrate is heated at 40^oC for 10 minutes, then titrated with 3M HCl solution until the pH approaches 7 and a silica-white precipitate is formed. The resulting silica precipitate is then filtered using filter paper to separate the filtrate from the precipitate. The precipitate was washed using 14 aqua deminerals aimed at removing impurities, and the SiO2 precipitate was dried at 100^oC for 2 hours.

3.2 Zeolite Preparation

The zeolite synthesis method from Lapindo mud uses the hydrothermal method. This method was chosen because this method is one of the most effective methods to be used in making zeolites. Zeolite extracted from Lapindo mud was mixed with Al_2O_3 (Merck) and aquademineral and stirred for 30 minutes until homogeneously mixed. Then the mixture was incubated for 24 hours and then put in an autoclave and heated in the oven for 48 hours at 90°C. The solids formed are washed with distilled water and crystallized with a hydrothermal reactor at a temperature of 100°C-110°C for 48 hours. The formed crystals are washed with distilled water to pH = 7-8, then dried at 100°C for 24 hours.

3.3 Zeolite Adsorption Power Test Against Pb (II) Ions

The zeolite qualitative test was carried out by adding 100 mL of Lead(II) Nitrate solution with a concentration of 0.01 M (colorless solution) and allowed to stand for 3 hours while occasionally stirring. Next, the solution in the beaker is filtered with filter paper, to form residues and filtrate. The filtrate is put into a test tube and 3-5 drops of hydrochloric acid (0.1 M) (colorless solution) are added. This test is positive for Pb^{2+} ions if there is a white precipitate in the form of $HgCl_2$ based on the equation:

$$Pb^{2+} + 2HCl \rightarrow PbCl_2 + 2H^+$$

Based on testing, qualitative and quantitative data are obtained as follows:

Table 2. Presence of deposits and sediment periods in the results of qualitative and quantitative tests.

No.	Zeolite Mass (g)	Precipitant Mass (g)
1.	0 (control)	0,0385
2.	0,05	0,0283
3.	0,1	0,0194
4.	0,2	0,0110
5.	0,4	0,00379
Final percentage (%)		9,8442
Percentage of Decrease (%)		90,1558

Information:
+ : Deposits are present
- : No deposits

Testing the presence of lead(II) ions is carried out by adding 3-5 drops of hydrochloric acid solution to the filtrate. If after adding hydrochloric acid white $PbCl_2$ precipitate is not formed, the adsorption test is qualitatively declared successful. The product of this research is zeolite. These compounds are compounds that can adsorb heavy metal ions such as Lead(II) (Pb^{2+}) ions.

In this study, the sludge which has been activated by HCl successfully binds and precipitates heavy metal ions. This is evidenced by the presence of a white precipitate in the filtrate test residual binding of the active ingredient by zeolites. Based on the tests that have been done, the mass of sludge produced decreases with increasing concentration in each treatment. The following is a graph of the results of the analysis of sediment mass data for each treatment:

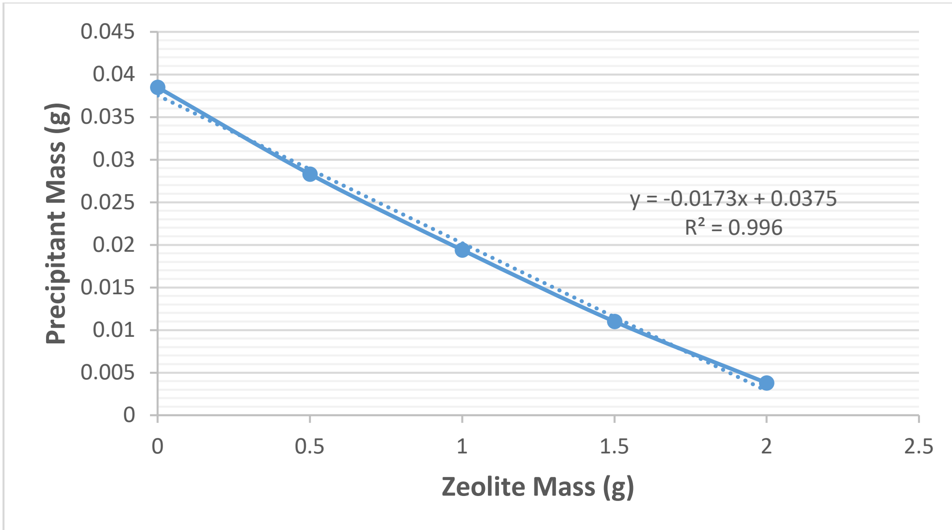

Figure 2. Graph of the effect of zeolite mass on sediment mass.

Based on Figure 2, the concentration of HCl activator is very influential on the binding capacity of sludge with lead ions. In the process of activation of Lapindo sludge shows that the greater the concentration of HCl, the greater the zeolite's binding capacity to lead(II) metal ions. According to the results obtained in this study, zeolite has a very good influence on the reduction of lead(II) heavy metal ion levels.

Zeolites are hydrated aluminosilicate minerals from porous structures with valuable physicochemical properties, such as cation exchange, molecular sifting, catalysis and absorption (Hedstrom, 2001). In zeolite structures, three relative components are found: an aluminosilicate framework, an exchangeable cation, and zeolytic water. The general chemical formula for zeolites is $M_{x/n}[Al_xSi_yO_{2(x+y)}]\cdot pH_2O$ where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is the cationic charge; y / x = 1–6, p / x = 1–4 (Agustina et al., 2014). The application of zeolites for water and wastewater treatment has been realized and is a promising technique in the environmental cleaning process. Zeolites are often used as a binding agent for ammonium ions and heavy metal removal because of the nature of ion exchange and several review papers have appeared (Wang & Peng, 2010). Apart from the presence of cations in water, anions and many organic compounds are served in wastewater.

The mechanism that occurs in the adsorption process in zeolites is physical adsorption. Lead(II) ions in the form of heavy metal ions are not completely bound to the surface of the adsorbent so that the adsorbate can move from one part of the surface to another. Adsorption occurs through heavy metal ions that enter the zeolite pore, then it is bound by negative ions found in the zeolite. In addition, a large surface area is certainly also related to the adsorption that occurs. With the increasing surface area of the zeolite, it will indirectly cause the negative charge contained in the zeolite to become more so that more heavy metal ions can be bound by the zeolite.

These negative charges are formed from the three-dimensional structure of tetrahedral silicate $[SiO_4]^{4-}$ and alumina $[AlO_4]^{5-}$ which are bound through oxygen atoms. The silicon atom is surrounded by 4 oxygen atoms so that it forms a network with a regular pattern. Some places in this network, silicon atoms are replaced with aluminum atoms, which are only coordinated with 3 oxygen atoms. The existence of this aluminum atom as a whole will cause zeolites to have a negative charge that can be used as an ion exchange with heavy metals. The ion is then captured in the zeolite pores and attached to the zeolite, so the concentration of metal ions in the solution can be reduced.

4. Conclusions and Recommendations

4.1 Conclusions

Lead (Pb) heavy metal content in industrial waste can be reduced by adding zeolite. In the adsorption process, it shows that the greater the mass of zeolite, the greater the decrease in lead content (Pb). The most effective zeolite mass in absorbing Pb^{2+} metal in $PbNO_3$ is at mass 2 grams with an effectiveness of 90.15%.

4.2 Recommendations

It is recommended for researchers or reviewers of this material, including characterization of zeolites such as using XRD and SEM-EDX instruments, to be able to find out the character of the zeolites produced and to apply zeolite adsorbents that have been developed in industry, so that the problem of lead waste in the industry can be immediately resolved.

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Biography / Biographies

Sigit Trimayanto is an Educator in Education Laboratory Indonesia majoring in Chemistry. Mr. Trimayanto holds a Bachelor of Education in Chemistry from State University Surabaya. He is a project leader in this research at State University of Surabaya, East Java. He once won various awards, one of which was third place in the Chemical Engineering Paper Competition 2019 held at Riau University, Indonesia. He is also one of the researchers who has published various scientific works in various national and international journals and proceedings.

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