The effect of the natural bentonite to reduce COD in palm oil mill effluent by using a hybrid adsorption-flotation method

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Abstract—Palm oil mill effluent is waste produced from palm oil processing activities. This waste are coming from condensate water, process water and hydrocyclone water. The high levels of contaminants in the palm oil mill effluent causes the waste becomes inappropriate to be discharged to water body before processing, one of the most major contaminants in wastewater is fats, oils and COD. This study investigated the effectiveness of chemically activated bentonite that serves as an alternative to reduce the COD in adsorption and flotation based palm oil effluent waste processing. Natural bentonite was activated by using nitrit acid and benzene. In the existing adsorption material to improve COD reduction capability whereas the flotation method was used to further remove residual effluent which is still remain after the adsorption process. An adsorption columns which operated in batch was used in the present study. By varying the circulation time and adsorbent treatment (activated and non-activated), it was shown that percentage of COD reduction reached 75% at the circulation time of 180 minutes for non activated adsorbent. On the other hand the percent of COD reduction in adsorption and flotation process using activated bentonite reached as high as 88% and 93% at the circulation time of 180 minutes.

1. Introduction

Indonesia is currently a country with the largest oil fields in the world. The area of oil palm in Indonesia in 2009 amounted to 8127 million hectares [2] and continues to increase every year. Increasing oil palm plantations will result in increasing the amount of palm oil mill to process the palm fruit. Palm oil mill effluent will produce a number ranging between 600-700 liters/ton of fresh fruit bunches (FFB). This waste comes from drab water, condensate water, process water and water hydrocyclon. The materials contained in the waste, among others, oil-grease, NH3-N, TOC, COD, BOD, and TSS with high concentrations which need to be processed before discharged to the environment.

Palm oil wastewater treatment is conventionally done biologically by using pond system, where the liquid waste is processed in a pond by utilizing anaerobic and aerobic microbes. This process takes 120-140 days to break down the organic material with efficiency of 60-70%. Required land area reaches up to 7 ha to process 30 tons/hour of fresh fruit bunches (FFB) and it limitate the availability of land, more over, in the rainy season the pond will be overflow. Therefore it is necessary to have a process that can cultivate the oil palm waste water efficiently. One of the methods that can be used is
the adsorption which using natural adsorbent (in this case the bentonite) combined with flotation process.

Research adsorption using bentonite as the adsorbent has been done by several researchers [4,6-8,11-13,17-21]. Weishan (2013) used bentonite to remove polyvinyl alcohol in water, so did Ishq, M (2015), he also used bentonite to remove oil in water. Similarly, the preliminary study of hydrocarbon compounds in the wastewater by flotation process has also been carried out [1,3,5,11,14,16]. The study of adsorption studies using other adsorbent has been done to remove oil in water using activated carbon and zeolite as adsorbents [14]. While the use of organic clay to eliminate petroleum hydrocarbons in industrial waste have also been studied [10]. From the above explanation, it can be seen that the adsorption method is suitable for setting aside hydrocarbon compounds in the water, especially for levels of COD.

In this study, a modified natural bentonite is used as an adsorbent hydrocarbons (such as fats and oils) in the palm oil mill effluent (POME). Based on the results of previous studies, it is known that the adsorption method was only able to adsorb free hydrocarbons in the water, but for bounded hydrocarbons in water it is necessary to give an additional alternative process, namely the flotation method.

2. Procedure
The study was conducted in a laboratory scale, using adsorption column with a circulatory system and proceed with the flotation process. The sample used is palm oil mill effluent from Cot Girek.

2.1 Materials and Equipment
Materials used in the study is the effluent waste palm oil, Bentonite (activated and non-activated), Crystal K_{2}CrO_{4} 0.1 N H_{2}SO_{4} (Merck), HNO_{3} 0.5N (Merck), benzene (Merck), Ag_{2}SO_{4} (Merck), HgSO_{4} (Merck), indicator Ferroin (Merck), and Fe(NH_{4})_{2}(SO_{4})_{2}.6H_{2}O (Merck). While the tool used is the adsorption column and flotation (adsorption column made of acrylic), pumps, flow meters, sewage tank, aerator, diffuser as well as the supporting tools of analysis.

2.2 Bentonite Adsorbent Preparation
Natural bentonite originated from Nisam area of North Aceh is crushed and sieved to obtain the appropriate size (± 1 cm). Bentonite is dried in a furnace at a temperature of 600°C for 2 hours, cooled to room temperature and stored in a desicator. Bentonite then was activated with 0.5 N nitric acid and benzene, each for two hours, washed with distilled water until the pH is neutral. Bentonite is dried in an oven at temperature of 105°C for two hours thus ready to use as an adsorbent.

2.3 Experimental Procedure
In the adsorption process the waste tank, liquid waste was included as much as 10 liters of POME. Adsorption column was filled with bentonite with a 30 cm bed height. Waste was inserted through the top of the column by using a pump with a flow rate (1 L/min). COD changes were observed in the variation of circulation time for 15-180 minutes during the adsorption process was taking place. While in the flotation process palm oil effluent was included from the adsorption process results in a flotation tank as much as 5 liters, aerator was include which has been connected with the diffuser using a hose. The changes were observed for each waste COD adsorption process results. The series of adsorption and flotation unit is shown in Figure 1.
2.4 Analysis
In this research, analysis of the waste after adsorption and flotation processes, namely COD levels measured at the time variation of circulation. The methods used are closed reflux method (titration) with the analysis tool COD reactor.

3. Results
A. The characteristic of palm oil mill waste
Based on the study conducted in laboratory of unit operation and water processing, the result showed the analysis of COD level and fat in the water of palm oil mill waste in the waste reservoir tank in Cot Girek before and after the process of adsorption and flotation using activated bentonite. The analysis is as shown in table 1.

| Parameter | Unit     | Value         |
|-----------|----------|---------------|
| TOC       | mg/L     | 5065.13       |
| COD       | mg/L     | 18739.776     |
| pH        |          | 5             |
| TSS       | mg/L     | 15000         |
**B. Characteristic of Bentonite**

Characteristic of bentonite was conducted by measuring the value of Cation Exchange Capaticity (CEC) and the particle size of bentonite. CEC was done by using methilen blue method, while the size of bentonite pore was measured by using SEM. The result of CEC measurement is displayed in table 2.

| No.  | Type of Adsorbent                                                                 | Cation Exchange Capacity CEC (meq/100 gr) |
|------|-----------------------------------------------------------------------------------|------------------------------------------|
| 1.   | Bentonite after heating process in 600°C                                          | 30                                       |
| 2.   | Bentonite after being activated by using nitric acid and heating process in 600°C | 42                                       |
| 3.   | Bentonite after being activated by using benzene and heating process in 600°C     | 48                                       |

The following characteristic bentonite beside by using the measurement of CEC value is by determining the pore size of bentonite by using SEM in 4000x enlargement, and the result gained is as in figure 2.

![Figure 2. The result of pore measurement using SEM](image)

Based on the measurement of pore size by using SEM, the result gained is as displayed in table 3.
Table 3. Size of Bentonite Pore.

| No. | Type of Bentonite                                                                 | Range of Pore (µm) |
|-----|----------------------------------------------------------------------------------|--------------------|
| 1.  | Bentonite after heating process in 600°C                                        | 0.610 – 2.030      |
| 2.  | Bentonite after being activated by using nitric acid after heating process in 600°C | 0.728 – 3.780      |
| 3.  | Bentonite after being activated by using benzene after heating process in 600°C   | 1.861 – 6.990      |

From the adsorption and flotation process obtained the results of COD removal as shown in Figure 3. From the Figure it is seen that the longer the contact time given, the removal efficiency COD liquid waste palm mill obtained greater.

![Figure 3](image.png)

**Figure 3.** Graphic of COD removal based on circulation time variation in adsorption process

In flotation process, flotation tank with six liters capacity is used and oxygen is in through diffuser. The waste that will be processed is originated from the output of effluent in adsorption column with contact time for 30 minutes. The result of COD removal in flotation process is explained in figure 3.
4. Discussion
From the analysis of table 1, it can be seen that the value of TOC and COD from the liquid waste of palm oil mill is still beyond the maximum limit of the standard quality for liquid waste of palm oil mill that has been set by Bapedal, KEPMEN LH No.51/MenLH/10/1995 that 500 mg/l for COD. While the TOC value if referred to the standard quality of oil and gas waste, it has the limit for 100 mg/L. Based on those TOC and COD values, it is necessary to conduct the process for waste water of Palm Oil Mill and in his study, the removal of COD is observed through the adsorption and flotation process by using bentonite as the adsorbent.

In table 2, it showed the varies value of CEC of bentonite. Based on physical and chemical activation, the bentonite has CEC as much as 30, 42 and 48 meq/100 gr for the bentonite that has been heated in 600°C, by using nitric acid and benzene respectively. Chemical activation to the heated bentonite raised up the value of CEC where benzene is better than nitrit acid. The value of CEC is relatively small due to the heating process in 600°C in the furnace that caused the the broken of misel in the bentonite. However the heating in the furnace is neccesary because the used bentonite is in adsorption coloumn, without the heating process, the bentonite will be smashed and cause the blockage in the coloumn. In pre-research, it has been done vary of heating temperature treatment to get the stable bentonite to the adsorption process especially to the liquid waste of palm oil mill. The result of pre-research showed that the heating temperature in 600°C produced the stable bentonite and it is not smashed during the adsorption process.
From figure 3. It showed the percentage of COD removal after adsorption process by varying contact time from 15 minutes to 180 minutes. From the graphic, it can be seen clearly that in 180 minute. It also can be seen that in 180 menit the biggest removal of COD was gained for the three types of adsorbents, however the optimum time is still not be reached considering the given trend is continously raising. For the activated bentonite physically through the heating process in 600°C, it is gained the COD removal as much as ± 75%, while for the both physical and chemical activated bentonite, the removal reached up to ± 86% and ± 89%, each for nitric acid and benzene as the activator. The duration of contact time between adsorbate and adsorbent would effect the capaticy of adsorption. The longer contact time, the more organic compound will be adsorpted until it become balance. On the other hand, when it has been balanced, the contact time will no longer give effect to the capacity of adsorption.

This study used three types of treatment for the bentonite, there are ; bentonite activated physically through the heating process in 600°C (adsorben 1), adsorbent activated phisically and chemically by using nitric acid (adsorben 2) and benzene (adsorben 3) as activators. The heating process in furnace is conducted to keep the form of bentonite stable in adsorber column during the adsorption process. From Figure 3, it showed that the adsorbent is only activated physically which is by heating in furnace in 600°C for one hour, it gave the smallest percentage of removal. While the bentonite that has been activated both physically and chemically gave the better result, especially the activation using benzene. This is also supported by the each CEC values of bentonite as displayed in table 2. In thermal activation, high temperature can omit water molecule and other impuritie. The change of structure and composition during the heating process can vary based on the chemical composition of natural bentonite and time of heating. The over heating can cause the short space in structure and interlayer of bentonite, the small interlayer space can cause the particle diffusion closer to another atom that can affect the space surface and CEC value of the bentonite. This is supported from CEC data in table 2.

The purpose of chemical activation by using nitric acid is to exchange Ca$^{2+}$ that exist in Ca-bentonite become ion H$^+$ and release ion Al, Fe, dan Mg and other impurities in the bentonite structure, so that the bentonite become active. For that purpose, beside nitric acid, sulfate acid and choride acid are chemical compound that also commonly used. During the activation process, Al, Fe, and Mg are dissolved in solution, then the acid adsorption occured to the bentonite structure, so the structure series have wider space.

Beside activated with acid, in this study the bentonite is also activated by using organic compound, benzene. Generally, bentonite is modified with organic compound to raise its afinity to organic compunds that trigger COD and TOC in liquid waste. The organic cation that is used shoul have the positive contain. The organic cation will replace the anorganic cation in bentonite interlayer area so it can increase its activity to the organic compound.

The modified bentonite with organic compound is namely organo bentonite. The addition of organic compound can also create organo bentonitewhich has spesific character, one of its important characters is thermal stability. In this study, the activated bentonite using benzene has higher thermal stability compared to the activated bentonite using nitric acid and heated in furnace. The CEC value of the organobentonite as much as 48 meq/100gr, bigger that the bentonite activated with HNO$_3$ and heated in furnace which is as much as 42 meq/100gr and 30 meq/100gr (table 2.).

From Figure 4, It was resulted the COD removal after flotation process. The coloumn effluent of adsorption in 180 minutes with activated bentonite after being processed in flotation tank and resulted
the average COD removal for ± 93%. Studies about flotation method have been done by several researchers, Hong Zhong et al, 2015 studied the removal of mine ore by using flotation method and managed to remove up to 100%. So did Jinzhou Qu et al (2015), he observed the characterization of flotation in distributing coal particle, while I Wayan Budiarsa (2012) analyzed the COD removal of industrial waster which resulted the efficiency more than 90%. From the several previous researchers and the result from this study, it showed that the flotation method is the appropriate method to remove COD in liquid waste of palm oil mill.

5. Conclusion
The combination between adsorption and flotation process showed the significant effect to the decreasing of COD level in liquid waste of palm oil mill. The percentage of COD removal of Palm oil mill liquid waste after adsorption process gained up to 88.76 %, that is in contact time 180 minutes with bentonite activated with benzene. The using of nitric acid and benzene as the bentonite activator gave the very good removal COD, where benzene as the activator was able to absorb better. The flotation process was able to remove COD in liquid waste of palm oil mill mainly 93% with contact time 30 minutes.

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