INDONESIAN MINING JOURNAL Vol. 15, No. 2, June 2012 : 70 - 78

STUDY OF BATCH SCALE-UP BENTONITE ACTIVATION USING SULFURIC ACID

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ABSTRACT

As a commodity for industrial applications, bentonite is needed in a large number of tonnages. Indonesia retains about 6 hundred million tons of bentonite resources, but its quality does not yet satisfy industrial spesification. Most Indonesian bentonite is calcium-bentonite type. Therefore, it is necessary to activate the material to enhance its absorption ability for decolorizing crude palm oil in cooking oil industries. This research was aimed to obtain the optimal bleaching power in order to decolorize the crude palm oil effectively. The batch scale bentonite activation used raw material from Sarimanggu, Tasikmalaya district, West Java. Since 40 %-solid gave a better average bleaching power value than that of 20 %, the activation was then focused at seeking the best condition with regards to the activition time (hour) and reagent dosages (sulfuric acid). The batch up scale of this research refered to the use of a 100-kg bentonite as the feed. The feed size was -10 mesh. The use of sulfuric acid was 2.5 to 20 % (equivalent to 0.13 to 1.02 N) for 20 % solid and 2.5 to 15 % (equivalent to 0.34 to 2.04 N) for 40 % solid. A series of activation times was 1, 2, 3, 4, and 5 hours. It started when sulfuric acid has been depleted. Sampling was completed for each hour when a sample was neutralized until pH = 7. The sample was dried and the rest of bentonite slurry was flowed into a dilution tank to be neutralized using water. Condition of 1-hour activation and 7.5 %-sulfuric acid (equivalent to 1.02 N) provided the best bleaching power value (88 %).

Keywords: batch scale-up, bentonite, activation, bleaching power

INTRODUCTION

Bentonite, a smectite group of clays minerals, contains an octahedral sheet between two tetrahedral sheets (Kirali and Lacin, 2006). The mineral has been widely used in a number of applications such as adsorbents, foundry, drilling fluids, iron ore pelletizing, agronomy, building, refining industries, etc. Indonesia has abundant bentonite resources. It is predicted to be 611,351,020 tons (Daranin and Haryadi, 2010). In 2008, about 148,859.90 tons of raw bentonite was produced in Indonesia with average consumption of 129,412.50 tons. Indonesia currently imports bentonite mainly from China and Malaysia because, in most cases, Indonesia bentonite receives minimum treatment after mining activities such as milling and drying. Normally, it has low natural bleaching power. The bleaching power of bentonite can be improved by acid activation using sulfuric acid or hydrochloric acid at certain concentration, temperature and time (Rossi et al., 2003 and Rozic et al., 2010). As a significant demand, processing the bentonite is a major task to improve its quality for domestic requirements. According to Miswanto et al. (2006) and Daranin (2010), bentonite production tended to remain constant at about 150 thousand of tons per year. Meanwhile bentonite consumption tended to increase linearly, exceeding the annual average bentonite production. Therefore, it must be supplied by the large number of quantity with high quality bentonite, especially the local raw bentonite.

The quality of local raw bentonite can be enhanced by activation process using ion exchange mechanism; through porosity and surface area techniques (Ciullo, 1996). The activation is required if the bentonite is used for bleaching earths, decolorizing crude palm oil and fats (Gupta, 1985). Yet, a lot of industries use the bentonite for not only bleaching earths but also other purposes such as adsorbents, foundry, drilling fluids, binder in iron ore pelletizing, agronomy, building industries, refining etc. (Bergaya et al., 2006).

Received : 18 January 2012, first revision : 20 March 2012, second revision : 07 June 2012, accepted : June 2012

The research objective is to study the bleaching power of the activated bentonite at large equipment capacity but still in batch process. It is targeted that the bleaching power should be increased into minimum 81 % as compared to the previous researches. The feed was set a 100 kg for one time of a process. The achieved bleaching power was then compared to the bleaching effectivity of 95 % of the Germany bentonite Tonsil. At R&D Center for Mineral and Coal Technology, research on bentonite activation had been done in 1998, 2001, and 2002. Zulkarnain (1998) sought the optimal condition of the bentonite activation using sulfuric acid as the activating media at laboratory-scale. The sulfuric acid concentration were 1, 1.25, 1.5, 1.75, and 2.0 N, meanwhile the feed were 20 grams and - 150 mesh in size. The activation took place in 25 % solid at boiling water temperature (100 °C) in 3 hours. The bleaching power of the activated bentonite varied between 78.30 to 80.10 %. Husaini (2001) repeated the research in a larger scale at the same variables as the previous one. If resulted the same bleaching power values. In 2002, Husaini conducted similar-research as that in 2001, however, concentration of the sulfuric acid was 1.088 N and the feed size was - 100 mesh, while other variables were similar (25 % solid, 3 hours activation, and 100 °C). The bleaching power of the activated bentonite increases from 23.26 to 72.54 %.

METHODOLOGY

Research was conducted at Citatah Mineral Centre and Mineral Processing Laboratory as well. The feed for the process was originated from Sarimanggu, West Java. At least 100 kg of dry bentonite performing size of -10 mesh was used for the feed and placed in a reactor at room temperature. The solid percentage was determined for 20 and 40 %. The use of sulfuric acid was 2.5 to 20 % (equivalent to 0.13 to 1.02 N) for 20 % solid and 2.5 to 15 % (equivalent to 0.34 to 2.04 N) for 40 % solid. Both feed (dry bentonite) and sulfuric acid were operating in a batch system. A series of activation times was 1, 2, 3, 4, and 5 hours. It started when sulfuric acid has been depleted. Sampling was completed for each hour when a sample was neutralized until pH = 7. The sample was dried and the rest of bentonite slurry was flowed into dilution tank to be neutralized using water. The slurry was then pumped by a diaphragm pump into the filter press to get cake materials. The cake was transferred into an extruder to get a noodle-like material and then dried in a rotary drier. A flow sheet regarding bentonite activation is shown in Figure 1.

The taken sample was then calculated its Bleaching Power (Capacity) by the equation below (Foletto et al., 2011):

$$BP(\%) = \frac{(A_0 - A)}{A_0} \times 100$$

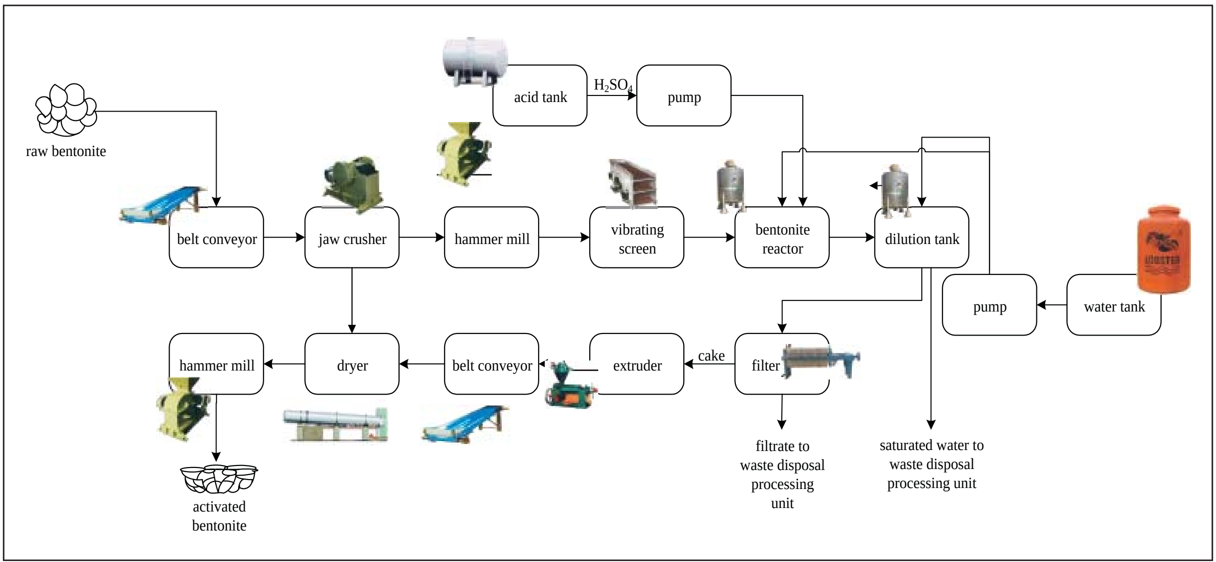


Figure 1. A flow sheet of bentonite activation that employ Sarimanggu bentonite as the feed

where A_0 and A are the absorbance of neutral oil and bleached oil, respectively at the maximum absorbance wavelength of neutral oil (420 nm).

RESULTS AND DISCUSSIONS

Laboratory analysis shows chemical composition of Sarimanggu bentonite (Table 1). It can be inferred from Table 1, that based on SiO_2/Al_2O_3 ratio which approaches 4 : 1, the material from Sarimanggu is bentonite. The material is a calcium bentonite type as shown by higher CaO. Iron and the alkaline elements such as K and Mg at their oxides state are not considered as impurity materials since they can be difussed away from bentonite lattice by H^+ ion from sulfuric acid.

Table 1. Chemical composition of Sarimanggu bentonite

Composition	Content (%)
SiO_2	59.10
Al_2O_3	16.22
Fe_2O_3	2.09
K_2O	0.077
Na_2O	0.12
CaO	0.42
MgO	3.95
TiO_2	0.30
LOI	17.04
H_2O^-	28.88

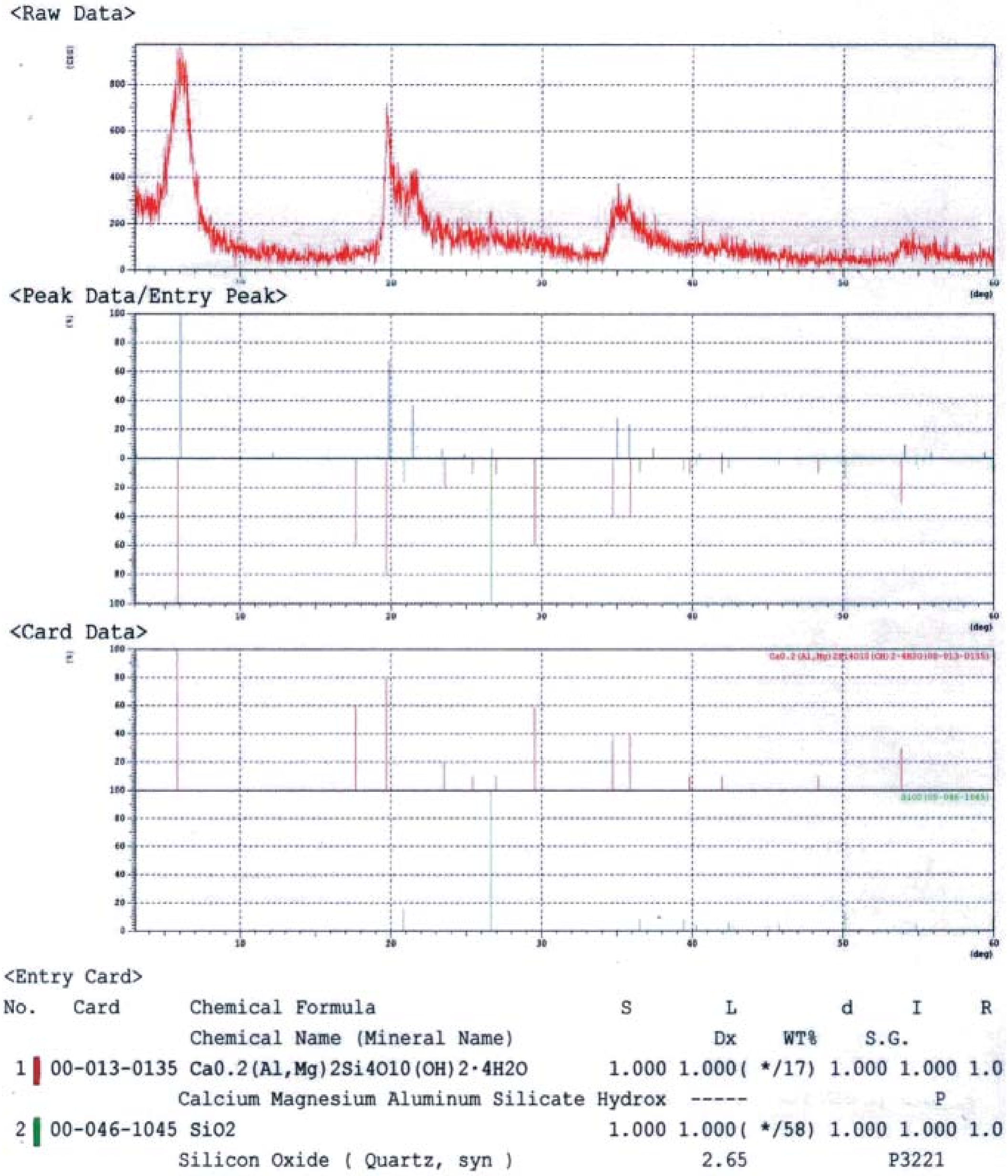
Basically, Sarimanggu bentonite contains montmorillonite and quartz as shown in Figure 2. The montmorillonite shows lamellar structures that indicate an aluminina dioctohedral sandwiched by two opposing silicate tetrahedral layers. These structures stack then form a group of montomorillonite sheets. The fact that Sarimanggu bentonite is a calcium bentonite is also supported by XRD analysis (Figure 3). The figure also states that in such a deposit contains quartz.

X-Ray Mapping, an EDS SEM analysis, explains that Sarimanggu bentonite contains elements such as aluminum (Al), silicon (Si), magnesium (Mg), niobium (Nb), and fluor (F). Silicates is the dominant element among these elements according to Figure 4. It does not show CaO and Na_2O because both of them have small amount of content (below 0.5 %) in the detected specimen (according to Table 1). Since Na, Ca and Mg have the same typical alkaline characteristics, the content of CaO and Na_2O are hidden by MgO content intensity in x-ray mechanism that has significant amount according to Table 2 (3.95%).

Figure 5 also presents petrographic analysis of raw bentonite. It shows that the bentonite depicts fine (darker color) until ultra fine grains (brighter color), masive structure and fine relief. The picture also indicates the solution residue (black). Its composition includes quartz and clay mineral as well as a small amount of opaque minerals.

Laboratory analysis using sodium hydroxide and crude palm oil states that raw bentonite has 44 % bleaching power compared to 95 % Germany

Figure 2. SEM photomicrograph of Sarimanggu bentonite at 5000 x magnification



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<Entry Card>
No.   Card        Chemical Formula                          S      L        d     I     R
                  Chemical Name (Mineral Name)                     Dx   WT%    S.G.
 1  00-013-0135 Ca0.2(Al,Mg)2Si4O10(OH)2·4H2O            1.000 1.000( */17) 1.000 1.000 1.0
               Calcium Magnesium Aluminum Silicate Hydrox -----             P
 2  00-046-1045 SiO2                                     1.000 1.000( */58) 1.000 1.000 1.0
               Silicon Oxide ( Quartz, syn )                   2.65            P3221
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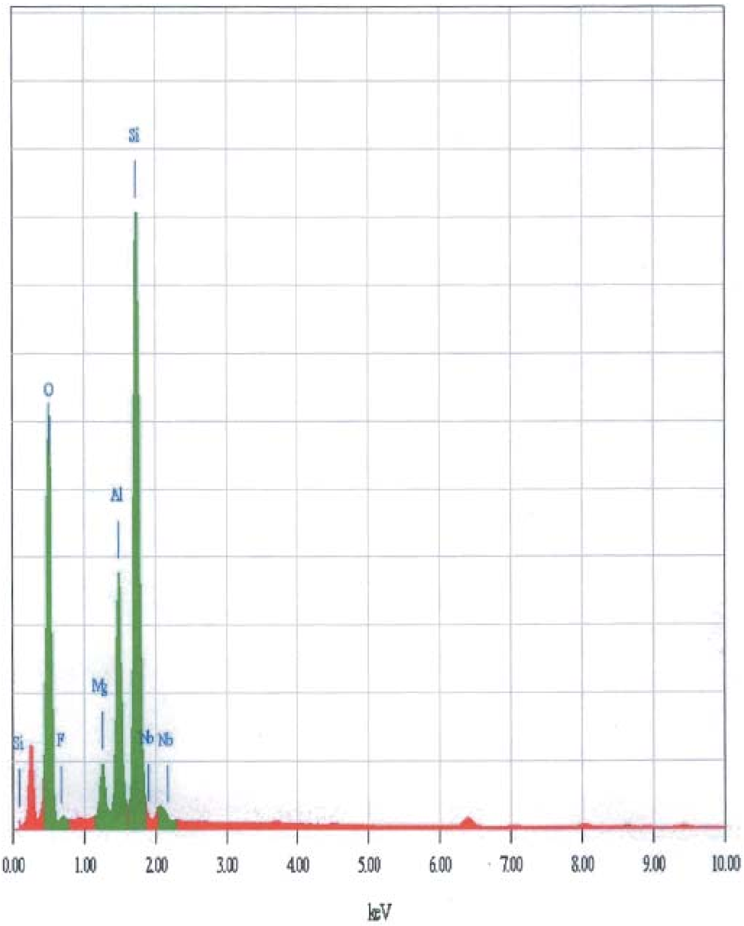
Figure 3. XRD analysis of Sarimanggu bentonite presenting montmorillonite and quartz minerals

tonsil. Based on such a condition, the study employed 20 % solid. A 100-kg raw material basic was loaded into a reactor then stirred to get homogeneity. The sulfuric acid (H_2SO_4) was then poured into the reactor as much as 2.5 % (w/w) or equivalent to 0.13 N. The activation then was started for 1 hour and sampled. Similar sulfuric acid dosage was re-applied for 2-hour activation process and second sample was then taken. The process was repeated for 3, 4 and 5 hours. Different sulfuric acid dosages were also applied for next processes; started from 1 to 5 hours as shown in Figure 6. The best process was conducted for 5 hours at 17.5 % sulfuric acid dosage (Figure 6). However, such a condition was not good enough due to time and energy consuming. As a result, it will increase the operational cost. Next process utilizes 40 % of bentonite. The result is shown in Figure 7.

Fluctuation of bleaching power is caused by bentonite submicroscopic platelets effectivity to perform cation exchanges. As the sulfuric acid dosage increases, the H^+ will replace K^+, Na^+



Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O		49.60							
F K	0.677	2.55	1.30	8.26	F	2.55	0.00	1.2878	
Mg K	1.253	3.24	1.07	8.20	MgO	5.38	1.03	6.0157	
Al K	1.486	13.40	1.22	15.26	Al2O3	25.32	3.85	27.9810	
Si K	1.739	31.20	1.36	68.27	SIO2	66.75	8.60	64.7155	
Nb L									
Total		100.00		100.00		100.00	13.48		

Figure 4. X-Ray Mapping of bentonite from Sarimanggu mine

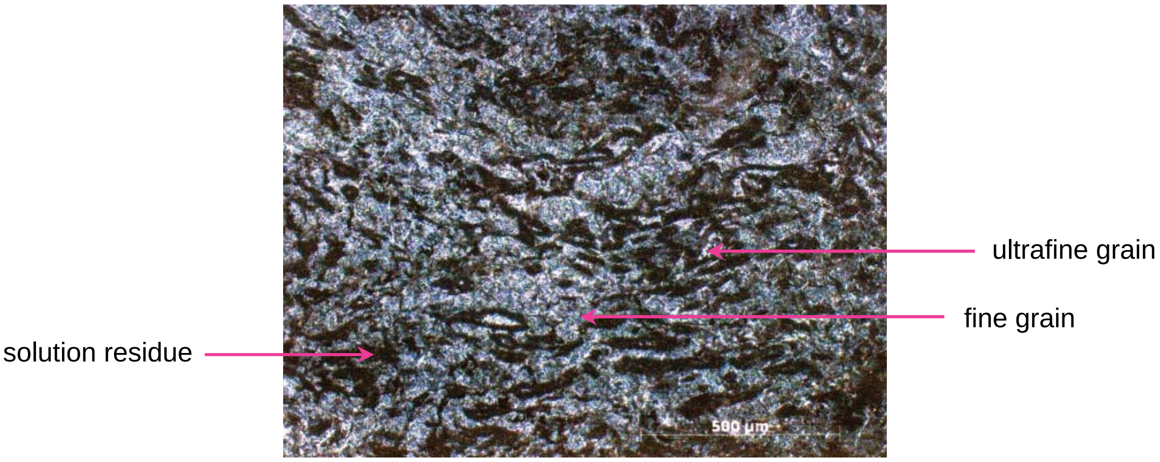


Figure 5. Photomicrograph of thin cross section of Sarimanggu bentonite

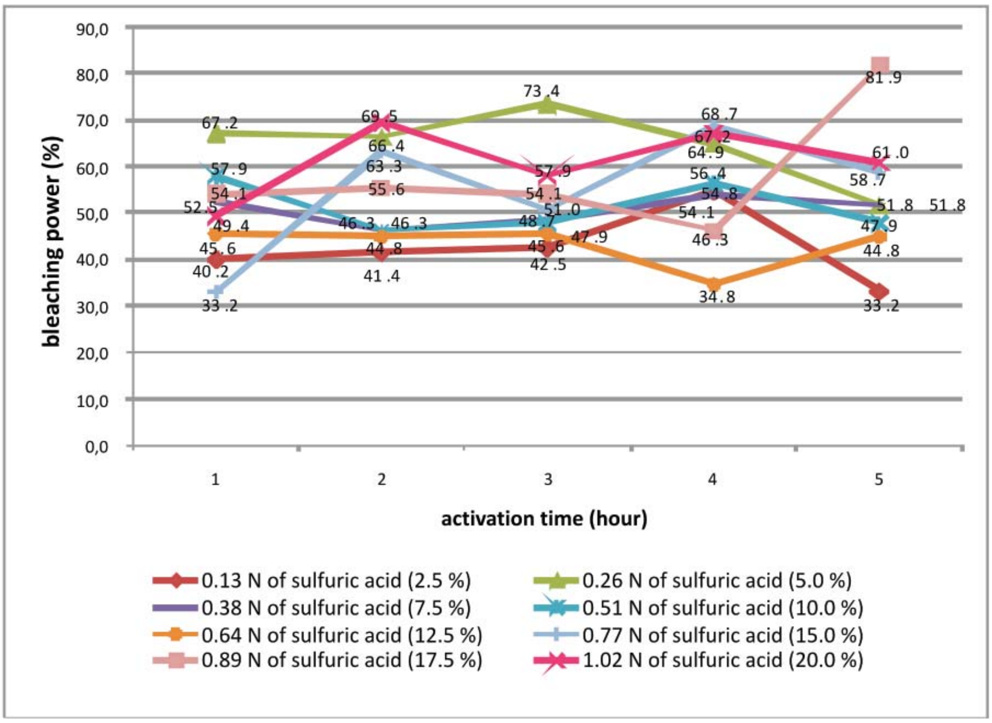


Figure 6. Bleaching power vs activation time at different sulfuric acid dosages using 20 % solid

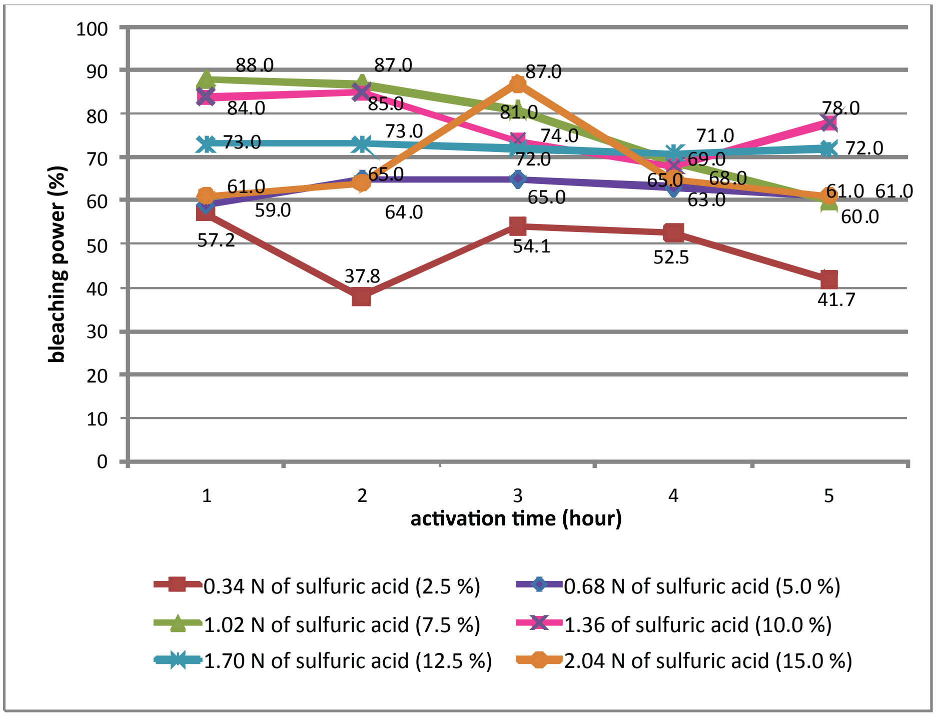


Figure 7. Effect of reagent dosages on bleaching power at each hour activation using 40 % solid

and Ca^{2+} within interlamellar spaces causing the electrical-charged lattice to share that will affect water from acid solution entering the spaces. As long as the lattice of the platelet shares, the swellability and absorptivity increase. As a result the bleaching power also increases. This lasts until the interlamellar spaces are saturated by water and the form the van der waals bonding between H^+ and hydroxil ion at the edges of the platelets. At this stage, the bleaching power will decrease because no share or movement from those of the platelets. This van der waals bonding is weak and can be broken by drying the activated bentonite at room temperature. The disuniformity of the dried-platelets of the bentonite contributes to the fluctuation of the bleaching power value when it is measured in bleaching power test.

As one of the factors that influences bentonite absorptivity (Didi et al., 2009), the best solid percentage should be determined between the two values of solid percentage. Referring to Figure 6 and 7, a 40% solid provides the highest average bleaching power (67.64%) as shown in Table 2.

Tabel 2. Bleaching power and solid percentage of Sarimanggu bentonite

solid percentage (%)	Average Bleaching Power (%)
20	53.32
40	67.64

High solid percentage will increase the interaction between the alumina octahedral and water. It makes water molecule will be absorped between alumina octahedral with silica tetrahedral layers. Water and its hydroxil group will enter the lattice of the bentonite that is easy to remove by heating process. Bentonite lattice will be wider as an effect of ionic bond between oxygen atom at SiO_4^{2-} and silicon and aluminum atoms within the bentonite itself. The influence of bentonite's swellabilty (Ciullo, 1996) and low bulk density (0.45-0.75 g/ml) (Gupta, 1985) also widen the bentonite lattice. Although low bulk density is one of bentonite properties, it doesn't mean that the solid percentage in the reactor should be low to get the bleaching power increase the feed in this batch scale research, are bigger than that of the laboratory scale. This condition shoul be compensated with much more water. A 40% solid is adequate to perform alumina-water interaction supported by stirring action of the reactor's impeller. Contact between alumina octahedral with water molecule at a 40% solid is more effective than that of a 20% solid.The lattice, that is left by water molecule at heating process, will grow its capacity and increase the bleaching power capacity.

Figure 7 shows that a tendency of decreasing bleaching power to decrease in the long run of activation time. More activation time will damage bentonite submicroscopic platelets (sheets) due to excessive acid-platelets contact. This will result in decreasing the bleaching power. According to Figure 7, a condition of 100 kg bentonite, one hour activation and 7.5 % dosage of sulfuric acid or equivalent with 1.02 N resulted in the highest bleaching power (88 %).

The resulting high bleaching power was represented by the montmorillonite sheets that tend to grow massively into interlamellar structures, as Figure 8 depicts. If compared to Figure 2 (before activation), Figure 8 describes the massively growth of montmorillonite sheets into interlamellar structures after activation, remaining only a few montmorillonite sheets. Actually, the growth associated with the share of plated-interlamellar structures that were affected by the occupation of the water from sulfuric acid solution. Activation proceeds with partial dissolution of bentonite and includes initial replacement of the interlayer cations by H^+, and is followed by dissolution of the octahedral and tetrahedral sheets with subsequent release structural cations. These series of processes altered the structure of the initial bentonite (before activation).

Figure 9 shows that the a 7.5 %-sulfuric acid (H_2SO_4) dosage or equivalent to 1.02-N concentration and one hour activation are the best condition to optimize the bleaching power of Sarimanggu bentonite. Increasing reagent dosages results in increasing the ionic exchange capacity until it reaches the optimal value (a 7.5 %-sulfuric acid dosage) that means that no more H+ concentration will replace the alkaline cations at the edges of bentonite platelets. The bleaching power tends to decrease when exceeding that optimal value. According to Suhala and Arifin (1997), the acidity will influence the exchanges of K^+, Na^+, and Ca_2^+ with H^+ within interlamellar space, and diffuse Al^{+3}, Fe^{3+}, and Mg^{2+} away from

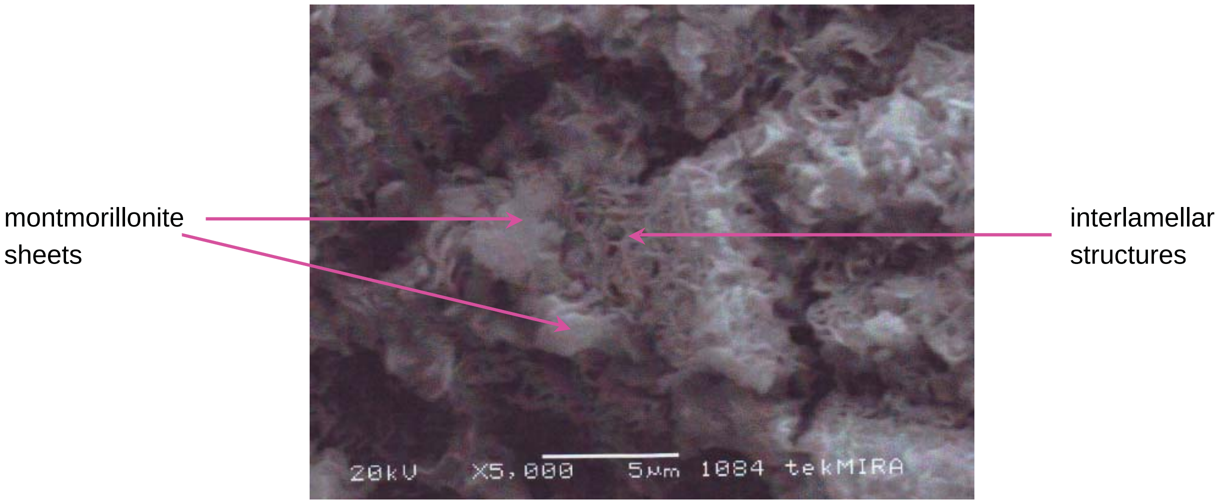


Figure 8. SEM photomicrograph of the best activated-bentonite (1-hour activation, 1.02 N sulfuric acid concentration) at 5000 x magnification

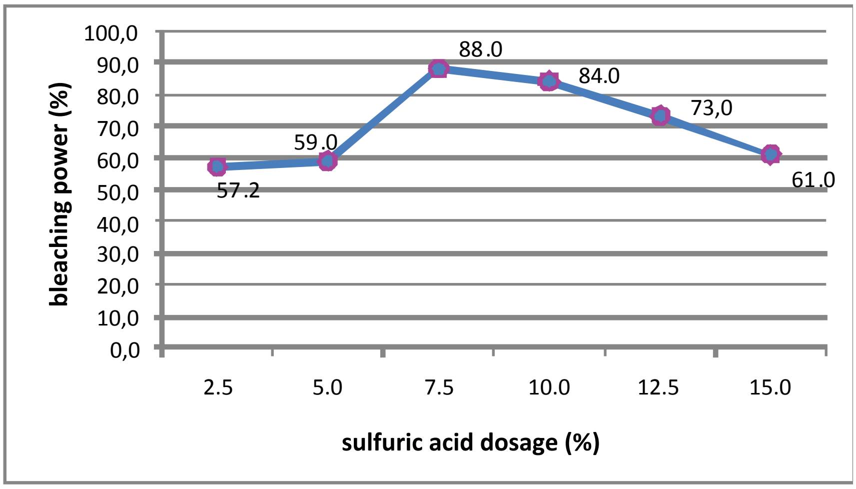


Figure 9. The influence of sulfuric acid to bleaching power in 1 (one) hour activation in 40 % solid

their lattice. It will make the clay more swellable and absorptive. The optimum point of dosages is 7.05 %, however, addition of reagent dosages affects the bentonite lattice and results in descending the absorptivity of the bentonite and bleaching power.

Compared to the previous researches regarding bentonite activation, there is a significant difference in bleaching power attainment. The previous ones (Zulkarnain, 1998; and Husaini, 2001) achieved the highest bleaching power at 80.10 % but the present research achieves 88 % bleaching power, even without heating treatment and shorter activation time. The thicker slurry of the activated bentonite (40 % seems solid) facilitating the sulfuric acid solution to interact with the bentonite platelets more effective than that of a 25% solid. When the interactive between effective acid solution and bentonite submicroscopic platelets occurs, the water penetrates the area between the platelets and forces them farther apart. Meanwhile, the major exchange ion (Mg^{2+}) as studied in Table 1, substitutes the Al^{3+} in octahedral positions and Al^{3+} for Si^{4+} in tetrahedral positions (Ciullo, 1996). As the influence of the major exchange ion, the platelets separate or swell farther apart and the exchange ions begin to diffuse away from the platelet faces (lattice) that are negatively charged. Further penetration of water between the platelets then proceeds in an osmotic manner until they are completely separated. Thus, in this present experiment, heating application to endorse bentonite submicroscopic platelets movement is not required.

Without heating treatment, a 7.5% reagent dosage and 1 hour activation; are more benefit as the fuel consumption can be eliminated. Finally, it will reduce the operational cost. This activating condition is more competitive for medium to small scale bentonite processing industries.

CONCLUSION

The best condition for processing the bentonite using sulfuric acid is 40 % solid, 7.5 % sulfuric acid and 1 hour activation time. Such condition provides 88 % bleaching power.

SUGGESTION

This optimal condition should be validated through repetitive experiments, starts from 100 kg to the maximum capacity of the reactor (300 kg). Not only for validation, this experiment repetitions will give information and feedback to improve the bleaching power capacity of the Sarimanggu bentonite until it approaches 95 % Germany bentonite tonsil. Continuous tests should be required.

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