

Recovery of H₂SO₄ from spent acid waste using bentonite adsorbent

Marwan Asof^{1,*}, Susila Arita Rachman², Winmy Andalia Nurmawi³, Cindy Ramayanti²

¹Department of Mining Engineering Universitas Sriwijaya, 30662 Palembang, Indonesia

²Department of Chemical Engineering Universitas Sriwijaya, 30662 Palembang, Indonesia

³Department of Industrial Engineering, Universitas Tridinanti, 30145 Palembang, Indonesia

Abstract. Spent acid waste is produced in the petroleum processing industry at the alkylation process unit that requires sulfuric acid as a catalyst to produce iso-octane. Therefore, spent acid contains sulfuric acid attached to a long chain carbon and other compounds. This compound is corrosive and has a pH below 1.0, so that it cannot be directly discharged into the environment. The processing and utilization of spent acid to meet environmental quality standards need to be conducted. This study aimed to conduct waste treatment of spent acid and to recover sulfuric acid from the spent acid solution because the level of H₂SO₄ is high at about 82%, then the sulfuric acid can be reused in the alkylation process or other processes. Adsorption method was selected to process the waste using bentonite as adsorbent in 3 stages adsorption columns. The results showed that the recovery of H₂SO₄ was successful in which the purity of H₂SO₄ generated after distillation reached 94.94%.

1 Introduction

The production process of petroleum processing industry, especially in the alkylation unit produces spent acid waste. Spent acid waste is classified as hazardous and toxic material and belongs to B3 waste. According to the regulation of Ministry of Environment Republic of Indonesia No 18/2009, industries must manage or perform waste treatment of B3 wastes in order to meet the Indonesian National Standard (SNI) or international standards, or other standards that apply nationally and internationally. Spent acid is one of the B3 waste that requires special treatment to be able to be reused in the process or transformed into other useful products.

The spent acid used in this study consists of compounds of waste from the alkylation unit in the petroleum processing industry. The main component of the spent acid is sulfuric acid, a major catalyst in the reaction between iso-butane and iso butylene that will react to form isooctane. Some of the constituent formed from alkylation unit other than sulfuric acid are distillate, alkylate, diethyl sulfate and dimethyl sulfate. The physical properties of spent acid are dark, smelled very sharp with a pH <1, wherein the initial concentration of sulfuric acid in the spent acid treated solution is 82%.

Problems in managing acid waste from oil and gas industry process are very important things to be resolved, so that the environment can be protected from contamination. Management of acid waste in this study

is focused on recovery of H₂SO₄ contained in the waste solution using bentonite adsorption methods. In this case, bentonite is activated by physical adsorption in a stratified adsorbent column.

Researches on the treatment of spent acid wastewater have been performed by many researchers, among others, [1] conducted a spent acid recycle process to recover molybdenum contained in the mixture of waste in a way to neutralize the ammonia gas in the spent acid containing molybdenum, and then followed by crystallization and filtration. Hydrogen reduction of molybdenum oxide produces commercial products such as molybdenum metal powder. Fluid that contains a lot of nitrogen from this process can be used as fertilizer. [2] was successfully recovered the acid from the spent acid of steel industry (electroplating) which contains heavy metals included in B₃ category with a high enough concentration.

[3][4] succeeded in recovering HCl, Fe and ZnCl₂ from iron material production waste (galvanizing plants) using merger technology between ion exchange with membrane electrowinning, while [5] and [6] tried to minimize the spent acid from galvanic plant using hydrochloric acid as an impurities cleaning compound from metals by conducting hydrochloric acid regeneration using Kleingarn acid management system. It showed a positive result because it can reduce the spent acid wastes discharged into surface water.

*Corresponding author: marwan_asof@yahoo.com

Bentonite is a potential mineral and is scattered in almost every island in Indonesia. On the Sumatra island, bentonite is spread almost throughout the region, especially in the Jambi area. [7] showed that bentonite in Jambi is generally composed of four types of minerals; kaolinite, monmorillonit, quartz and cristobalite. Bentonite of clay type having a major content of smectite minerals (montmorillonite) with levels of 85 -95%, is soft with a hardness 1 on the Mohs scale, the density between 1.7 to 2.7, breakable, plastic, and high colloidal.

Based on the physical properties, bentonite is differentiated as Na-bentonite and Ca-Bentonite. Na bentonite or swelling bentonite can swelling up to eight times when immersed in water and will be suspended when dispersed in water. In the dry state the colour is white or cream. In a wet state and when exposed to sunlight, it will turn shiny. High ratio of soda and high lime will produce colloidal suspension having a pH of 8.5-9.8 and cannot be activated. The exchange positions are occupied by sodium ions (Na^+) that have a large content of Na^+ between the layers and have swelling properties.

In the Ca-Bentonite-non swelling, bentonite content of Ca^{2+} and Mg^{2+} is relatively higher when compared with the content of Na^+ . This kind of bentonite is less swell when immersed in water, remain dispersed in the water and will quickly settle or not form a suspension, but naturally or after being activated it has a good adsorption property [8]. Comparison of Na and Ca content is low and colloidal suspensions have a pH: 4-7. Ion exchange position is more occupied by ions of calcium and magnesium. In the dry state, it is rapid slaking, gray, blue, yellow, red and brown. This bentonite can be used as a catalyst support, whereas the modified bentonite can be used as a catalyst.

Indonesia needs bentonite as the filler or fillers in the paint industry, metal casting, oil drilling and as one type of adsorbent frequently used as a purification material of palm oil or coconut oil (bleaching agent) to absorb the stain and impurities in oil continuous increase. Absorption capability of bentonite can be enhanced by activation both physically and chemically that are useful to increase the surface area and modify the structure of bentonite. [9] Liisa Carlson, 2004 stated the nature and characteristics of bentonite are highly dependent on the geographic location of the region and the largest content is Na-montmorillonite, other parts are hematite, smectite, iron, pyrite and others. Smectite mineral type composed of aluminosilicate framework and form a layered structure has a negative charge evenly across its surface and a good cation exchanger.

An adsorption is an event of adsorption of molecules at the surface or between phases, where the molecules of the material are collected on the adsorbent. The materials to be adsorbed and adsorbent materials are two distinct phases. Then in the event of adsorption, the adsorbed material will be collected at the interface of the two phases. Adsorption is very widely used in industry, especially in wastewater treatment at industrial level. Adsorption known is chemical adsorption and physical adsorption. Chemical adsorption occurs because of the chemical bonding

between the solute molecules (solute) and adsorbent molecules usually progresses slowly but irreversibly, while physical adsorption occurs because of the weak attraction of molecules between the two objects by Van der Waals forces on the surface of the adsorbent, so that it will form a thin layer of fine particles on the surface. The numbers of substances absorbed depends on the partial pressure of the molecule (PA). Some molecules diffuse laterally or may react on the surface (chemisorption). The speed of adsorption and desorption determines the equilibrium on the surface. The success rate of adsorption process on the surface of solids is highly dependent on the characteristics and concentrations of the compound to be absorbed, the molecular size of the adsorbate (the material to be absorbed), the surface area of solids (adsorbent), the degree of acidity of the solution [10], temperature, mass and particle size, contact time and others. To recover H_2SO_4 that the levels are still high, this research is used adsorption using bentonite adsorbent that has been activated physically.

2 Materials and methods

2.1. Materials and equipment

The raw material used was a solution of spent acid from alkylation unit of the oil and gas industry. The adsorbent used was bentonite originating from Jambi with a particle size of $100\mu\text{m}$. Research equipment used was adsorber column operated in 3 stages as shown in Figure 1. Columns made of pyrex with a column diameter of 5 cm with a height of 70 cm. The top of columns were equipped with liquid distributor made of perforated plate, and the below were given sponge and installed vacuum pumps to accelerate the flow down.

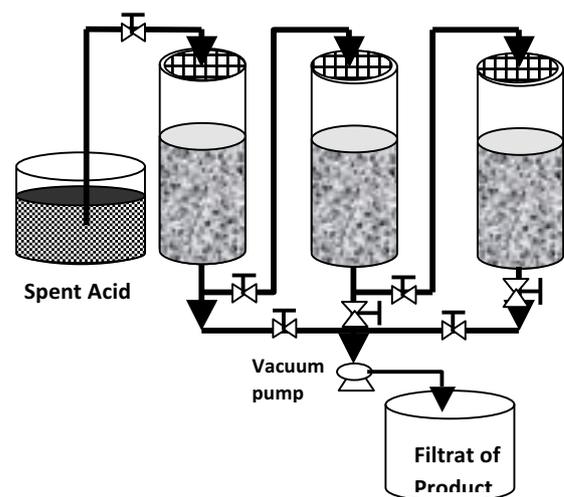


Fig.1. The schematic representation of the Series Adsorber Column

1.2 Research procedure

Physical activation of bentonite was conducted by heating at a temperature of $850\text{ }^\circ\text{C}$ for 3 hours, then the adsorbent

was washed with distilled water and dried in an oven at 110°C for 3 hours. The adsorption capacity of the adsorbent was investigated by conducting a variation of the adsorbent weight of 100, 150 and 200 grams that were inserted into the adsorption column.

Adsorption column was filled with 100 grams of bentonite adsorbent with a size of 100 µm. Above the column was mounted a liquid distributor so that the flow entered evenly through all the volume of the adsorbent. Under the column was mounted vacuum pump in order to make the spent acid penetrate more quickly into the adsorbent and was collected as filtrate under the adsorbent column. Slowly the spent acid from column 1 was filtrated and to be input in the 2nd column and the 2nd column output became the input to the 3rd column. Filtrate from at each output column was measured its volume and analysed its H₂SO₄ concentration. Then repeat the same procedure for the adsorbent weight of 150 grams and 200 grams.

The analysis of H₂SO₄ concentration was done by titration method. This method aimed to determine the changes in the sulfuric acid concentration of spent acid solution after passing through several stages of the adsorption process. SEM-EDS was performed to observe the structure of bentonite to determine bentonite morphology and the composition of the constituent elements in the bentonite.

3 Results and discussion

3.1. The effect of adsorbent mass on the filtrate volume and H₂SO₄ purity

Research results in Figure 2 show that the filtrate volume that can be recovered using adsorbent of bentonite is quite large. The highest and the lowest percentages of filtrate volume on the first output column are 72% and 40%, respectively. In the 2nd column, the highest and the lowest percentages are 53.4% and 29.4%, respectively. While on the 3rd output column, the highest percentage is 18% and the lowest is 10.8%. The heavier the adsorbent mass, the smaller the percentage of filtrate recovered, but the greater the concentration of sulfuric acid produced. It could be seen in Figure 3.

In Figure 2 and Figure 3 are shown how the mass of adsorbent affects filtrate volume and H₂SO₄ concentration produced. The heavier the adsorbent mass, the smaller the percentage of filtrate recovered. It indicates that the performance of the adsorbent is quite excellent at absorbing water and hydrocarbon impurities contained in the spent acid.

The resulting filtrate was distilled at a temperature of 110°C until the water in the solution evaporates completely so that the remaining solution in the distillation flask was analyzed. Subsequently, the result obtained was the increase in the concentration of H₂SO₄ up to 94, 94% with an adsorbent mass of 200 grams.

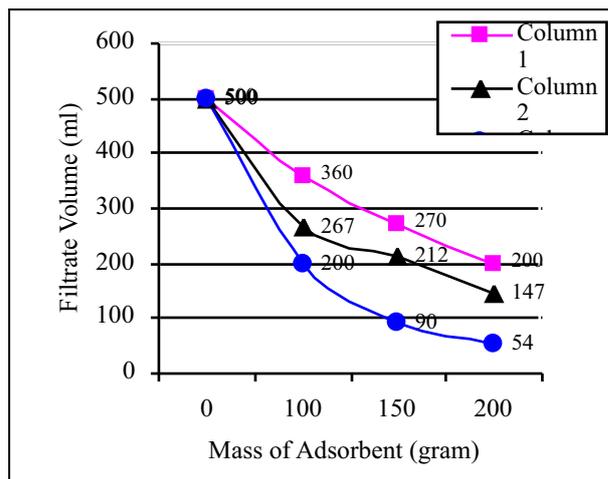


Fig.2. Results of the filtrate versus adsorbent mass

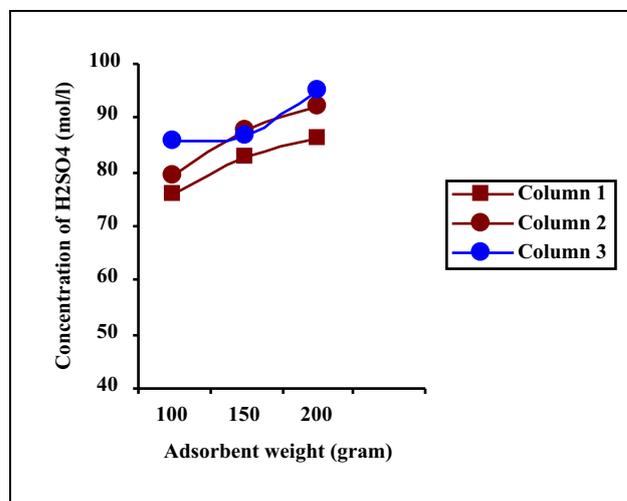


Fig. 3. Concentration of H₂SO₄ output of series adsorber column versus adsorbent mass

The purity of H₂SO₄ generated in this research was quite high. The next research would attempt to use this recovery result to activate bentonite as it has been researched by Hulya et al, 2007 and Muserref et al, 2007 who have activated bentonite with various concentrations of H₂SO₄. Their results indicate that activation by H₂SO₄ concentration > 50% can increase the ability of bentonite as a bleaching agent in soybean oil up to 70%.

3.2. Characterization of Bentonite Adsorbent

The characteristic of bentonite as adsorbent was investigated using Scanning Electron Microscopy (SEM) and Energy Disvertive Spectroscopy (EDS).

The analysis shows that the constituent elements of bentonite consist of silica, alumina, Oxygen, Nitrogen and Fe as shown in Figures 4 and Figure 5.

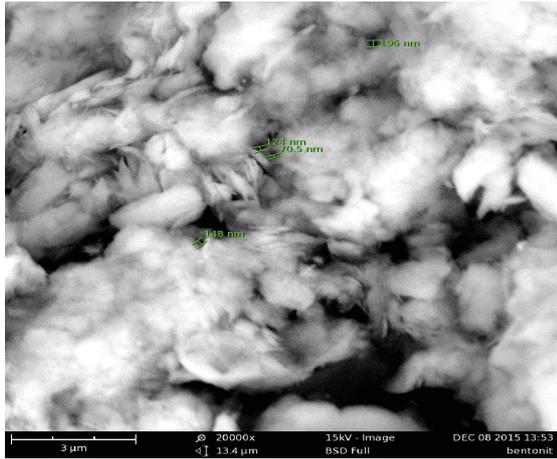


Fig. 4. Analysis of Scanning Electron Microscopy (SEM) bentonite before Adsorption Process

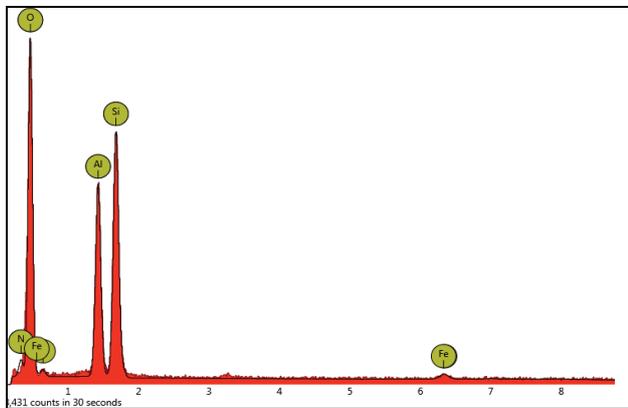


Fig. 5. SEM-EDS Spectrum of Bentonite before Adsorption Process

In the Figures 5, bentonite solids shaped layers of clay mineral mixture with a pore size of 70.5 nm to 148 nm. Meanwhile, the composition of each constituent element can be seen in the table below.

Table 1. The constituent elements of bentonite before adsorption

Element Number	Element Symbol	Element Name	Confidence	Concentration
8	O	Oxygen	100.0	68.2
14	Si	Silicon	100.0	14.8
13	Al	Aluminium	100.0	13.4
7	N	Nitrogen	100.0	2.7
26	Fe	Iron	Manual	1.0

In Figure 6 and Figure 7, it shown that after adsorption of spent acid solution, bentonite was contained increasing percentage of sulfur, molybdenum and potassium, while the pore sizes enlarged between 157 nm to 254 nm. The increase of bentonite pores may be due to the nature of the reactive sulfuric acid towards bentonite so as to make the bentonite lattice decays and bentonite pores enlarge. The small residual sulfur bonded to the surface of bentonite

showed that most of the sulfur is adsorbed as the filtrate so that it can be recovered.

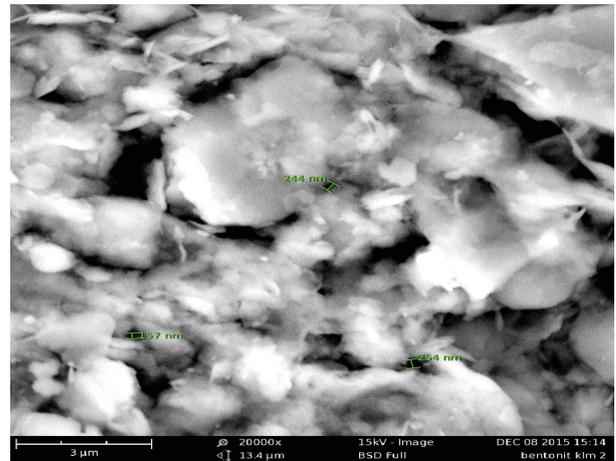


Fig.6. analysis of Scanning Electron Microscopy (SEM) bentonite after adsorption proses

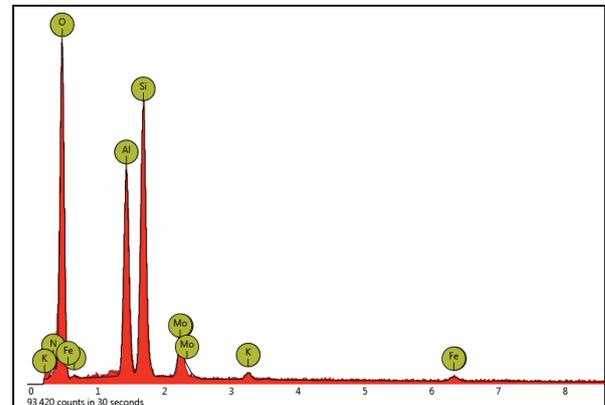


Fig.7. EDS Spectrum of Bentonite after Adsorption Process

Table 2. The constituent elements of bentonite after adsorption

Element Number	Element Symbol	Element Name	Confidence	Concentration
8	O	Oxygen	100.0	66.2
14	Si	Silicon	100.0	13.8
13	Al	Aluminium	100.0	12.5
16	S	Sulfur	Manual	0.5
42	Mo	Molybdenun	100.0	3.6
7	N	Nitrogen	100.0	2.2
19	K	Potassium	Manual	0.4
26	Fe	Iron	Manual	0.8

4 Conclusion

Recovery of sulfuric acid from the spent acid of alkylation results can be achieved by adsorption method using adsorbents of bentonite that are activated physically with a temperature of 850 ° C for 3 hours. Adsorbent mass affects the filtrate volume and sulfuric acid purity produced, where adsorption processes at 3 stages are capable of raising sulfuric acid purity of 82% to 94.94%.

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