Electro-oxidation as Tertiary Treatment Techniques for Removal of Palm Oil Mill Effluent

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Abstract. The production of palm oil, though, results in the generation of huge quantities of polluted wastewater normally referred as palm oil mill effluent (POME). It gives adverse impacts to the environment, particularly if it is not properly treated. POME are known to have various types of liquids, residual oil and suspended solid as it has very high strength waste in its untreated form. Although conventional biological processes are normally efficient for the degradation of pollutants occurring in wastewater, most of these compounds are not effectively removed. As a result, further treatment is needed to meet more stringent discharge standards of Department of Environment (DOE), Malaysia. This research focused on treatment of POME by using electro-oxidation process (EO). It was done to identify the performance of EO process for colour, chemical oxygen demand (COD), suspended solids (SS), and Ammoniacal-nitrogen NH₃-N) removal as well as the relative effects of different operational parameters such as pH, type of electrodes and contact time. The pH was varied between 3 and 11, using Ferum (Fe) and Aluminium (Al) electrode, and contact time from 0 to 120 min. The most suitable pH, contact time and type of electrode were pH 3, 120 min and Aluminium electrode, respectively. Therefore, EO process at specified level can be used as an efficient and effective post-treatment technology to meet the standard regulatory requirements.

1. Introduction
Large demand of products of oil palm by China, European Union, United State of America and Vietnam has contributed to economic boost of Malaysia [1]. However, other effects might arise from production of palm oil if not well controlled. Normally, there were two types of wastes produced in palm oil industry, which are firm and liquid wastes. The residues of oil palm tree such as trunks, fronds, empty fruit branches, fibres, kernel shell and palm oil mill effluent (POME) are the wastes produced from those industries. POME needs an effective treatment before to be discharged into watercourse due to its highly polluting properties. This is because of the rapid growth of development of oil palm plantation in Asian countries that includes Malaysia [2]. The conventional practice of treating the wastewater would be the biological treatment, which is usually aerobic and anaerobic processes are applied. However, due to its complex composition, this treatment is time consuming and usually ineffective in degrading high molecular weight fraction.
Recently, tertiary treatment methods are being used instead of conventional chemical and biological method. Among tertiary treatment are the advanced oxidation processes (AOPs). AOPs involves the generation of a strong oxidant, hydroxyl radicals (OH) with oxidation potential of 2.8 V that exploits and further degrade organic pollutants [3]. During the degradation process, the produced hydroxyl radicals attack the contaminants and transform into $\text{H}_2\text{O}$, $\text{CO}_2$ and inorganics [4]. Hence, the aims of this research are to evaluate electro-oxidation (EO) as one of AOPs as post-treatment for POME removal. Furthermore, to investigate the effects of operational parameters such as type of electrodes, pH, contact time, and determine the efficiency of the process.

2. Experimental

2.1 Sample Collection
POME 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 wastewater was collected using a 10 L bottle. The collected samples were then transferred to the laboratory and were stored at 4°C to minimize the biological and chemical reaction in samples and to avoid inaccurate results.

2.2 Reactor Set-up
The type of electrodes that used in this process is fixed with the usage of the iron (Fe) and aluminium (Al) electrode plate with a dimension of 12 cm x 4.5 cm, respectively with a total area of 54 cm². Exactly half of each electrode length (6 cm) was immersed in the 500 ml sample, thus this will bring to a total area of 27 cm² that were contacted with the electric. Meanwhile, the magnetic stirrer speed was set to 300 rpm so that it allows homogeneous mixing of the POME sample while reacting with the anode and the cathode terminal of the cell. Other than that, the sample was cooled to room temperature before used in the experiment. The distance between the two electrodes was set to 3 cm apart from each other due to the fact that the magnetic bars that were stirring occupy some spaces and also to allow for the reaction to occur in between which is direct anodic oxidation whereby the pollutants were absorbed on the anode surface and destroyed by the anodic electron transfer reaction [5]. A DC power supply was adopted to consistently supply a constant voltage of 12 V and 60 mA of current density (optimize value). Before the treated samples were tested for percentage removal, it will first let to settle for approximately one hour to allow for sedimentation of the sludge and to extract the supernatant and filtered off for any suspended solids.

2.3 Analytical Method
The samples were analysed according to the method prescribed in the Standard Methods for the Examination of Water and Wastewater [6] and Hach method.

3. Results and Discussions

3.1 POME Characterization
Table 1 shows the initial characteristics of biologically treated POME. The initial pH was 7.85, COD was 1,409 mg/L, color was 3,217 PtCo, NH$_3$-N was 220 mg/L, and SS was 326 mg/L.
Table 1. Characterization of POME sample.

| Parameter                          | Value     |
|------------------------------------|-----------|
| Color                              | 3,217 PtCo|
| Chemical oxygen demand (COD)       | 1,409 mg/L |
| Ammoniacal-nitrogen (NH3-N)        | 220 mg/L  |
| pH                                 | 7.85      |
| Suspended solid (SS)               | 326 mg/L  |

3.2 Preliminary Experiment
The preliminary experiment was carried out in order to determine optimum values for the parameters of the features. The initial pH of the sample was taken without being adjusted. The optimum value from the preliminary experiment were used to carry out the characteristic analysis and then to proceed with EO process. The biologically treated POME was tested with different current density and the distance between electrodes of 3 cm as shown in table 2.

Table 2. Different current density with regard to color removal and COD concentration.

| Current density | Color (PtCo) | COD concentration (mg/L) |
|-----------------|--------------|--------------------------|
| 30 mA/cm² (0.81 A) | 897          | 652                      |
| 60 mA/cm² (1.62 A) | 492          | 524                      |
| 90 mA/cm² (2.43 A) | 588          | 560                      |

Based on the results, the optimum value which is at 60 mA/cm² current density was applied throughout the EO experiment. From the above three conditions, it can be seen that the second condition, which is by using 60 mA/cm² of current density the difference in COD removal decreasing from 1,409 mg/L to 524 mg/L and colour removal from 3,217 PtCo to 492 mg/L were the most significant comparing with the other two conditions. Next, the biologically treated POME was tested with different distance between electrodes as shown in table 3.

Table 3. Distance between electrodes with regard to color removal and COD concentration.

| Current density | Color (PtCo) | COD concentration (mg/L) |
|-----------------|--------------|--------------------------|
| 30 mA/cm² (0.81 A) | 572          | 652                      |
| 60 mA/cm² (1.62 A) | 492          | 524                      |
| 90 mA/cm² (2.43 A) | 517          | 560                      |

The distance between electrodes which are 3 cm were used as optimum value in term of color and COD removal. The reason of this to occur was the same with the previous result which is the preliminary experiment. The removal efficiency of color and COD is much greater by using 3 cm distance between electrodes compared to 2 and 4 cm.

3.3 Effect of Operational Parameters

3.3.1 Effect of Contact Time
Pre-determined current density was being used as it is shown to have the optimum effect towards the varying time of reaction conducted. To achieve the optimum conditions, sets of contact time ranging from 0 to 120 min were carried out. From the ranges of contact time, 120 min were the best optimum contact time. This can be support by [7] studies which also stated that their optimum reaction time on their Fenton process also achieved 120 min, with no significant change in efficiencies above this reaction time [7]. However, throughout the observation, it is confirmed that the treatment with longer time would
obviously provide a better removal efficiency of all parameters. It is no doubt that elevating the contact
time gives out greater removal efficiency. However, the operational cost is one of important factor to be
considered along with the treatment efficiency.

3.3.2 Effect of Initial pH
Adjustment of the pH was carried out using the optimum time of 120 mins and two types of electrodes
which are Fe and Al. It is anticipated that lower pH would provide better removal efficiency upon the
interaction of the acid and the sample. Figure 1 shows the effects of pH on the removal efficiency of EO
process by using Fe electrode. It shows that lower pH which is pH 3 provide better removal efficiency
in terms of colour, COD, SS, and NH$_3$-N were 90.2, 84.7, 83.8, and 64.9%, respectively. After pH 3, the
removal percentage was declining.

Figure 1. Effect of pH on the removal of color, COD, SS, and NH$_3$-N (Fe electrode).

For Al electrode as in figure 2, the best possible reduction in colour, COD, SS, and NH$_3$-N that are
obtained from the data sheet is at pH 3, whereby the removal efficiency of 95.2, 90.7, 85.8, and 60.9%
are achieved. But there is a slack between pH 3 and 5 in terms of turbidity and NH$_3$-N. However, the
values the removal percentages of these parameters are not too significant. Low pH is suitable because
it can helps to increase the oxidation process as acidic condition contributes to oxidation. Upon great
consideration, pH 3 was chosen as the optimum due to its effective overall removal and it was aligned
with previous study [8, 9]. It is because pH range of 2-4 produce the high oxidizing potential as it exhibits
stable hydroxyl radicals.

Figure 2. Effect of pH on the removal of color, COD, SS, and NH$_3$-N (Al electrode).
3.3.3 Effect of Electrode

Electrode assemblies as the heart of the EO process and for that reason, it is very concern and crucial to find the suitable material selection. The two materials which are Fe and Al were used in this study. The experiments were conducted at different electrodes by using pH 3 that have been determined at earlier stepped. The comparison of colour removal efficiency was showed in figure 3. By using Fe electrode, colour removal reaches its optimum level of 90.2 % as compared to the 95.2 % by using Al electrode in 120 min.

![Figure 3. Effect of electrodes on color removal efficiency.](image)

Figure 3 shows the effect of electrodes on COD removal efficiency. It can be seen that COD removal is more when Al electrode is used (90.7 %) as compared to COD removal of Fe electrode is used (84.7%) at 120 min.

![Figure 4. Effect of electrodes on COD removal efficiency.](image)

Figure 4 shows the result of the different electrode on SS removal efficiency. Based on the results, the SS removal for 120 min towards Al is 85.7%, which is higher than Fe (83.8%). Moreover, as suitable material of electrode is used, where both the material and sample are in contact, reaction can be seen and this might prove to be affecting the overall reaction. This eventually led to the affected composition inside the sample and thus produces a varying effect upon the actual experiment.
The effects of electrodes on NH$_3$-N removal efficiency have been observed during the EO process. The common type of electrode is represented in figure 6. It shown that iron electrode (64.9%) is better removal than aluminium electrode (60.9%) at 120 min.

In conclusion, Al has better removal than Fe electrode for all parameters except NH$_3$-N. From previous study which is conducted by [10], EO process using Fe electrode rather than Al is a feasible treatment for POME due to the presence of H$_2$O$_2$ as oxidation agent and Polyaluminum chloride (PAC) as additional coagulant [8, 10].

3.3.4 Effectiveness of EO Process

Table 4 and 5 summarized the removal efficiency of all parameters. It can be justified that Al electrode gives higher percentage removal than Fe electrode such as 95.2 % of color, 90.7% of COD, 85.8% of SS, and 60.9% of NH$_3$-N within 120 min contact time. However, for 60 min the results obtained only achieved 78.0, 70.8, 67.4, and 53.9% for the respective parameters.
Table 4. Summary of the removal efficiency of all parameters by using Fe electrode.

| Parameter    | Initial | Final | Removal (%) |
|--------------|---------|-------|-------------|
| Colour (PtCo) | 1409    | 216.0 | 84.7        |
| COD (mg/L)   | 3217    | 315.3 | 90.2        |
| SS (mg/L)    | 326     | 52.8  | 83.8        |
| NH$_3$-N (mg/L) | 220     | 77.2  | 64.9        |

Table 5. Summary of the removal efficiency of all parameters by using Al electrode.

| Parameter    | Initial | Final | Removal (%) |
|--------------|---------|-------|-------------|
| Colour (PtCo) | 3,217.0 | 154.0 | 95.2        |
| COD (mg/L)   | 1,409.0 | 131.0 | 90.7        |
| SS (mg/L)    | 326.0   | 46.0  | 85.8        |
| NH$_3$-N (mg/L) | 326.0   | 46.0  | 85.8        |

The comparison between raw POME sample and the electro-oxidation treated sample were carried out in order to know their properties. It was then discovered the removal efficiency of the process towards color, COD, SS, pH and NH$_3$-N can be said to be promising as most of them are in compliance with the discharge standard.

4. Conclusions

In this study, the optimum operational conditional for the post-treatment of POME using EO were determined, which are Al electrodes for contact time 120 min and pH 3 were recorded. Upon these findings, the specified level can be used as a post treatment technology as they are effective. They will give considerable results of discharging so that it will comply with the requirements. EO process is recommended because it can be operated at ambient temperature and pressure. They require no auxiliary chemicals and do not produce waste. It also can be adapted to various applications, and can be easily combined with other technologies. In addition, this research has been contributed to society and sustainable environment by reducing the toxicity of POME. Therefore, it will contribute to save the earth. The results conclude that electrode material play an important role in electro-oxidation method for treatment of POME.

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