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Activation of Kaolin Minerals from Ketapang Regency as Cu Metal Adsorbent Material

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ABSTRACT

Kaolin is a term given to a group of phyllosilicate minerals whose layers have a 1:1 structure with $Al_2Si_2O_5(OH)_4$ composition. This type of kaolin phyllosilicate mineral is commonly known as a clay mineral. The kaolin clay group consists mainly of the kaolinite mineral or better known as white clay. Kaolin is widely applied in industries such as paper, ceramics, rubber, plastic, paint, fiberglass, cosmetics, etc. The processing of kaolin as an adsorbent can be carried out using physical activation, where the kaolin is washed and separated from the impurities and dried into a powder. Then the chemical activation of kaolin will go through a leaching process using HCl with optimal concentrations aimed at separating kaolin from impurities that are still chemically bound to kaolin. The results of the characteristics show recovery of 71.42% to 81.2% and moisture content <2%. The chemical composition of kaolin containing SiO_2 was 53.32–67.32%, Al_2O_3 was 28.22–30.47%, Fe_2O_3 was 1.32%, CaO was 0.03%, MgO was 0.20%, MnO_2 was 0.01%, K_2O of 0.86%, NaO of 0.01%, Cr of 0.01%, LOI of 11.03%. The adsorption test results on Cu metal in $CuSO_4$ solution showed the absorption of 62–93% of Cu metal which was adsorption.

Keywords: kaolin, physical activation, chemical activation, adsorbent, metal adsorption.

INTRODUCTION

Kaolin is a clay mineral formed by phyllosilicate-structured aluminum silicate hydrate with $Al_2Si_2O_5(OH)_4$. Kaolin is generally gray, orange-yellow, or reddish. This kaolin contains very fine grains, soft and less plastic when mixed with water. Potential kaolin reserves in Indonesia are around 66.21 million tons consisting of 12.95 million tons of proven reserves, 26.57 million tons of indicated reserves, and 26.70 million tons of inferred reserves [1]. The potential reserves are distributed in several areas, including West Kalimantan, South Kalimantan, Bangka Belitung Islands, and other potentials are located on the island of Sumatra, particularly North Sumatra, Java Island, and North Sulawesi [2].

Kaolin minerals consist of kaolinite, nacite, and halloysite, with kaolinite being the main mineral. Oxides like Fe_2O_3, TiO_2, CaO, MgO, K_2O, and Na_2O are often present in kaolin as impurities. The composition of pure kaolin is SiO_2 46.54%, Al_2O_3 39.5%, and H_2O 13.96% [3].

Ketapang is one of the West Kalimantan Province districts with great potential in providing kaolin materials. Kaolin from West Kalimantan contains quartz, kaolinite, and illite minerals, with a whiteness value of 87.74 and a CEC (Cation Exchange Capacity) value of 38.74 meq/100 grams. The kaolin is slightly brownish (slightly gray) because it is

influenced by geographical conditions, which are peatlands [1].

Kaolin has many benefits, not only as a ceramic, brick, tile, paper coating barrier, or pharmaceutical material, but the use of kaolin has experienced development along with the various studies on the benefits of kaolin. Currently, kaolin is also widely used as an adsorbent [4], catalyst buffer [5], ion exchanger [6], and many more, depending on the physical and chemical properties of the kaolin.

One way to produce kaolin that can be used and utilized is by activation. The activation process is critical in determining the quality of kaolin produced, both surface area and its adsorption ability. The surface area is closely related to activity because the reaction occurs on the surface. A large surface area will cause more and more reagent molecules to adsorb on the surface so that the activity will increase.

Processing kaolin as an adsorbent is performed by physical activation, where the kaolin is washed and separated from its impurities and dried into a powder. Then, kaolin is chemically activated, where kaolin samples go through a leaching process using HCl, which aims to separate kaolin from impurities that are still chemically bound to kaolin. Adsorbent products are then characterized and tested against metals by calculating the adsorption capacity of the absorbed metals. If the adsorption capacity is good, then the adsorbent can be used as a metal absorbent material (Adsorbent) [8]-[14].

METHODS

The kaolin samples were from CV Surya Prima Kaolin, Bangkal Serai Village, Kendawangan District, Ketapang Regency, West Kalimantan. Initial characterization was carried out to determine the chemical composition of the newly taken kaolin using X-Ray Diffraction (XRD) characterization. The kaolin activation method is divided into two stages, the first activation process is carried out physically, and the second process is carried out chemically. Kaolin that has undergone physical and chemical activation is then tested with kaolin adsorbent activity test with adsorption capacity test using Cu (Copper) metal.

Activation of Kaolin by Physics

First, kaolin minerals were weighed and washed with water (10% Solid: 90% Liquid), then filtered with an 80 mesh sieve, and the filtration results were deposited for one day (Figure 1). The precipitated kaolin is separated and dried in the sun (Figure 2). After drying, weighing, and grinding were carried out until 200 mesh. The sample was analyzed using ICP (Inductive Couple Plasma) to determine kaolin's mineral content after physical activation.

Figure 1. Kaolin was weighed and washed with water.

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Figure 2. Kaolin dried in the sun.

Activation of Kaolin by Chemical

In the second stage, kaolin derived from the physical activation process is then leached by stirring the magnetic stirrer into a beaker glass covered with aluminum foil with HCl solutions of various concentrations of 2, 4, 6, 8, and 10 Molarity at a temperature of 900^{o}C and leaching time for 2 hours. Furthermore, the neutralization stage occurs when the leached kaolin is washed with distilled water until ph 6–7 (neutral). After that, the sample was filtered and dried using an oven at 1300^{o}C for 5 hours and continued with the calcination process using a furnace at 7000^{o}C for 1.5 hours. Grinding and sieving were carried out to a size of 200 mesh, and the samples were ready for adsorption tests on metal samples. The samples were analyzed using ICP (Inductive Couple Plasma) to determine kaolin's mineral content after chemical activation.

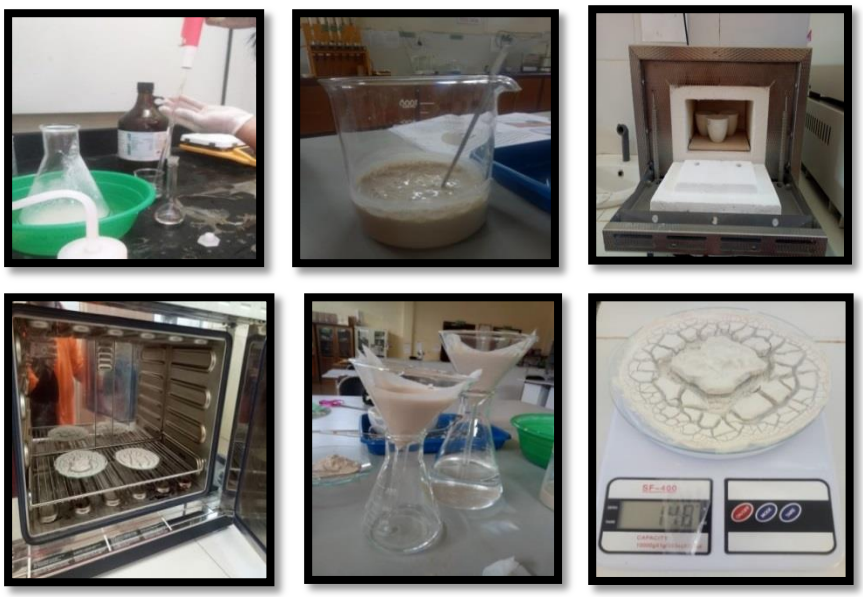

Figure 3. Activation of kaolin processes by chemical.

$CuSO_4$ Metal Solution Adsorption Activity Test

The adsorbent activity test was carried out by weighing the kaolin adsorbent of 5 grams which was then added to the $CuSO_4$ metal solution with a concentration variation of 0.25 ppm; 0.5 ppm; 1 ppm; 3 ppm, and 5 ppm (Figure 4). After that, each sample was stirred for 2 hours, and the stirring results were taken for testing using AAS (Atomic Absorption Spectrophotometer). The AAS method is a quantitative analysis method that aims to determine the levels of absorbed metals, in this case, Cu metal as a parameter.

Figure 4. Concentrate variation for $CuSO_4$ test.

RESULTS AND DISCUSSION

Kaolin Characterization

Kaolin characterization is carried out because kaolin generally consists of a mixture of several types of minerals and mineral content composition. It is necessary to do an initial characterization to find out kaolin's constituent elements/compounds using X-ray Diffraction (XRD) analysis. The results of X-ray diffraction (XRD) analysis can be seen in Figure 5.

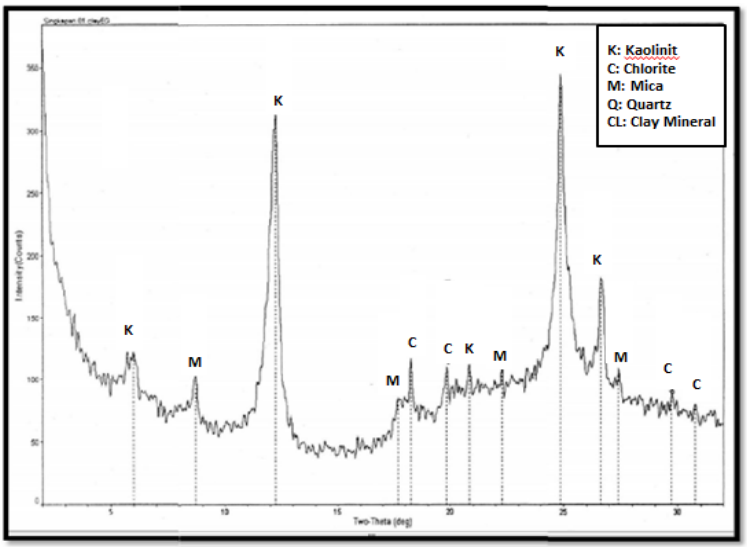

Figure 5. The XRD Diffractogram of kaolin samples.

The XRD diffractogram results of kaolin samples (Figure 5) provide information about the type of mineral and the degree of crystallinity of the structure of the components that compose the sample. The theta (deg) absorption peak pattern shows the sample's mineral type. At the same time, the level of crystallinity of the component structure is reflected by the peak intensity. The main peaks that appear are characteristic peaks of kaolinite and chlorite which are the most kaolin constituent minerals. These minerals are indicated by the highest peak that appears at peak d (Å) = 7.2250 on kaolinite two-Theta = 12.24 and the second highest at peak d (Å) = 3.5786 on kaolinite two-Theta = 24.86. In addition, the XRD analysis provides information on the content

or composition of the minerals in it, as seen in Table 1. The results of the chemical composition test using XRD, as in Table 1, show some of the mineral components contained, such as kaolinite, which has the highest content among other mineral components, namely 74.13% chlorite have a content of 10.38% mica 8.42% and quartz has a content of 6.71%, as well as 0.35% clay minerals.

The qualitative analysis of kaolin samples uses organoleptic methods, including shape, color, taste, and hardness tests. The test results show the shape of the kaolin mineral is solid, slightly white-gray, has no taste (tasteless), and has a hardness level between 2–2.5 Mohs Scale (Table 2).

Table 1. Mineral composition in kaolin samples.

No	Minerals	Test Results (%)
1	Kaolinite	74.13
2	Quartz	6.71
3	Chlorite	10.38
4	Mica	8.42
5	Clay Minerals	0.35

Table 2. Kaolin mineral characteristic test result using organoleptic methods.

No	Test Parameter	Results
1	Shape	Solid
2	Color	Grey/ White
3	Taste	Tasteless
4	Hardness	2 – 2,5 Mohs Scale

Physical Preparation of Kaolin Mineral Sample

Kaolin preparation begins with crushing kaolin mineral chunks into fine-size and washing them. This washing is done using distilled water. This washing removes impurities like quartz sand, iron oxide, titanium oxide, mica, and other impurities such as roots. The use of distilled water is based on the nature of distilled water which is a solvent with a very high level of polarity and has little mineral content so that it does not interfere with the washing process.

After physical preparation, the results obtained are products or kaolin in white flour that has no taste (tasteless) and is clean from impurities. The recovery of kaolin that has gone through the physical preparation process is 71.42%. The physically prepared kaolin was analyzed using ICP. The analysis results show that the chemical composition of kaolin minerals is 53.32% SiO_2, 30.47% Al_2O_3, 1.32% Fe_2O_3, 11.03% LOI, and 1.47% MC. LOI (Loss of Ignition) is a compound lost in the combustion process, while MC (Moisture Content) is the water content contained in kaolin minerals from physical preparation. Complete analysis results can be seen in Table 3.

Table 3. Chemical composition of kaolin from ICP analysis after physical preparation.

No.	Compounds	Test Results (%)
1	SiO_2	53.32 %
2	Al_2O_3	30.47 %
3	Fe_2O_3	1.32 %
4	CaO	0.03 %
5	MgO	0.20 %
6	MnO_2	0.01 %
7	K_2O	0.86 %
8	NaO	0.01 %
9	Cr	0.01 %
10	LOI	11.03 %
11	Mc	1.47 %

Chemical Preparation of Kaolin Mineral Sample

Kaolin samples that have been physically activated are then leached with HCl (hydrochloric acid) concentrations of 2, 6, 8, 10, and 12 Molarity. Leaching aims to separate kaolin from impurities that are still strongly bound to the kaolin structure. In addition, the acid will also dissolve metals trapped in the pores and interlayer spacing on kaolin to clean and enlarge the surface area of kaolin.

Kaolin which has been chemically activated obtained a recovery of 87.1% and the remaining 12.9%. The mineral content of kaolin that has been chemically prepared by ICP analysis shows the composition of kaolin constituent mineral content, which can be seen in Table 4. The analysis results show the constituent elements of kaolin are 67.32% SiO_2, 28.22% Al_2O_3, 0.05% Fe_2O_3 and 10.97% LOI, and 1.25% MC.

Based on the analysis results, it can be seen that the amount of SiO_2 and Al_2O_3 in kaolin samples that have been physically and chemically processed has increased. It shows that the sample preparation is effective enough to clean and activate the kaolin. However, in this case, it has not been done up to the BET analysis stage, which aims to determine how large the pore size (nm), surface area (m^2/g), and total pore volume (cc/g) is.

Table 4. Chemical composition of kaolin from ICP analysis after chemical preparation.

No.	Compounds	Test Results (%)
1	SiO_2	67.32 %
2	Al_2O_3	28.22 %
3	Fe_2O_3	0.05 %
4	CaO	0.01 %
5	MgO	0.13 %
6	MnO_2	0.01 %
7	K_2O	0.82 %
8	NaO	0.01 %
9	Cr	0.01 %
10	LOI	10.97 %
11	Mc	1.25 %

Copper Sulfate ($CuSO_4$) Metal Adsorption Activity Test

The CuSO4 metal adsorption activity test using kaolin aims to determine how much kaolin's ability to absorb $CuSO_4$ metal is. If the ability of kaolin is sufficient in the absorption of $CuSO_4$ metal, then one of the samples can be used to remove the metal contained in groundwater. Metals in water can cause the water to become cloudy, corroded, and scaled. The common technologies used to remove metals like Fe, Mn, Cu, etc., include membrane technology, adsorption, ion exchange, and precipitation. Adsorption is one of the effective water treatment processes and is often used to remove heavy metals.

The adsorption activity test was conducted using Cu (copper) metal. Cu metal is based on the availability of chemicals found in the laboratory. Cu metal in the $CuSO_4$ compound with the concentration of the parent solution used is 50 ppm, where the variation in solution concentration for five adsorbent samples to be tested is a solution of 5 ppm, 3 ppm, 1 ppm, 0.5 ppm, and 0.25 ppm. The $CuSO_4$ metal adsorption test results using Atomic Absorption Spectrophotometer (AAS) can be seen in Table 5.

Based on the test, it can be seen that the ability of kaolin to absorb copper sulfate is excellent compared to before adsorption. It is because kaolin has a large pore or surface area. Kaolin also has a distance between layers in the structure/framework. In the framework/structure of kaolin, there is a negatively charged O group (-) so that it can attract positively charged ions such as Fe^{2+}, Na^{+}, Cu^{2+}, etc.

Table 5. $CuSO_4$ metal adsorption test results using AAS

No	$CuSO_4$ Samples (ppm)	AAS Results (ppm)	Adsorbed (%)
1	0.25	0.030	88
2	0.5	0.0350	93
3	1	0.379	62
4	3	0.36	88
5	5	0.71	85.5

After adsorption with kaolin, the test results showed that the $CuSO_4$ levels decreased (Figure 6). In the initial sample,

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$CuSO_4$ before adsorption amounted to 0.25 ppm; after adsorption and AAS testing, the results obtained were 0.030 ppm, where $CuSO_4$ adsorbed by 88%. In the second sample, the initial $CuSO_4$ content was 0.5 ppm; after adsorption, the results obtained were 0.0350 ppm, where $CuSO_4$ was adsorbed by 93%. The third sample of $CuSO_4$ had initial levels of 1 ppm; after adsorption, the results obtained were 0.379 ppm, where $CuSO_4$ adsorbed by 62%. The fourth sample of $CuSO_4$ had initial levels of 3 ppm; after adsorption, the results obtained were 0.36 ppm, where $CuSO_4$ adsorbed by 88%. For the fifth sample, the initial level of $CuSO_4$ was 5 ppm; after adsorption, the results obtained were 0.71 ppm, where $CuSO_4$ was adsorbed by 85.5%.

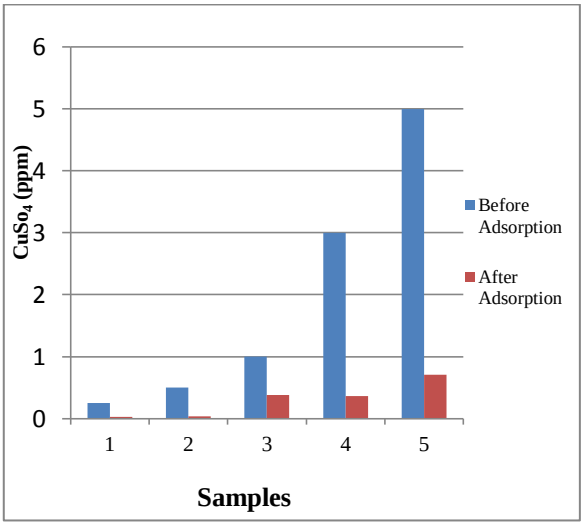

Figure 6. Adsorption test result of $CuSO_4$ test graph.

This condition can occur because kaolin has a skeletal structure containing empty spaces occupied by cations and free water molecules that allow ion exchange and absorption of charged metal ions. Due to the evaporation of water content during physical and chemical activation, the space occupied by free water molecules becomes empty so that when adsorption is possible, the absorption of copper sulfate ($CuSO_4$).

CONCLUSION

Based on the results of experiments, calculations, and observations, it can be concluded that kaolin minerals from Ketapang regency can be activated by physical and chemical activation so that kaolin minerals are produced in the form of adsorbents in optimal conditions. The results of adsorption tests on Cu metal in $CuSO_4$ solution showed absorption of 62–93% adsorbed.

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