Effect of electrode materials on the degradation of palm oil mill effluent by electro-oxidation process

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Abstract. In the recent decades, Malaysia has been known as the one of the palm oil producers and exporters. The increasing of the production and demand of palm oil tends to increase the Palm Oil Mill Effluent (POME). Undeniably, the conventional biological treatment has been implemented to reduce the organic matters but insufficient to satisfy the discharge standard by the local authority. Consequently, the biological treated POME has to be treated further to meet the stringent discharge standard. Hence, an advanced oxidation processes (AOPs), electro-oxidation process (EOP) has been applied to treat further the biologically treated POME. There are two stages in this study, EOP carried on with catalyst and electrode (Al and Fe). Therefore, the performance of EOP is evaluated by investigating the removal efficiency on the organic parameters like COD, colour, suspended solid and NH3-N. The operational parameters are the pH adjustment (pH 3, 5, 7 and 9), contact time ranging from 0 to 60 min and the dosage of catalyst (H2O2 and TiO2). The highest degradation of the parameters was obtained under the most acidic solution pH 3, with addition of TiO2 by using Al electrode. The percentages of removal are 96.58 % of colour, 98.74 % of SS and 84.85 % of COD.

1. Introduction
Palm oil is the largest produced and traded vegetable oil in the global oil market. Malaysia produced 27 % out of 72.08 million tonnes of the total palm oil in year 2018. On the other hand, it will tend to increase of the Palm Oil Mill Effluent (POME). POME is an incurable non-toxic wastewater which a concentrate dark brownish slurry. It consists of 95 % water, 4 % oil and 30-70 % solid material [1]. The temperature of the POME discharge normally around 80 to 90 °C, which mixed with water, oil and suspended solid composition [2]. Also, POME contains residual oil so that it cannot be easily separated using conventional gravity-based treatment.

Wastewater like POME is needed to be treated before discharge to the environment which conform the standard limit of Department of Environmental (DOE) Malaysia. Normally, conventional biological treatments were applied to treat the POME in Malaysia such as oxidation pond with aerobic and anaerobic. However, it was insufficient to reach the standard limit due to the remaining of the non-biodegradable organics which are metabolized and degraded slowly.
Post treatment is to further treat the POME due to the biological treatment is inefficient to remove the COD and colour. Recently, the advanced oxidation processes (AOPs) has been implemented to further treat the recalcitrant organic compound contains in POME. Electro-oxidation is an effective process for the organic degradation which using the anodic absorbed oxidant to generate oxidants in the bulk solution to conduct direct or indirect oxidation.

Thus, to treat the biologically treated POME (BIOTPOME), AOPs is implemented to complete the task to reduce the environmental pollution problems. The mechanism of AOPs like electro-oxidation process (EOP) is works by generating highly reactive radicals (•OH) which can destroy the organics chemicals due to the reactive electrophiles [4]. The highly reactive radicals who can decompose the organic compound are due to the high potential oxidation (2.87 eV). EOP is one of the AOPs which are a combination process with electro-coagulation and electro-flotation [5]. The preparations for EOP are arranged by using a pairs of metal sheet which are anode and cathode to perform as electrode and connect to the DC power supply. Reduction and oxidation are occurs at cathode and anode. Furthermore, the EOP can be enhanced by addition of catalyst like hydrogen peroxide (H$_2$O$_2$) and titanium oxide (TiO$_2$) due to the highly generation of reactive radicals.

2. Materials and methods

2.1. Sample collection
BIOTPOME samples were collected from an aeration pond of the Malpom Industries Sdn Bhd, Pulau Pinang, Malaysia. The aeration pond is where the oxygen was supplied to allow bacteria respiration to proceed rapidly. The collected samples were then transferred to the laboratory and were stored at 4 °C to minimize the biological and chemical reaction in samples as well as to obtain more accuracy experimental data.

2.2. Experimental procedure and analysis
The operational parameters involved in the EOP are pH adjustment of pH 3, 5, 7 and 9, the ranges of contact time from 0 to 60 min, the type of electrode as well as dosage of catalyst. The electrodes used for each batch are same which is cut into a size of 12 cm x 4.5 cm in dimension. 6 cm of electrode is immersed into the 500 ml sample beaker during the EOP and the distance between electrodes set to 3 cm. A magnetic stirrer is used in 300 rpm to drive the reaction between anode and cathode. The electrodes are connected to the DC power supply with a 1.62 current density and 12 V, constantly. The second stages of the experiment are involved in catalysts which are H$_2$O$_2$ and TiO$_2$. Preliminary experiment was carried to obtain a suitable dosage of catalyst by determining the effective removal efficiency on the organic parameters such as chemical oxygen demand (COD), colour, suspended solid (SS) and Ammoniacal nitrogen (NH$_3$-N). The oxidation processes were carried out under ambient temperature. The data were taken after the process is done as well as the sediment was settled down. The standard method which used to test the data is according to the Hach Water Analysis Handbook and the Standard Method for Examination of Water and Wastewater.

3. Results and discussion

3.1. Characterization
The initial characteristics study on the BIOTPOME is very important to obtain the range of the operational parameters in order to achieve the objective. By comparison of both initial characterization and typical value of BIOTPOME, it is noticed that the value for COD still acceptable and satisfy to the stringent discharge limit of DOE. In contrast, the value for SS, colour and NH$_3$-N are higher than the typical value of BIOTPOME.
### Table 1. Characterization of BIOTPOME.

| Parameter | Unit    | BIOTPOME | Typical Value [6] |
|-----------|---------|----------|-------------------|
| SS        | mg/L    | 984      | 130-352           |
| Colour    | Pt/Co   | 4,939    | 500-5,240         |
| COD       | mg/L    | 1,353    | 2,420-4,500       |
| NH\(_3\)-N| mg/L    | 403      | 53-123            |
| pH        |         | 8.44     | 8.0-8.5           |
| Temperature | °C     | 28       | 25-30             |

#### 3.2. Effect of pH

In order to study the operational parameter, adjustment of the initial pH value is the critical parameters to carry on. The experiment was conduct by adjust the initial pH value to the pH 3, 5, 7 and 9. Consequently, the sample was adjusted by sulphuric acid or sodium hydroxide in the beginning before undergo EOP. Figure 1, shows a decline of removal efficiency on the few organic parameters when using aluminium as electrode. In the condition of pH 3 without addition of catalyst, the removal efficiencies are 77.8 % for COD, 74.0 % for colour, 64.0 % for NH\(_3\)-N and 82.4 % for suspended solid. The decrease of the removal percentages with the increase of initial pH value is due to the organic substances can be removed efficient in an acidic solution compared to alkaline condition.

![Figure 1. Removal efficiency for Al electrode without addition of catalyst.](image_url)

#### 3.3. Effect of electrode

Based on figure 2, the COD removal depict that the Al electrode have better removal efficiency compared to Fe electrode. It shows that the removal efficiencies for iron plate are 52.8 % which lower than Al which contributed 60.0 %. This is due to the Fe (II) is easily oxidized to Fe (III) in the acidic solution. Hence, the decline for removal efficiencies occurred [7].
3.4. Effect of contact time
In the preliminary experiment, the optimum contact time from 0 to 60 min is used for every EOP. Thus, operational cost can be controlled and minimized due the cost also an important factor needed to consider rather than removal efficiency. As the figure 2 shows that the removal efficiency for COD is increasing as the time increased. This is due to the anode will generate more MO₄(¬OH) in bulk solution to strengthen the degradation of organic matters [8].

3.5. Effect of catalyst dosage
As shown in figure 3, the removal performance of suspended solid and colour removal shows an optimum during the EOP with addition of H₂O₂ catalyst. The removal efficiency was obtained at the peak for suspended solid and colour which are 89.97 % and 85.28 % respectively. However, it shows a fluctuated result on removal performance for COD and NH₃-N. Slight decline for COD and NH₃-N removal when adding catalyst into the process are from 75.6 % to 67.0 %, and 69.4 % to 52.0 %, respectively. For the observation on the experiment of EOP with H₂O₂, the bubbles were form vigorously compared to the pH reagent like H₂SO₄ contact with the sample. This is due to the efficient of degradation of organic compound by cathodic reduction of hydrogen ions (H⁺) [9]. Also, it can describe as the decomposition of the recalcitrant organic matters of POME.

Figure 2. Effect of different electrode on removal efficiency of COD.

Figure 3. Effect of dosage of H₂O₂ with Al electrode at pH 3.
To comply with the objective, effect on dosage of catalyst shown in the graph above with aluminium plate at pH 3. The optimum dosage obtained by preliminary experiment study. It depicts that the organic substances in the wastewater removed significantly in the catalyst condition for COD, colour and SS due to the high percentage removal. This is because the anatase form of TiO$_2$ is the most efficient photocatalyst to generate free radicals [10].

**Figure 4.** Effect of dosage of TiO$_2$ with Al electrode at pH 3.

4. Conclusion

From the result obtained in the research, the EOP perform better in low pH condition with Al electrode compared to Fe due to the higher removal efficiency of the organic parameters. Based on the result, the removal percentages by using Al electrode are 77.82 % for COD, 73.69 % for colour, 63.69 % for NH$_3$-N and 82.37 % for SS. Meanwhile, it is complied with the objective to purpose the removal efficiency of parameters such as SS and colour with addition of catalyst hydrogen peroxide. This is due to the removal competence of both SS and colour can meet 70 %. In the contrary, the removal efficiency with addition of TiO$_2$ giving a good result on parameter such as SS, colour and COD. Hence, the EOP performs well based on the constant current density, contact time, variable operational parameter. The final pH of the sample is in between the neutral condition. In the nutshell, the AOPs like EOP is suitable to be applied to further treat the industrial effluent like POME. As a result, it comply the stringent regulation by DOE as well as provide a good aesthetics view of the environment.

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