

Enhancement of Kaolin Adsorbent Capability of Modification Result with Organic Compound in Absorbing Pb^{2+} Metal in Water

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ABSTRACT : In this research was conducted by increasing the absorption of kaolin in reducing Pb^{2+} metal in water by modifying kaolin with polyphosphate, surfactant, and modified Chitosan we call it are organokaolin. The aim of this research to optimize the more specific metal absorption in absorbing Pb^{2+} metal in water using kaolin that had been modified with organic compound, so that the absorption power increased. Before being modified, the kaolin was activated using HNO_3 . The method used here was to mix kaolin with organic compound in ratios of: 1:0, 1:2; 1:3; 2:1 (g of solid : ml of liquid). The metal concentration was determined at 10 mg/L, and the stirring speed was 100 rpm with the stirring time (contact time) varied which were 0, 30, 60, and 90 minutes, at the temperature of 55°C. The metal concentration was measured using Atomic Absorption Spectrophotometer (AAS), while the characteristics were using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). The results of this research indicated a decrease in Pb^{2+} level in water between 78% - 85.63%, and could increase absorption by 78%.

KEYWORDS-Adsorbent, kaolin, chitosan, polyphosphate, metal, surfactant

I. INTRODUCTION

Kaolin is a type of clay, and is widely available in Aceh Province, where its utilization has not been carried out to the fullest. Meanwhile, with the development of science and technology, it has an impact on environmental pollution, especially the presence of metal in water that can interfere with health. The potential of kaolin in Indonesia is around 66.21 million tons, consisting of 12.95 million tons of proven reserves, 26.57 million tons of designated reserves, and 26.70 million tons of inferred reserves. Those potential reserves are scattered in several regions such as West Kalimantan, South Kalimantan, Bangka and Belitung, with good enough quality, especially to be used as ceramic raw material. Therefore, one of the efforts is the use of kaolin as an adsorbent in absorbing metal in water. However, in the utilization as an adsorbent media, a treatment is needed so that the absorption of the metal can increase, and the absorption

is maximum. Increased absorption, or optimization of zeolite and kaolin as adsorbents, can be done through physical and chemical activation. The physical activation process is carried out by heating (calcination). This heating aims to vaporize the water trapped in the pores of zeolite and kaolin crystals thus the number of pores and specific surface area increases. Chemical activation can be done by using a solution of hydrochloric acid or sulfuric acid which aims to clean the surface of the pore, to remove disruptive compound, and to rearrange the location of atom that can be exchanged.

Kaolin is an inorganic polymer which is a natural mineral from the silicate group with a layered structure belonging to the inorganic ion exchanger, so it is able to capture ions from the outside with the aid of water. The presence of negative ions is due to the relatively small ratio between silica and alumina (Si/Al), and also the presence of oxygen and

hydroxyl groups on the surface of kaolin. Kaolin is still a type of zeolite and bentonite, but zeolite and bentonite have better or higher absorption compared to kaolin, especially when compared to activated carbon, therefore, some efforts are needed to increase the absorption of kaolin. Kaolin itself has been widely used as an adsorbent such as adsorption of lead, zinc, and cadmium, by modifying kaolin and polyphosphate [1], Absorption in Gas polluter [2].

Kaolin is widely used in various industries such as the paper industry, ceramics, and so on. Clay is also widely used as an alternative adsorbent because it has a large surface area, high porosity, high abundance, and a relatively cheaper price, compared to other adsorbents. However, if it is not modified first, and when applied as an adsorbent, kaolin gives less than optimal results due to its easy-to absorb water, and the pores are often not uniform.

From the information above, the use of kaolin as an adsorbent for water treatment in general is still very minimal, except the use of kaolin as metal absorption. Apart from being a metal remover, kaolin also has the potential to reduce color and odor in water, and the absorption of SO₂ gas from residual gas. The use of activated charcoal by using H₃PO₄, H₂SO₄, and HCl activation to eliminate odors in tapioca waste, has been carried out where optimal results are obtained using H₂SO₄ as its activator [3] Another application for the use of modified adsorbent, as a color removal of congo red (CR), is by modifying bentonite with surfactant. The addition of surfactant aims to increase the absorption, where bentonite before being modified can absorb CR of 37.10 mg/g, and after modification with surfactant, an increase in absorption becomes 210.10 mg/g [4]. The removal of direct yellow 50 (DY50), direct red 80 (DR80), and direct blue 71 (DB71) dyes from aqueous solutions, has been carried out by varying various types of adsorbents namely activated carbon, raw kaolin, and montmorillonite. The results of this research showed that raw kaolinite and montmorillonite, which were effective in removing direct dyes from aqueous solutions in the concentration range, were investigated. Because clay types are abundant and inexpensive adsorbents, this can be considered for removing dyes directly from aqueous solutions,[6].

In this study will learn several treatments for kaolin in increasing its absorption by physical treatment, namely by the process of calcination.

Another treatment is by modifying kaolin with several organic compounds such as polyphosphate, surfactant, and chitosan. This research also studies the mechanism of increasing the absorption of kaolin which will be modified with organic compound applied in water treatment containing metal, as well as how the mechanism of increasing active power and increasing the ability of absorption in its application in the water treatment process. In addition, the characteristics of some metals that are absorbed in adsorbent will be studied by using Fourier Transform InfraRed (FTIR), while the changes that occur due to the presence of adsorption metal on adsorbent are done by using the Scanning Electron Microscope (SEM) test.

III. METHODOLOGY

In this research, the material used was Kaolin from Sawang District, North Aceh Regency; K₂HPO₄ polyphosphate; Surfactant; and Chitosan, derived from commercial materials used for the modification process of activating kaolin as an adsorbent. Making metal waste was done by making stock solution. Distilled water, KOH, and HNO₃, were used in the activation process using bases and acids to remove the level of metal and the organic compound contained in kaolin to increase their absorption. The experiment was carried out using kaolin that had been mashed with a size of 80 mesh before the initial activation process. The initial metal concentration of 100 mg/L as a stock solution then diluted to up to 10 mg/L, with the stirring speed of 100 rpm. In the contacting process between adsorbent with metal, the sampling times were varied, 0, 30, 60, and 90 minutes, with the ratio of kaolin to surfactant and polyphosphate, which were 1:0, 1:2, 1:3, and 2:1. The data to be taken was the concentration of metal ion after the adsorption process using AAS equipment; the characteristic of the modified adsorbent was carried out using FT-IR (Fourier Transform Infrared Spectroscopy); and used Scanning Electron Microscopy (SEM) to see the morphology.

Initial Activation of Kaolin

Kaolin was crushed and sieved to obtain 80 mesh particles, then heated at 300°C for 3 hours in the furnace. After cooling, it was mixed with KOH at a ratio of 2:1 (kaolin in g : KOH in ml), and allowed to stand for 1 hour at a temperature of 200°C. The result of mixing was then dissolved with distilled

water (100 gram/1000 ml water); after stirring, ripen for 12 hours. Then the ripening result was reacted at 90°C for 4 hours. Then being washed with distilled water until neutral, and dried in an oven at 110°C for 2 hours. Being washed again with HNO₃ in a ratio of 2:1, then allowed to stand for 1 hour at a temperature of 110°C. The result of mixing was then dissolved with distilled water (100 gram/1000 ml water); after stirring, allowed to stand for 10 hours, and stored in a desiccator.

Modification of Kaolin with organic compound and examination

Kaolin solids were mixed with organic solutions (Polyphosphate, Surfactant, and Chitosan) in the ratio of 1:0, 1:2, 1:3, and 2:1 (g of solid : ml of liquid). The mixture was stirred using a shaker for 3 hours at a speed of 100 rpm. After that, the precipitate was filtered and washed with *aquabides*, and dried for 4 hours; kaolin that had been modified with organic compound was then stored in a desiccator. The metal absorption step was carried out by inserting 2 grams of *organokaolin* into the *erlenmeyer*, then 100 ml of artificial waste sample was put into the 250 ml *erlenmeyer*, and mixed with *organokaolin* with a certain ratio (according to the experimental design). After that, it was closed using aluminum foil, then put into the incubator shaker with a stirring speed of 90 rpm. Sampling was carried out at intervals of 0, 30, 60, and 90 minutes; the taking time at 0 minutes was intended to determine the initial conditions of the sample, so that the absorption efficiency can be known. Metal content was tested using AAS, and the characteristic of the adsorbent was analyzed using FTIR.

IV. RESULT AND DISCUSS

Performance of Kaolin-Polyphosphate Adsorbent

The modification of kaolin as an adsorbent was modified with polyphosphate to see the ability of the adsorbent to reduce level of lead metal in two types of waste, namely artificial waste and actual waste. The use of actual waste was done to see the performance of the adsorbent modification, because in the actual waste there was not only Pb²⁺, but there were also other metals or other organic compounds as confounding compounds that can affect the adsorbent absorption. For more details, see Figure 4.1. below:

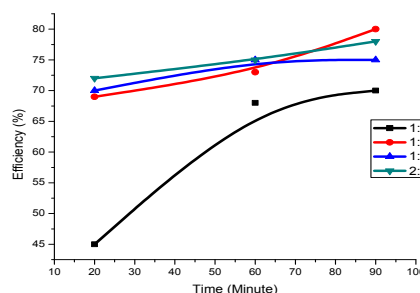


Figure 4.1. Decreased level of Pb²⁺ metal with increasing contact time by modification of kaolin-polyphosphate adsorbent.

An efficiency of Pb²⁺ metal reduction also occurs at From Figure 4.1. The modification performance of kaolin adsorbent with polyphosphate has the same tendency to occur with *organokaolin* surfactant. The optimum condition occurs at a ratio of 1:2. A very significant increase in the efficiency of the Pb²⁺ removal occurs up to 30 minutes, subsequently the efficiency improvement is very slight, and tends to approach a constant condition. That is because the adsorbent starts to saturate so that there is no increase in efficiency, and the graph tends to be constant. The most significant increase in the contact time of 30 minutes, where the adsorbent without modification is lower in efficiency than the adsorbent that has been modified with polyphosphate. The greater efficiency increases with increasing contact time, this happens because the longer the contact time, the more adsorbent is able to absorb Pb²⁺ metal in water. Over time, the adsorbent conditions will saturate due to all the cavities of the adsorbent have been filled with Pb²⁺ metal, and negative ion in polyphosphate has as much binding to Pb²⁺ metal in water.

Performance of Kaolin Adsorbent Modified with Surfactant

In this research, surfactant was modified with kaolin adsorbent; the type of surfactant used is the anionic type. The use of anionic surfactant was due to the use of artificial waste which would be absorbed by the adsorbent that was Pb²⁺ metal waste which contained positive ion. Research data can be seen in Figure 3.2. below

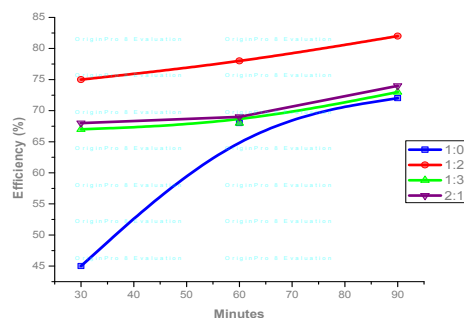


Figure 4.2. Decreased level of Pb^{2+} metal with increasing contact time by modification of Kaolin-Surfactant adsorbents.

The increase in the efficiency of the reduction of Pb^{2+} metal escalates with increasing contact time for the whole modification in different ratios. The most significant increase occurred at contact time of 30 minutes, between the unmodified kaolin adsorbent, and the modified kaolin with surfactant. This shows that there is an increase in the performance of adsorbent due to the presence of anionic kaolin which gives an increase in the number of negative ion (anion) in the adsorbent, thereby capturing more Pb^{2+} metal in water.

In the adsorbent modified with surfactant, a significant decrease in lead metal was seen in *organokaolin* adsorbent in a ratio of 1:2, with a reduction capacity of 78.72%, and with a contact time of 90 minutes. The reduction phase occurred from a concentration of 100 ppm to 24.6321 ppm at 30 minutes contact time, then in the 60th minute to 24.2405 ppm, and at the 90th minute to 21.2847 ppm. Based on the lowest concentration reduction, the optimum condition of *organokaolin* adsorbent from surfactant was at a ratio of 1:2 at the 90th minute.

Performance of Modified Kaolin Adsorbent with Chitosan.

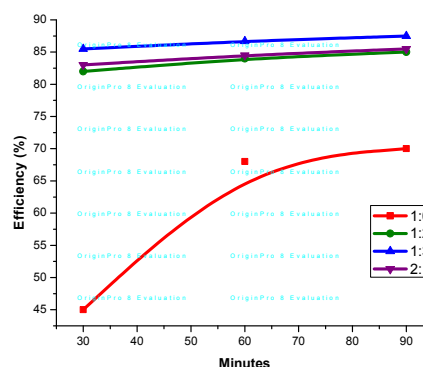


Figure 4.3. Decreased level of Pb^{2+} metal with increasing contact time by modification of Kaolin-Chitosan adsorbent.

An increase in the performance of adsorbent occurs very significantly, between before being modified by chitosan; this can be seen in Figure 3.3. The ability of kaolin adsorbent modified with chitosan can reduce Pb^{2+} metal content by 85.63%. This is due to artificial waste having no anion, thus kaolin modified with chitosan is more efficient at absorbing Pb^{2+} metal in water.

From Figure 3.3., it is also seen that the use of chitosan, that is suitable for reducing Pb^{2+} metal content, is the use of chitosan in the ratio of 1:3. This is because the kaolin active group is covered by chitosan so that the active group which plays a lot is the active chitosan group. The more chitosan is used, the higher the percentage of absorption, due to the number of chitosan active group and kaolin active group that play a role in binding Pb^{2+} metal ion, therefore the chitosan active group can adsorb more than the kaolin active group.

Performance of Fourier Transform Infrared Spectroscopy (FTIR)

The result from FTIR analysis

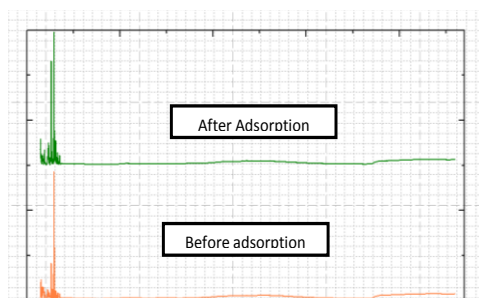


Figure 4.4. FTIR analysis result, before and after modification between Kaolin and Polyphosphate in absorbing Pb^{2+} metal in water.

At the first peak in the natural kaolin curve, there is an H_2O group with a wavelength of 206.38 cm^{-1} ; but at the first peak in the preparation kaolin curve, the group is transformed into a Si-O-Si group with a wavelength of 688.59 cm^{-1} . The loss of the H_2O group is caused by a heating of 200°C when kaolin is prepared. At the next peak, in natural kaolin there is a Si-O functional group with a wavelength of 750.31 cm^{-1} ; but in kaolin preparation, the group is transformed into OH deformation group which is bound to a cation with a wavelength of 914.26 cm^{-1} . That is because kaolin preparation is activated with HNO_3 and KOH so that the functional group changes. But at the last peak, both curves show that there is the same functional group, O-H Octahedral with different wavelengths.

The same condition was also seen in the result of the modification between kaolin and surfactant; the results of the FTIR analysis can be seen in Figure 4.5. below.

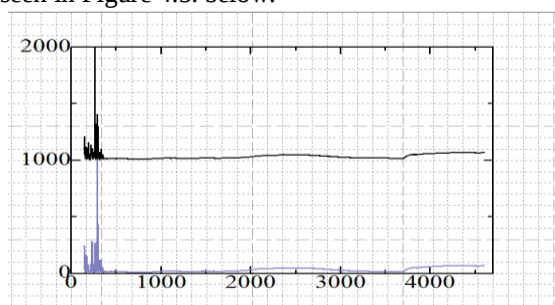


Figure 4.5. The result of FTIR analysis, before and

after modification between Kaolin and Surfactant in absorbing Pb^{2+} metal in water.

From Fig. 4.5. it is seen that at the first peak in the curve, kaolin is modified with surfactant before the adsorption process, there is a Si-O-Al group with a wavelength of 493.78 cm^{-1} ; and at the first peak in the curve, kaolin is modified after the adsorption process does not change, but with a different wavelength of 489.92 cm^{-1} . At the next peak, on the kaolin before adsorption, there is a Si-O functional group with a wavelength of 1112.93 cm^{-1} ; but on kaolin after adsorption, it turns into a stretching C-O group with a wavelength of 1182.36 cm^{-1} . That is because kaolin has been contacted with lead ion so that the functional group changes. However, at the last peak of the two curves, it shows that there is the same functional group, O-H Octahedral with different wavelengths.

CONCLUSION

The conclusions from the results of this research can be drawn as follows:

1. The modification among kaolin-surfactant, kaolin-polyphosphate, and kaolin-chitosan, can reduce the Pb levels up to 78% - 85.63% with various conditions.
2. The modification of kaolin and modifier can increase the Pb absorption efficiency from 44% to 78% in the comparison.
3. The efficiency and the adsorption capacity are directly proportional to the concentration of waste; meaning that the greater the concentration of waste, then the greater the efficiency and the adsorption capacity.

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