Using Fly Ash And Bottom Ash Boiler Of Palm Oil Factories As Adsorbents For Adsorption Of Color In Artificial Liquid Waste

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ABSTRACT
This study aims to determine the ability of bottom ash and fly ash in adsorbing artificial wastewater dye (PtCo) and chemical oxygen demand (COD) with three variations of adsorbent used in adsorption column. This research begins with the process of washing, drying and sieving adsorbent. Then proceed with the activation process of adsorbent using HCl 1 M which is heated at 90 °C for 1 hour accompanied by stirring. The adsorption system used is continuous (column) with up-flow flow pattern and using the pump to provide pressure so that the influent can pass through the adsorbent contained in the column. The characteristic analysis of adsorbent was done on moisture content, ash content, and iodine absorption. The highest moisture content and ash content obtained were 0.6% with fly ash adsorbent before activation and 0.285% with fly ash adsorbent after activation. Compared with SNI 06-3730-95 has been appropriate, while the iodine drainage from bottom ash was 35.38 mg/g and fly ash of 50.76 mg/g and none meet SNI 06-3730-95 of 750 mg/g. The highest efficiency results in dye and COD were found in adsorption column with fly ash adsorbent with color value of 96.96% and COD concentration of 83.26%, followed by stratified columns with combined adsorbent between bottom ash and fly ash with color values of 53, 93% and COD of 62.82%, and adsorbent by using bottom ash efficiency of highest color value of 53.03% and COD of 71.08%. The highest adsorption capacity was obtained by using adsorption column with bottom ash and fly ash (BF) adsorbent of 8.42 mg/g, followed by fly ash (FA) of 7.53 mg/g and bottom ash (BA) of 7, 37 mg/g.

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1. INTRODUCTION
Palm oil in Indonesia is a vegetable commodity as a producer of Crude Palm Oil (CPO) with an area of 4,763,797 hectares of oil palm with production 11,267,161 tons based on Indonesia's plantation statistics in 2016. With such a large area of oil palm cultivation, oil palm plantations and their processing plants have the potential to produce CPO and besides that, they also produce a
very large amount of organic waste compared to other plantation crop wastes. These abundant
natural resources are scattered in various parts of Indonesia, especially in Sumatra and
Kalimantan.

The development of the palm oil industry that continues to increase will have an impact on
solid waste generated from processing fresh fruit bunches (FFB). F. Irene. (2010) said that solid
waste in the form of palm kernel shells and fibers has been used as fuel in palm oil mills since the
factory was established to produce electricity and water vapor used for processing in the factory.
Shell burning, as well as FFB, produce waste in the form of ash which is not utilized and managed
properly so that it can cause environmental damage. The combustion ash from the boiler is called
Palm Oil Fuel Ash (POFA) (Farandia., 2015).

Liquid waste comes from factories which usually use a lot of water in the production process.
Water from factories carries a number of solids and particles, both dissolved and settled. Some of
these materials are rough and some are smooth. Often the factory effluent is cloudy and has a high
temperature. Polluted wastewater has visually identifiable characteristics from turbidity, color, taste,
or other indications (Muthawali, 2013).

Color in water is due to the characteristics of the substances present in the water and not to
the water molecules themselves, from metals in rocks and soil, from soil organic matter and plants.
Colors in water and wastewater are divided into two, namely true colors and false colors. True color
comes from dissolved organic substances, minerals, chemicals in water that cannot be separated
by filtration, water color is caused by heavy metals, generally because iron, copper or manganese,
leaves and peat can add tannins, glucose, and others, which can produce yellow or brown zones.
While the pseudo color comes from suspensions and colloidal materials that can be separated by
filtration, and comes from industrial waste which usually produces various chemicals and colors.

From the description above, it can be concluded that the ash from palm oil mills can be used
as an adsorbent to adsorb dissolved and insoluble substances in wastewater. In addition, palm ash
is easy to obtain, available in large enough quantities and cheap so that it is very effective to use
as an adsorbent. In this study, boiler ash was used to adsorb dyes in artificial liquid waste. Boiler
ash used in this study is bottom ash and fly ash which have been activated with 1 M HCl solution
and use a column system with an up-flow pattern. Because in the column system, the solution is
always in contact with the adsorbent so that the adsorbent can adsorb optimally until the saturation
condition is when the effluent concentration approaches the influent concentration.

2. RESEARCH METHOD

2.1 Research Flowchart

The research to be carried out is an experimental research with a laboratory scale. This study
was conducted to determine the ability of BA and FA from palm oil mills as adsorbents that have
been activated using 1 M HCL to absorb artificial liquid waste using the up-flow column method.

2.2 How Adsorbent Preparation and Activation Works Adsorbent Preparation

The adsorbent preparation process begins with washing the BA and FA of the palm oil mill
using water to remove impurities and separate the shells contained in the ash and after that the
ash is dried in an oven until the ash is dry. Furthermore, BA and FA were sieved to obtain 140
mesh or 105 m.

2.3 Adsorbent Activation Process

Before the activation process is carried out, the BA and FA boilers are first washed with
distilled water, then dried in an oven at 110 0C for 3 hours, after which the ash is weighed dry.
Furthermore, the BA and FA boilers were activated with 1 M HCl solution accompanied by heating
at 90 0C for 1 hour. The activation process is carried out by comparing BA and FA with HCl, which
is 1:4. After that, the BA and FA boilers were drained from the HCL solution and washed again with
distilled water until the pH of the ash became neutral. The BA and FA boilers were then re-dried in
the oven at 110 0C for 3 hours.

2.4. Sampling Method
The adsorbent samples in the form of BA and FA were taken before and after the activation process and then stored in a closed container for testing the characteristics of BA and FA with water content, ash content, and iodine absorption. The next sample, namely effluent from the adsorption process with BA and FA, was collected in a closed container which was taken every 16 minutes, then tested for COD concentration and color. This was done for the effluent in the adsorption process of column I, column II and in the adsorption process carried out with a stratified system, namely column III.

2.5 Data analysis
Data analysis was carried out on the characteristics of the adsorbent originating from the bottom ash boiler and fly ash of the palm oil mill. The data analysis was carried out on each adsorbent with the same activation process. Data analysis was also carried out on dyes using the color value measurement method (PtCo), COD removal efficiency, breakthrough curve for color and COD values, and COD adsorption capacity obtained by numerical integral equations based on Simpson’s method.

3. RESULTS AND DISCUSSIONS
3.1 Preparation and Activation of Bottom Ash and Fly Ash Boiler Boiler Adsorbents for Palm Oil Mills
This study used bottom ash (BA) and fly ash (FA) adsorbents sourced from two PKS. Fly ash was obtained from PTPN III Sei Mangkei and bottom ash was obtained from PTPN III Sei Silau. Both of these ashes were chemically activated using 1 M HCl to remove impurities or by-products that covered the ash pores. Activation is carried out to increase the adsorption ability to absorb dyes and Chemical Oxygen Demand (COD) contained in artificial tea wastewater. The size of BA and FA used in this study was 105 μm or passed on a 140 mesh sieve which can be seen in Figure 1.

![Fly Ash Activated with 1 M HCl](image)

Figure 1. Fly Ash Activated with 1 M HCl

In Figure 1, the color of BA is darker than FA, it is because the ash source comes from a different factory and BA has relatively a lot of impurities mixed under the furnace. The combustion temperature of BA is between 700-800 °C, while FA has a combustion temperature of 800-1000 °C and FA is finer in color with a grayish white color.

3.2 Characteristics of Bottom Ash and Fly Ash

a. Water content
The water content test aims to determine the hygroscopic nature of the ash. Water content testing was carried out on bottom ash and fly ash before and after activation. BA and FA ash was heated at 110 °C for 3 hours to evaporate the water still contained in the ash which can be seen in Figure 2.
Based on the water content of BA and FA, coconut mills are relatively low because high water content will affect the absorption of liquid. Low water content is expected to have good absorption because the pores are not closed by water so that it has a large absorption. The data in Figure 4.2 shows that the highest water content value is fly ash before activation of 0.6% and followed by bottom ash after and before activation and fly ash after activation. The high water content in fly ash before activation was due to the ash storage not being carried out in a closed manner so that the water around the ash absorbed into the ash as it is known that the preparation of BA and FA ash from sieving and storage was carried out in an open state.

When compared with activated charcoal-based adsorbents, the water content is influenced by hygroscopic properties, the amount of water in the air, the length of the cooling, milling and sieving processes. High water content can reduce the adsorption power of activated charcoal to liquids and gases (Wibowo, et al. 2009).

According to Mu’jizaz (2010), the lower the water content, the more space in the pores that can be occupied by the adsorbate so that the adsorption takes place optimally. The binding of water molecules on the adsorbent by the activator causes the pores in the carbon ash to get bigger. The larger the pores, the larger the surface area of the adsorbent. This results in an increase in the adsorption ability of the adsorbent.

b. Ash Level

Ash content testing aims to determine the content of metal oxides and minerals in BA and FA ash which is not wasted during combustion and activation. Ash content testing is carried out on BA and FA before activation and after activation with 1 M HCl.

The results of the ash content test showed that the ash content of BA was smaller than that of FA both before activation and after activation in a furnace at 600°C for 4 hours. The high ash content after activation is because the activator reacts with the metals that cover the surface of the adsorbent to form salts that can dissolve into the activator solution so that when heated at a temperature of 600°C, the salts also burn.

According to Budiono (2006) the high and low ash content is influenced by the activator in dissolving inorganic minerals contained in activated charcoal. The ash formed is because the material has mineral elements such as calcium, potassium, sodium, and magnesium. The content
spreads in the activated charcoal lattice so that it covers the activated charcoal pores (Pari et al., 2001).

According to Herlandien (2013), the remaining minerals will cause blockage of the activated charcoal pores so that it affects the adsorption that occurs.

c. **Iodine Adsorption**

Lodine absorption aims to determine the ability of the adsorbent to adsorb adsorbates with small molecular sizes ranging from 10 Angstroms. The level of adsorption of the adsorbent on iodine can be seen from the number of iodine obtained. The iodine number indicates the amount of iodine (mg) that can be absorbed by one gram of the adsorbent. Iodine adsorption is an important parameter to determine the quality of the adsorbent, related to its use in the process of purification, cleaning and blanching and other uses. Determination of iodine absorption was carried out on BA and FA which had been activated with 1 M HCl.

![Figure 4. Lodine Adsorption of Bottom Ash and Fly Ash](image)

Based on SNI 06-3730-95 for activated carbon-based adsorbents, the minimum iodine adsorption capacity is 750 mg/g, thus BA and FA adsorbents that have been activated with 1 M HCl do not meet the requirements because their absorption capacity is below 750 mg/g. This is due to the presence of impurities that cover the pores of the BA and FA ash and the ash has not enough micropores to adsorb the iodine solution. In Figure 4.3 there is a difference in the value of the iodine adsorption capacity of BA and FA, this difference is influenced by the temperature and length of combustion time in the palm oil mill boiler, so it greatly affects the quality of the ash in removing impurities and the formation of ash pores. Different ash collection sites also affect the size of the particles used as adsorbents because BA has a relatively larger size while FA has a relatively smaller size than BA. According to Idrus, R. (2013) The greater the value of the iodine number, the greater the adsorption power of the adsorbent.

3.3 **Adsorption Process in Column Fixed Bed Adsorbers**

The tea solution is passed on the adsorption column in an up flow manner, the adsorbent will bind the dye and COD contained in the solution, then the solution is passed continuously through the adsorbent which is initially free of adsorbate. The bottom of the bed that first received the solution would be very effective at absorbing the dye and COD and the dye and COD that escaped would be absorbed by the next bed. Sampling of the adsorption column effluent was carried out every 16 minutes after the adsorption process took place until it approached the adsorption column effluent concentration with the adsorption column effluent concentration (Ce/C0) approaching 1 (saturated).

From Figure 4, the fluctuation of COD removal efficiency indicates the occurrence of a deasorption process due to the pressure generated in the up-flow flow of the adsorption column. Due to the flow pressure, the adsorbate that has been absorbed by the adsorbent can be released again. Based on the measurement of the color and COD values of each adsorption column effluent, a breakthrough curve was obtained for each adsorption column which can be seen in Table 1.

| Effluent Adsorption | Color Value (Pt Co) | COD concentration (mg/L) |
|---------------------|---------------------|--------------------------|
|                     |                     |                          |
### Adsorption Capacity

The contact time of the solution with the adsorbent in the column was different even though the initial flow rate was set the same, namely 20 ml/min. The longest contact time is when the column is stratified with bottom ash and fly ash media of 39 minutes, followed by bottom ash column of 32 minutes and fly ash of 29 minutes. The difference in contact time is influenced by the design of the column used, the adsorbent column still has leakage so that it affects the flow rate, the size of the adsorbent is very small so that the solution passed is difficult to find a gap to exit, and the influent flow that first enters the adsorption column is upflow. is still relatively smooth because the adsorbent condition is dry, The next influent flow will not be as smooth as the first influent flow because it is blocked by the pressure generated by the weight of the adsorbent in a wet state so that the time increases but the flow rate decreases. From the available data, it can be concluded that the removal of color and COD values is not only influenced by contact time but also by particle size, combustion process and adsorbent activation.

#### 3.4 Adsorption Capacity

The adsorption capacity was used to determine the COD adsorption capacity with BA, FA and BF adsorbents. The adsorption capacity calculation was only carried out on the COD value, because the COD value already described the overall organic and inorganic materials contained in the artificial tea liquid waste.

Figure 5 shows the highest COD adsorption capacity possessed by adsorbent BF of 8.42 mg/g, followed by FA of 7.53 mg/g, and the lowest COD adsorption capacity of BA adsorbent of 7.37 mg/g. If viewed from the results of iodine adsorption, the value of FA adsorption capacity is

| Adsorbent | Intake Time | Contact Time (Minute) | Influent | Effluent | Ce/Co |
|-----------|-------------|-----------------|---------|---------|-------|
| Bottom Ash | t1 | 32 | 775 | 0.47 | 133 |
| Fly Ash | t2 | 48 | 1650 | 0.65 | 460 |
| Batman Ash and Fly Ash | t3 | 64 | 1085 | 0.92 | 6 |
| | t4 | 80 | 1570 | 0.95 | 2 |
| | t5 | 96 | 1330 | 0.80 | 6 |
| | t6 | 112 | 1650 | 1.00 | 0 |

The adsorption capacity calculation was only carried out on the COD value, because the COD value already described the overall organic and inorganic materials contained in the artificial tea liquid waste.
higher than the value of BA adsorption, so the adsorption capacity value in Figure 4.14 is directly proportional to the result of iodine adsorption, while the BF capacity value which is higher than BA and FA is due to consisting of two different ash in one column, so that the molecules contained in the tea solution, both large and small can be adsorbed. FA has more micropores while BA does not have too many micropores, so the compounds that are not adsorbed by FA can then be adsorbed by BA, using two or more adsorbents in one column will allow the compounds contained in tea waste to be more adsorbed.

![Figure 5. COD Adsorption Capacity of Each Adsorption Column](image)

4. CONCLUSION
The water content obtained from the test results of the characteristics of the adsorbent, the FA water content before activation was higher than that of BA by 0.6% and 0.21%, while after activation, BA was higher than FA by 0.34% and 0.09%.

The ash content obtained from the test results of the characteristics of the adsorbent, FA ash content is higher than BA both after activation and before activation. The ash content of BA before activation was 0.035% and after activation was 0.069% and FA water before activation was 0.214% and after activation was 0.285%.

Iodine adsorption capacity of FA and BA adsorbents activated by HCl where FA has a higher adsorption capacity than BA, namely: 50.76 mg/g and 25.38 mg/g.

The highest color removal efficiency was obtained by using an adsorption column with an adsorbent FA pada t1 of 96.96% then followed by an adsorption column of BF at t1 of 53.93% and BA at t1 of 53.03%. The highest COD removal efficiency was using a column with FA adsorbent at t2 of 83.26% followed by BA adsorption column at t1 of 71.08% and BF at t1 of 62.82%.

The highest COD adsorption capacity was obtained using an adsorption column with adsorbent BF of 8.42 mg/g, followed by FA of 7.53 mg/g, and BA of 7.37 mg/g.

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