Mass Optimization Of Acid-Activated And Acid-Thermal-Activated Bentonite In Heavy Metal Adsorption

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Abstract.

Heavy metal pollution such as Cu, Fe, and Pb is a serious environmental issue because it is toxic and can harm living things and the surrounding environment. Adsorption is a potential method to address heavy metal problems with bentonite as an adsorbent. Before use, natural bentonite will be activated first. Activation aims to increase the surface area, porosity, and number of active sites on the bentonite surface. This study aims to determine the optimum adsorbent mass in heavy metal adsorption and compare the best activation method using acid-activated bentonite (H_2SO_4 1.2M) and acid-thermal activated bentonite, namely H_2SO_4 1.2M and continued heating using a 300°C furnace for 6 hours. In addition, comparing changes in the surface characteristics of acid bentonite and acid-thermal bentonite through characterization using SEM analysis. Adsorption was carried out using a single component synthetic solution containing Cu, Fe, and Pb metals with variations in adsorbent mass of 1, 2, 3, 4, and 5 grams. The results show that acid bentonite has an open and porous surface structure and has many active sites. In acid-thermal bentonite, the silicate structure becomes more stable despite slight damage to the Si structure and at a higher mass makes acid-thermal bentonite higher than acid bentonite. The optimum heavy metal degradation efficiency is achieved at an adsorbent mass of 1 gram with acid-activated bentonite which achieves a metal degradation efficiency of 45% Cu, 100% Fe and 88%.

Keywords: *Adsorption; Acid-Activated; Acid-Thermal-Activated; Bentonite and Heavy Metal.*

I. INTRODUCTION

Wastewater is often generated as a byproduct of various industrial, mining, and laboratory operations. In certain cases, metal pollution in water is caused by the indiscriminate discharge of metals into waterways. Heavy metals are hazardous to living organisms, especially humans and aquatic fauna, due to their poor biodegradability, tendency to biomagnify, and toxicity at high concentrations. Remediation alternatives for removing heavy metals from aqueous solutions include adsorption, coagulation, flocculation, electrochemical removal, ion exchange, bioremediation, membrane filtration, chemical precipitation, and others. Adsorption has demonstrated high efficiency in water treatment against various contaminants, especially heavy metals [1].Bentonite is a clay mineral primarily composed of montmorillonite with a 2:1 structural ratio, consisting of two tetrahedral silica layers sandwiching one octahedral aluminum layer [2]. Bentonite has the property of swelling when wet and high ion adsorption capacity [3].

However, natural bentonite has a high level of impurities, resulting in limited active surface area and low availability of adsorption sites, resulting in low metal binding rates [4]. To overcome these problems, modification through acid activation is needed because it can increase the specific surface area, porosity, surface acidity, and adsorption activity of clay minerals [2]. Impurities in bentonite such as calcite and dolomite, are removed from its structure due to the cations in bentonite can be exchanged by hydrogen ions and some Al ions in the tetrahedral layer dissolve some Fe, Al and Mg cations in the octahedral layer [2]. In addition to acid activation, thermal activation can remove water content and increase the surface area of bentonite so that the adsorption capacity of bentonite becomes more optimal [5].In this study, the authors focused on the comparison of chemical activation of bentonite with an acid solution, namely H_2SO_4 1.2 M and a chemical-physical combination, where after the acid solution was continued heating using a furnace for 6 hours at a temperature of 300°C in absorbing heavy metals in synthetic waste single component metal ions Cu, Fe, and Pb by varying the mass of the adsorbent to obtain the optimum mass.

II. METHODS

Acid Bentonite Activation

250 grams of bentonite was activated with 500 mL of 1.2 M H2SO4 and then stirred using a magnetic stirrer at 100 rpm for 1 hour at 60°C. The bentonite was then washed with distilled water until it reached a neutral pH. The bentonite was filtered and dried in an oven at 105°C for 3 hours. Cooled in a desiccator, then filtered through a 100-mesh sieve. Bentonite before and after activation was tested for characteristics using SEM analysis.

Acid-Thermal Bentonite Activation

250 grams of bentonite was activated with 500 mL of 1.2 M H2SO4 and then stirred using a magnetic stirrer at 100 rpm for 1 hour at 60°C. The bentonite was then washed with distilled water until it reached a neutral pH. The bentonite was filtered and dried in an oven at 105°C for 3 hours. The bentonite was then reheated in a furnace at 300°C for 6 hours. Cooled in a desiccator, the bentonite was then filtered through a 100-mesh sieve. Bentonite before and after activation was tested for characteristics using SEM analysis.

Single-Component Heavy Metal Adsorption

Adsorption was carried out in a batch system, with 100 mL of each single-component synthetic waste containing 20 ppm Cu, Fe, and Pb at pH 5 placed in separate Erlenmeyer flasks. In each Erlenmeyer flask, activated bentonite was added, either acidically or acid-thermally with various masses of 1, 2, 3, 4, and 5 grams, which were then stirred using a magnetic stirrer at a speed of 100 rpm at a temperature of 25 ^{o}C for 60 minutes. The sample was then filtered with filter paper with the help of a vacuum pump and tested for heavy metal content using AAS. The percentage reduction in heavy metal content was calculated by comparing the metal content before and after adsorption. Equation 1 shows the percentage reduction in metal content, with c0 as the initial concentration, and c1 as the final concentration.

Metal degradation percentage = = $\frac{c_0-c_1}{c_0} \times 100\%$ … (1)

III. RESULT AND DISCUSSION

Adsorbent Characteristics with SEM anlysis

Adsorbent characterization using a SEM instrument aims to observe the surface morphology and elemental content of various types of solid samples using the principle of electron beams. This instrument can magnify from 10x to 3,000,000x, has a depth of field of 4–0.4 mm, and a resolution of 1–10 nm [6].

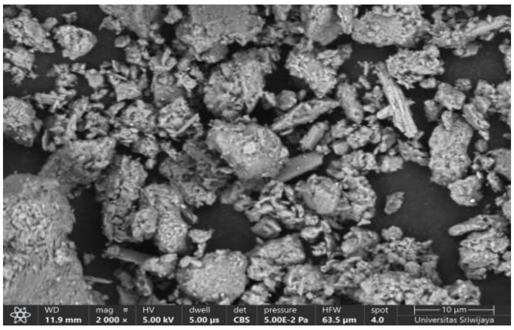

Fig 1. SEM of Bentonite before Activation Process with 2000x Magnification

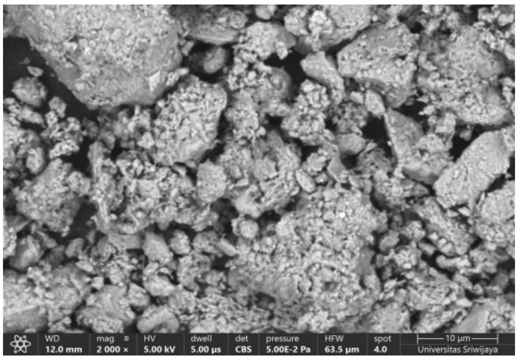

Fig 2. SEM of Acid-Activated Bentonite with 2000x Magnification

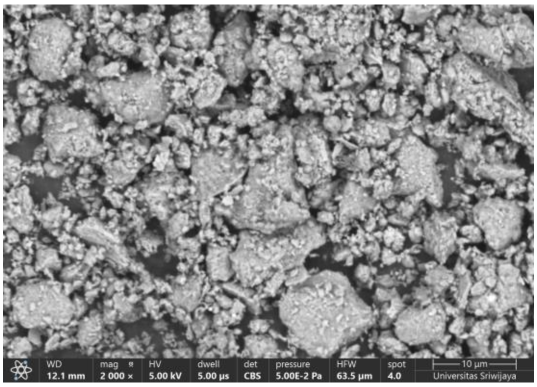

Fig 3. SEM of Acid-Thermal-Activated Bentonite with 2000x Magnification

Before acid activation, SEM analysis showed that bentonite had a dense, irregular surface, with most of the small pores blocked by impurities, and the particles tended to clump together. These characteristics indicate a relatively low surface area, which reduces adsorption efficiency due to the lack of open, accessible pores. There are quite significant changes in the morphology of the bentonite surface after being activated using 1.2M H_2SO_4. On the surface of the particles, the bentonite pores begin to open, making it appear less dense. As an acid activator, the use of sulfuric acid causes the dissolution of some cations such as Ca^{2+}, Mg^{2+}, Na^{+} in the bentonite structure and lifts impurities from the surface, thereby increasing the number of active sites [2]. Additional heating with a furnace can alter the structural model of the bentonite surface due to fragmentation. This results in a more porous bentonite surface and the opening of meso-macropores, which facilitates the entry of large ions into the clay structure[7]. A comparison of SEM images before and after activation shows that the activation process successfully breaks down the bentonite structure, making it more porous and dissolving cations and impurities. Bentonite with a more open structure and larger active surface area will provide better adsorption capacity for metal ions in wastewater. Therefore, the significant increase in adsorption performance after activation can be justified morphologically.

The Effect of Variation in Adsorbent Mass on Acid-Activated Bentonite and Acid-Thermal-Activated Bentonite on the Reduction of Heavy Metal Concentration

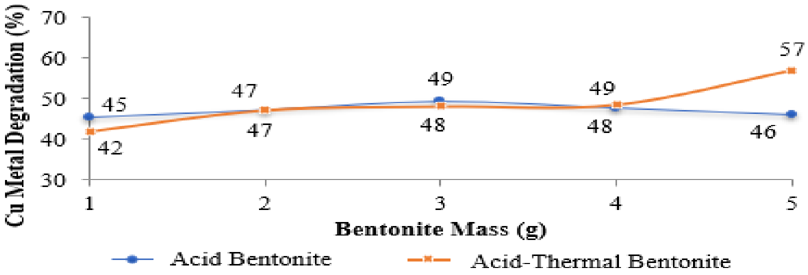

Fig 1. Effect of Adsorbent Mass on the Percentage of Cu Metal Degradation
Using Acid Bentonite and Acid-Thermal Bentonite

Figure 1 shows that the efficiency of Cu reduction in acid-activated bentonite and thermal-acid-activated bentonite increased with increasing adsorbent mass, but the most significant increase occurred with the addition of 0 to 1 g, both in acidic bentonite and acid-thermal bentonite, where Cu degradation increased sharply from 0% to 45% for acidic bentonite and from 0% to 42% for acidic bentonite. After the addition of 1 g of mass, Cu metal degradation increased in acidic bentonite up to the addition of 3 g of mass, although the increase was not significant. At the addition of 4 and 5 g of mass, metal degradation actually decreased. This pattern is a general characteristic of metal ion adsorption on negatively charged clays, where the addition of adsorbent mass increases the number of active sites, thereby increasing Cu ion adsorption.

However, at too large a mass, agglomeration or clumping occurs between particles, causing some pores and cation exchange sites to be closed, thus decreasing efficiency [8].In acid-thermal bentonite, the adsorption efficiency of Cu at 1–3 g is lower than in acid bentonite. This is due to dehydroxylation and partial shrinkage of the montmorillonite structure, which reduces the cation exchange capacity (CEC) and the number of –OH groups that act as Cu^{2+} adsorption centers [9]. However, at higher adsorbent masses, the total number of active sites increases significantly, so that the heat-modified structure actually becomes more stable and tends not to clump and increases the rigidity of bentonite grains, so that the Cu adsorption capacity can increase more than acid bentonite—in line with recent findings that thermal activation can produce oxide defect sites that are highly reactive to Cu^{2+} ions, especially at large adsorbent doses [10]. The optimum adsorbent mass for Cu metal remained at 1 g because this point resulted in the highest significant increase in efficiency. This indicates that the effect of increasing the adsorbent mass did not significantly affect the metal degradation efficiency.

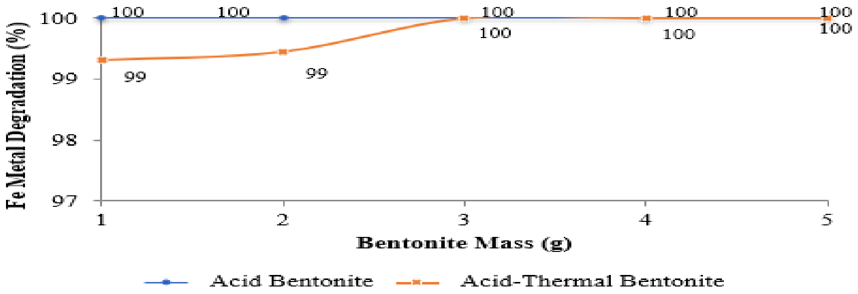

Fig 2. Effect of Adsorbent Mass on the Percentage of Fe Metal Degradation Using Acid Bentonite and Acid-Thermal Bentonite

Figure 2 shows that both acidic bentonite and acid-thermal bentonite are capable of significantly reducing Fe metal content, even starting from an adsorbent mass of 1 g. This phenomenon indicates that the optimum adsorbent mass for Fe metal is 1 g, because after that point the increase in efficiency is very small and not statistically or practically significant. Adsorption that occurs in acidic bentonite tends to be slightly more stable than acid-thermal bentonite, but the difference is not too striking for Fe metal. Acid activation successfully increases the number of surface-active groups—especially silanol (Si–OH) and aluminol (Al–OH) groups—and expands access to the interlayer space, so that Fe^{3+} ions are maximally adsorbed even at low adsorbent masses. Acid activation is known to increase the cation exchange capacity (CEC) and open the montmorillonite structure, making bentonite very efficient in capturing highly charged transition metals such as Fe^{3+} [8], [11]. In addition, this also shows that Fe^{3+} ions have a high affinity for the negative surface of bentonite so that once the active sites are available in sufficient quantities, the adsorption process takes place almost perfectly at various adsorbent doses [12].

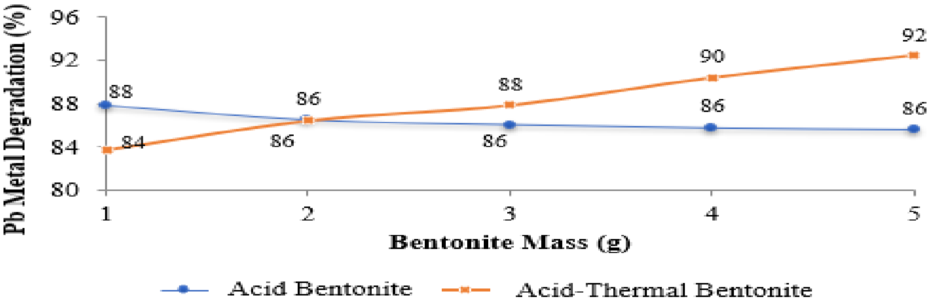

Fig 3. Effect of Adsorbent Mass on the Percentage of Pb Metal Degradation Using Acid Bentonite and Acid-Thermal Bentonite

Figure 3 shows that the Pb removal efficiency increased significantly with the addition of adsorbent from 0 to 1 g, where both acidic bentonite and acid-thermal bentonite reached efficiencies above 80%. After that, the increasing trend in efficiency continued for acid-thermal bentonite, while acid bentonite continued to decrease with increasing adsorbent mass, although not significantly. This decrease may be due to the phenomenon of particle agglomeration and overlap between bentonite particles, making some active sites less accessible to Pb ions at larger adsorbent masses. Acid-thermal bentonite showed an increase, with 84% degradation at 1 g, increasing with mass variation, reaching 92% degradation at 5 g. Heat activation helped prevent agglomeration. In addition, the stability of thermal bentonite particles at high masses and a more homogeneous material distribution allowed Pb^{2+} ions to access all available adsorption centers more efficiently. Consequently, greater adsorption efficiency was obtained at higher doses. This is in line with the research [13], stated that the higher Pb adsorption pattern on acid-thermal bentonite at large masses reflects the kinetic and thermodynamic advantages of the thermally altered structure, although at low masses some sites may be lost or become less reactive.

IV. CONCLUSION

This study shows based on SEM results that the surface morphology of bentonite after activation, both acid and acid-thermal, is more open, more pores and increased surface area and active sites that will absorb metal ions, compared to bentonite before activation. Then, in the chemical activation process with H_2SO_4 and a combination of chemical-physical activation (H_2SO_4 and heating with a furnace) on bentonite for the degradation of heavy metals Cu, Fe and Pb in synthetic wastewater gives the result that the optimum adsorbent mass is 1 gram with acid-activated bentonite and achieves the results of Cu metal degradation efficiency of 45%, Fe 100% and Pb 88%. While in acid-thermal bentonite with the same adsorbent mass, the degradation efficiency of heavy metals Cu 42%, Fe 99% and Pb 84%.

V. ACKNOWLEDGMENTS

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