Palm Oil Mill Effluent Treatment by Using Copperas as Physicochemical Treatment Agent

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Abstract. The palm oil mill industry in Malaysia are a huge agriculture industry which generates significant amount Palm Oil Mill Effluent (POME). POME is an oily wastewater which consist of various suspended components, the liquid are a combination of steriliser condensate and cooling water. The wastewater is very pollutant to human and environment, the coagulants applied to reduce the suspended materials in POME as following the stringent requirements of biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solid (TDS), total solid (TS) and turbidity as stated by the Department of environment. This paper analyses the use of ferrous sulphate heptahydrate as a coagulant as it was applied on the primary treatment and the results improvement upon physicochemical treatment parameters. Series of batch treatment for coagulation and flocculation with ferrous sulphate heptahydrate were conducted. Dosage and pH were conducted to determine the optimum conditions to apply the coagulants. The result of coagulants showed that ferrous sulphate heptahydrate have a good effect on BOD reduction at dosage 1500 mg/l pH of 3.4 before pH adjustment. There were eight different samples used for different concentration of coagulant, the sample of 250 ppm copperas feed till 1000 ppm feed has the COD result difference of 171 ppm. When the copperas feed increased the COD value will decreased gradually. For the second parameter, biological oxygen demands the BOD value are reduced successfully, the first sample with feed concentration 500 ppm of copperas has BOD value of 288 ppm. As we increase the feed of copperas to 2000 ppm the BOD value reduced to 13 ppm. Next the highest value of TSS reduction is at 2000 ppm of copperas feed, at the specific dosage the TSS reading was 7502 ppm

1. Introduction
The palm oil industry in Malaysia is the primary contributor from the rural segment to the national economy, which has contributed income of nearly RM63.5 billion of every 2014 from the export of palm oil-based products. This is regardless of the oil palm plantations just covers 16 percent of the in general planted horticultural zone in Malaysia, or proportionate to about 5.23 million hectares. The palm oil industry prepared 95.4 million ton of oil palm organic products Fresh Fruit Bunches (FFB) in 429 palm oil processes all through Malaysia that created 19.65 million ton of CPO in year 2014.

Higher crude palm oil (CPO) creation has expanded the measure of waste produced from the palm oil extraction process, the two solids and fluid waste. The major waste streams are POME that makes up roughly about 0.5 - 0.8 ton of POME from each ton of FFB handled in the event that the untreated effluent is released into water course, it is sure to cause significant ecological issues because of its high contamination load as biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, total solids (TS) and suspended solids (SS). The palm oil plant industry in Malaysia has in this way been recognized as the one releasing the biggest contamination load into the streams all through the nation (Asis, Affiq, Arifin, Ngteni, & Tahiruddin, 2016b).
2. Scope of study
This study consists of several lab experiments which utilize copperas (ferrous sulphate) as the coagulant to treat the primary treated palm oil mill effluent POME. The palm oil mill effluent sample was obtained from kilang sawit Panji Alam which is located in Kemaman, Terengganu. The efficiency of the coagulant was assessed based on biological oxygen demand, chemical oxygen demand, total suspended solid and final pH of the treated POME.

The main focus of this research is the application of ferrous sulphate heptahydrate as a potential coagulant for the treatment of POME. Physicochemical properties such as pH, temperature, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), Oil & Grease (O&G) Fresh POME turbidity from Sludge Pit (Primary POME), secondary anaerobic digester tank (Secondary POME), First tertiary aerobic pond (Tertiary POME) have been identified. The coagulation tests were conducted in accordance with standard coagulation-flocculation testing of industrial wastewater treatment (APHA, 2012) at different coagulation doses (200mg/L - 2000 mg/L), dilution factor (DF) at natural pH and temperature for 60 minutes. The coagulation capacity of ferrous sulphate heptahydrate and ferrous sulphate monohydrate were calculated by extracting BOD, COD, TSS, SS, turbidity in primary POME, secondary POME and tertiary POME treated.

The coagulation efficiency of coagulants ferrous sulphate heptahydrate and ferrous sulphate monohydrate has been compared and determined which coagulants and their optimal experimental conditions are most suitable for use as coagulants. POME coagulation was subsequently performed on a pilot scale using the optimum experimental conditions of copperas coagulant (coagulant doses of 750 mg/L - 1250 mg/L; natural pH, ambient temperature, reaction time of 3 h). Finally, the economic viability of the copperas coagulation of POME was determined and compared with the existing POME tertiary treatment cost.

3. Materials and Methodology
The sampling method and briefs procedure taken on the sample to be taken, the stage of effluent treatment that to be studied and the safety aspects of running the sampling, the analysis and data collection from sample test, following the parameter the primary effluent should be tested for Total Dissolved Solid (TDS), biochemical oxygen demand BOD, chemical oxygen demand COD. The jar test method is key to the research and conducted by using the most precise equipment in UC TATI laboratories.

3.1 Jar Test Method
Jar test used the treatment chemicals used in palm oil mill effluent coagulation process. This simulates the coagulation/flocculation process in a water treatment plant and lets operators decide whether they are using the correct amount of treatment chemicals, thus enhancing the performance of the plant. Jar conducted by adjusting the amount of coagulant and the sequence in which they are added to samples of raw water held in jars or beakers. The sample is then stirred in such a way that floc formation, development and settlement can be observed as it would be in the full-scale treatment plant. Flocculates formed when treatment chemicals combine with raw water content and clump together. The operator then conducts a series of tests to measure the effects of different quantities of flocculating agents at different pH values in order to assess the correct floc size for a specific plant. The right floc size varies according to the filter size. Figure 1 shows the setup of jar test equipment.
Figure 1: POME jar testing using setup rpm speed

3.2 **Determination of Chemical Oxygen Demand**

Chemical oxygen demand was used to determine the quantity of pollution in water after wastewater treatment. The value of COD indicated by testing the water sample using calorimetric analysis. In experiment for COD analysis the 1ml was treated clear solution with the COD reagent were heating for 2 hours at 150 °C using the COD reactor. COD reactor function was used to heat the COD reagent with the samples for 2 hours at 150 °C. After 2 hours, the samples were cooled down for a few minutes before testing the organic matter present in wastewater was oxidized by reagent material in the presence of Sulphuric acid to produce carbon dioxide CO2 and water H2O. The quantity of potassium dichromate used in the reaction is equivalent to the oxygen used to oxidize to organic matter of wastewater. The results of COD under this procedure are described as the mg of O2 consumed per liter of sample. The specimen is tested with Hach dr900 COD calorimeter which utilizes chromatography mechanism to which compared the reading between the blank sample and the wastewater sample that had been tested. Decomposition tracking by measuring the absorption at the correct wavelength (420 or 610 nm). Use a vial containing 5 mL of deionized water to zero the device in the absorbance mode and calculate the empty absorbance. The value is registered. Prepare a new blank when approximately 0.01 absorbance units have modified the absorbance.

3.3 **Determination of Biochemical Oxygen Demand**

Two BOD bottles were completely filled with dilution water. The correct specimen volume was carefully measured. Then the sample was put into the dilution before the containers are filled and the bottle was closed, the initial dissolved oxygen of one of the duplicate bottles are determined, including water dilution blank by one of the approved methods and record data. The bottles are placed in the incubator at 20°C and incubate for five days. The dissolved oxygen content of the incubated bottles was determined at the end of exactly five days. For each dilution, the biochemical oxygen demand was determined by using the formula. From those dilutions that have a depletion of at least 2 mg/L DO and at least 1.0 mg/L residual, the most reliable biochemical oxygen demand will be obtained. If there is more than one dilution that meets these criteria, the biochemical oxygen demand results should be averaged to obtain a final biochemical oxygen value. The blanks of the dilution water are only used to test the dilution water quality. The loss of dissolved oxygen will be less than 0.2 mg/L if the water value is decent and free of impurities. In either case, do not use the obtained depletion as a blank correction. Palm oil mill effluent are known for its high value in biological oxygen demand, as in the presence of dissolved oxygen aerobic bacteria used the organic materials founded in the effluent as a food. The calculation for the five day biochemical oxygen demand must conducted using the formula 3.1 , with $D0$ is the initial dissolve oxygen , $D5$ is the bod value after the fifth day , so the difference of dissolved
oxygen should be divided by $P$ which is the dilution factor of the used volume of sample. The BOD test is used because it measures the treatment plant efficiency in terms of BOD removal and control the plant process. It also used to determine the impact of the effluent discharge on the receiving waters. The final measurement of all oxygen consuming materials in a sample are termed as Total Biological Oxygen Demand (TBOD) and because the test are run in five days it is often referred as Five day BOD (BOD$_5$).

### 3.4 Determination OF Total Suspended Solid (TSS)

Very simply, by filtering supernatant from centrifugation (Figure 2) of the specimen through a particular pore size filter, TSS is anything that was captured. Suspended solids can range from silt or sand particles to pieces of plant material like leaves or stems. High amounts of TSS can cause a body of water to look aesthetically undesirable. Either the water's colour or overall turbidity will be adversely affected. There are several things that need to consider maintaining a good sample data. The effluent that are used may contain high concentration of metal waste and sulphates, those presence of impurities would make the sample absorb moisture from the area, so the sample are stored in air thigh container. Next, throughout drying process the sample may lose its constituents, the sample drying time were planned and the sample was cooled. The volume of residue over the whole sample were monitored, so much residue was entrapped water during evaporation.

3.5 Salinity Test of Copperas

There are two main methods of determining the salt content of water; Electrical Conductivity (EC), and Total Dissolved Solids (TDS). EC is a measure of how much electrical current can flow through a sample of water while TDS is a measure of the relative weight of dissolved materials in a sample of water. The salinity testing of copperas was conducted as one of the analysis that applied on the material. Copperas was tested using Hach conductivity meter. Electrolytic conductivity is the ion movement in a solution that generates an electrical current and is the reciprocal resistivity of the solution. The ions were derived from inorganic dissolved solids (e.g., chloride, nitrate, anions and sodium, calcium, magnesium, iron, and cations of aluminium). Organic materials such as oils, phenols, alcohols, and sugars were not conductive enough for a reasonable concentration calculation. Conductivity meters calculate the resistance in a solution area specified by the probe's physical design. A voltage was applied between the electrodes and was used to measure the conductivity for each centimetre by the voltage decrease induced by the solution resistance.

3.6 Determination of Moisture Content in Copperas

Since the copperas that used are ferrous sulphate hepta hydrate, the nature of the material is high moisture. By using thermalgravimetric method the percentage of moisture content were determined. During the procedure the samples were taken and by using cubicle, the samples were weighed for the initial measurement, later were being dried in oven.
4. Results and discussion

4.1 Chemical Oxygen Demand

The value of chemical oxygen demand was slightly reduced as every 250 ppm of copperas coagulants were applied (Figure 3). The required dosage of copperas needed can be considered high. To achieve a good state of settling, at 1000 ppm the result of the chemical oxygen demand value just achieved target. Since the copperas were acidic in nature and the treatment that was simulated are as aerobic condition the value of the palm oil mill effluent was reduced. To achieve a neutral condition pH of the effluent, further neutralization should be conducted. As the optimum operating pH for metal-based polymer coagulation are between 4 to 5, adjustment should also be applied during the process, as for the coagulation of the pome from kilang sawit Panji Alam, Kemaman, the pH are adjusted to 5 before it was applied with the copperas.

![Figure 3: The value of chemical oxygen demand versus the dosage of copperas](image)

4.2 Temperature

It was observed that the value of biochemical oxygen demand (BOD₅) was slightly decreased as we increase the dosage concentration of the copperas (Figure 4). The value was very significant as we compared to the reduction value of chemical oxygen demand (COD). The initial value of biochemical oxygen demand from the diluted palm oil mill effluent of factor of 0.02 give the value of average 400 ppm of BOD₅. At 250 ppm of copperas dosage the value of biochemical oxygen demand (BOD) was dropped to 288 ppm of concentration. The result prove that the copperas coagulant was very effective on biochemical oxygen demand reduction. The trends were almost same to the chemical oxygen reduction as both of the oxygen demand factors showing improvement of quality after the application of coagulants.
Figure 4: The value of biochemical oxygen demand (BOD$_5$) versus the dosage of copperas

4.3 Total Suspended Solid

The total suspended solid reduction was significantly reduced as the copperas treatment applied (Figure 5). The nature of the palm oil mill effluent is very high in total suspended solids. The oil and grease composition that exist in the palm oil mill effluent contributes on the high value of suspended solids. The initial reading of the palm oil mill test shows that more than 8000 ppm, for 1500 ppm of copperas dosage the reading of total suspended solid are at 7922 ppm. Total suspended solid was slightly reduced as the treatment was conducted.

Figure 5: TSS value against copperas dosage value

4.4 Copperas Analysis

From the moisture analysis result in Table 1 we can see the reduction of weight are a very visible hence we can measure the loss of water which is the moisture content that existed in the copperas. The nature for copperas, ferrous sulphate hepta hydrate prove that the material contains high amount of moisture. Table 1 shows the copperas after being overdried. The drying was conducted only to 4 hours at maximum, since the copperas was very reactive to the increased temperature the ferrous sulphate heptahydrate will turn into ferrous sulphate thermal heptahydrate in temperature more than 150°C that has different properties, the physical properties can be seen.
Table 1. Result of moisture analysis of copperas.

| Weight of container (g) | Weight of sample (g) | Total of weight (g) | Total weight After 2hrs (g) | Total weight After 4hrs (g) | Loss of water (%) 2 | Loss of water (%) 4 |
|-------------------------|----------------------|---------------------|-----------------------------|------------------------------|---------------------|---------------------|
| 41.89                   | 20.18                | 62.07               | 55.45                       | 51.23                        | 32.82               | 53.72               |
| 47.52                   | 20.66                | 68.18               | 61.70                       | 52.13                        | 31.35               | 77.69               |
| 45.74                   | 20.30                | 66.04               | 60.74                       | 52.20                        | 26.11               | 68.18               |

From the Table 2 we can observe the average salinity value was at 11.6 mS/cm. The salinity value was the conductivity value of the material. In this study 2 gm of copperas was diluted in 50 ml solutions with dilution factor of 0.04 respectively. The concentration of the ferrous sulphate can be determined by using this method as the concentration of soluble salt are proportional to the conductivity value of the test sample. Meanwhile the reading of the pH. value of the copperas was about 2, since the nature of the copperas acidic, the application during the coagulation process does make buffering effects, but this acidic properties of copperas also good in case the palm oil mill effluent pH value was more than five, since the effective pH for this coagulant are between 4-5 pH.

Table 2: The salinity and pH analysis of the copperas

| RUN no. | Salinity mS/cm | pH |
|---------|----------------|----|
| 1       | 11.72          | 1.8|
| 2       | 12.31          | 1.9|
| 3       | 12.06          | 2  |
| 4       | 8.80           | 1.9|
| 5       | 12.84          | 1.8|
| Average | 11.55          | 1.88|
demands the BOD value was reduced successfully, the first sample with feed concentration 500 ppm of copperas has BOD value of 288 ppm. As we increased the feed of copperas to 2000 ppm the BOD value reduced to 13 ppm. Next the highest value of TSS reduction was at 2000 ppm of copperas feed, at the specific dosage the TSS reading was 7502 ppm. The application of copperas as primary effluent treatment agent supposed to help reducing the biochemical oxygen demand (BOD$_5$) primarily and also improve others parameters which is in the studies, chemical oxygen demand (COD), and total suspended solids. With the improvement level gained in primary stage of the wastewater treatment the final discharge should be cleaner than before, hence making the palm oil mill effluent treatment more efficient.

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