Removal of palm oil mill effluent by using electro-oxidation process

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Abstract. Wastewater includes the Palm Oil Mill Effluent (POME) that gives adverse impacts to the environment especially for water pollution when it is not treated properly. 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). 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), ammoniacal-nitrogen (NH₃-N), and turbidity removal as well as the relative effects of different operational parameters such as pH, type of electrodes and contact time. The pH was varied from 3 to 11, the electrodes were aluminium and iron and the contact time was from 0 to 120 min. The most suitable pH, contact time and type of electrode were pH 3, 120 min and Al electrode.

1. Introduction

Large demand of products of oil palm by Saudi Arabia, Iran, Pakistan, India and the Philippines 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 bunches, 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.

The AOPs of electro-oxidation (EO) will usually goes with the role of hydroxyl radical to attack the pollutants present in effluent. This radical is produced at the electrode surface such as in the direct
EO process or in bulk solution such in the indirect electrolytic processes. For gaining both the treatment efficiency and the achievement of discharge standard, it is a possible ways to treat effluent.

2. Materials and Methods

2.1. Sample Collection
POME samples were collected from an aeration pond of the Malpom Industries Sdn Bhd, Pulau Pinang. 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. Experimental Procedure and Analysis
The type of electrodes that to be used in are fixed with the usage of the Al and Fe 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 stirrer speed was set to 300 rpm so that it allows homogeneous mixing of 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 [3]. 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. The treated samples were then taken to analyze according to the method prescribed in APHA [4] and Hach method.

3. Materials and Methods

3.1. 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 values for current density and the distance between electrodes can be obtained. The optimum value from the preliminary experiment were used to carry out the characteristic testing 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 1.

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

Based on the results, the optimum value which is at 60 mA/cm² current density was implemented for 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 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 for with different distance between electrodes as shown in Table 2.
Table 2. Distance between electrodes with regard to COD and colour removal

| Distance | 2 cm | 3 cm | 4 cm |
|----------|------|------|------|
| Electrodes | 652 | 524 | 560 |
| COD concentration | 572 | 492 | 517 |

The distance between electrodes which is 3 cm was implemented because of its optimum value in terms of COD removal and colour removal. The reason of this to occur was the same with the previous result which is the preliminary experiment. The removal efficiency of COD and colour is much greater by using 3 cm distance between electrodes compared to 2 cm and 4 cm.

3.2. POME Characterization

Table 3 shows the initial characteristics of biologically treated POME which was analysed according to the method prescribed in APHA method [4] and Hach method.

| Parameter      | Value      |
|----------------|------------|
| COD            | 1409 mg/L  |
| Colour         | 3217 PtCo  |
| NH₃-N          | 220 mg/L   |
| Turbidity      | 304 NTU    |
| pH             | 7.85       |
| Suspended Solid| 326 mg/L   |

3.3. POME Characterization

In this process, the operational conditions such as pH, contact time and types of electrode were studied for their effect in removing the parameters of POME such as COD, colour, NH₃-N, turbidity and SS. The oxidation processes were carried out under ambient temperature.

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 were conducted. To achieve the optimum conditions, a set of contact time ranging from 0 to 120 min were carried out. From the ranges of contact time above, 120 min were the best optimum contact time. This can be support by [5] 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. However, throughout the observation, the reaction of the different contact time, 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 pH adjustment. Adjustment of the pH was carried out using the optimum time of 120 min and two types of electrodes which are Fe and Al to run the varying pH in a set of experiment. When adjusting the pH, it is recommended that adding the acid buffer with care due to the pH from getting too low as it could affect the overall reaction and when acid buffer is added, there is a response occur upon contact and this would lead to an inconsistent results at the end of the day. Besides, the formation of bubbles seems to have sky-rocketed after the adjustment of pH and when the current are applied, the bubbles formed rather quickly and in a huge volume. 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 iron electrode. Figure 1 shows that
lower pH which is pH 3 provide better removal efficiency in terms of colour, COD, SS, turbidity and NH₃-N were 90.2, 84.7, 83.8, 71.7 and 64.9%, respectively. Furthermore, after pH 3 the removal percentage declined.

![Figure 1](image1.png)

**Figure 1.** Effect of pH on colour, COD, SS, turbidity and NH₃-N removal efficiency of (Fe electrode)

Moving on to the Al electrode as in Figure 2, the best possible reduction in colour, COD, SS, turbidity and NH₃-N that are obtained from the data sheet is working at pH 3 whereby the removal efficiency of 95.2, 90.7, 85.8, 72.7 and 60.9% are achieved. But there is a slack between pH 3 and 5 in terms of turbidity and NH₃-N. However, the value the removal percentage of these parameters is 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 [6, 7]. It is because pH range of 2-4 produce the high oxidizing potential as it exhibits stable hydroxyl radicals.

![Figure 2](image2.png)

**Figure 2.** Effect of pH on colour, COD, SS, turbidity and NH₃-N removal efficiency (Al electrode)
3.3.3. Effect of electrode. Electrode assembles as the heart of the EO process and for that reason, it is very concern and crucial to find the suitable material selection. The experiments were conducted at different electrodes by using pH 3 that have been determined at earlier stepped. Figure 3 shows the effect of electrodes on COD removal efficiency. It can be seen that COD removal is more when Al is used (90.7%) as compared to COD removal of Fe is used (84.7%) at 120 min.

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

Figure 3. Effect of electrodes on COD removal efficiency

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, the instance 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.

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

Figure 4. Effect of electrodes on SS removal efficiency

The effect of electrodes on turbidity removal efficiency is demonstrated in Figure 5. It shows that the Al has higher result between two electrodes with 72.7%, compared to the 71.7%.
Figure 5. Effect of electrodes on turbidity removal efficiency

The effects of electrodes on NH\textsubscript{3}-N removal efficiency have been observed during the EO process. The common type of electrode is represented in Figure 6, which concluded that Fe (64.9\%) is better removal than Al (60.9\%) at 120 min.

Figure 6. Effect of electrodes on NH\textsubscript{3}-N removal efficiency

In conclusion, Al has better removal than Fe for all parameters except NH\textsubscript{3}-N. From previous study by [8], EO process using Fe electrode rather than Al is a feasible treatment for POME due to the presence of H\textsubscript{2}O\textsubscript{2} as oxidation agent and PAC as additional coagulant [6, 8].

3.4. Effectiveness of EO Process

Table 4 and Table 5 show the summary of the removal efficiency of all parameters. It can be justified that Al electrode gives higher percentage removal than Fe such as 95.2\% of colour, 90.7\% of COD, 85.8\% of SS, 72.7\% of turbidity and 60.9\% of NH\textsubscript{3}-N within 120 min contact time. However, for 60 min the results obtained only achieved 78.0, 70.8, 67.4, 72.8 and 53.9\% for the respective parameters.
Table 4. Summary of the removal efficiency of all parameters by using Al electrode

| Parameters      | Initial | Final | Removal % |
|-----------------|---------|-------|-----------|
| COD (mg/L)      | 1409.0  | 131.0 | 90.7      |
| Turbidity (NTU) | 304.0   | 83.0  | 72.7      |
| Colour (PtCo)   | 3217.0  | 154.0 | 95.2      |
| SS (mg/L)       | 326.0   | 46.0  | 85.8      |
| pH              | 7.8     | 8.4   | -         |
| NH$_3$-N (mg/L) | 220.0   | 86.0  | 60.9      |

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

| Parameters      | Initial | Final | Removal % |
|-----------------|---------|-------|-----------|
| COD (mg/L)      | 1409    | 216.0 | 84.7      |
| Turbidity (NTU) | 304     | 86.0  | 71.7      |
| Colour (PtCo)   | 3217    | 315.3 | 90.2      |
| SS (mg/L)       | 326     | 52.8  | 83.8      |
| pH              | 7.85    | 8.7   | -         |
| NH$_3$-N (mg/L) | 220     | 77.2  | 64.9      |

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

4. Conclusion

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 EO method for treatment of POME.

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References

[1] MPOB 2017 *Overview of the Malaysian oil palm industry* http://bepi.mpob.gov.my/images/overview/Overview_of_Industry_2017.pdf, accessed on 14 November 2019

[2] Varkey H 2012 *Oil Palm Industry Economic Journal* 12(2) pp 1-13

[3] Awang Z B Bashir M J K Kutty S R M and Isa M H 2011 *Research Journal Chemical Environmental* 15(2) pp 229-232

[4] APHA-AWWA-WEF 2005 *Standard Methods for the Examination of Water and Wastewater* 21st edn APHA Washington DC
[5] Mohajeri S Aziz H A Isa M H Bashir M J K Mohajeri L and Adlan M N 2010 Journal of Environmental Science and Health Part A Toxic / Hazardous Substances & Environmental Engineering 45 pp 692-69

[6] Vedrenne M Medrano R V Garcia D P Uribe B A F and Ibanez J G 2012 Journal of Hazardous Materials 205 pp 208-215

[7] Barbusinki K and Pieczykolan B 2010 Architecture Civil Engineering Environment 3 93-100

[8] Nasrullah M Singh L Mohamad Z Norsita S Krishan S Wahida N and Zularisam A W 2017 Water Resources and Industry 17 pp 7-10