Electrochemical Treatment of Palm Oil Mill Effluent using Graphite as Electrode Materials

Rakhmania¹, M A Yuzir”*, F F Al-Qaim²

¹Department of Chemical and Environmental Engineering (ChEE), Malaysia-Japan International Institute of Technology (MJIT), Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra 54100 Kuala Lumpur, Malaysia
²Department of Chemistry, Faculty of Sciences for Women, University of Babylon, Hilla-Iraq

*Corresponding author: muhdaliyuzir@utm.my

Abstract. Palm oil mill effluent (POME) is one of the largest wastes produced by palm oil industries. The electrochemical process offers an alternative to treat POME with several advantages. Anodic oxidation as one of the mechanisms from the electrochemical process has high efficacy to oxidize the organic content. This oxidation ability depends on electrode materials. In this study, graphite was used as electrode materials. The effects of voltage, electrolysis time and electrolyte support was investigated. The results show the highest removal efficiency obtained were 71% of COD reduction and complete color removal at optimum condition. Using graphite as an electrode was found efficient compared to other traditional materials and capable to reduce time the POME treatment compared to conventional methods.

1. Introduction
Malaysia has a total production of crude palm oil (CPO) 19.8 million tons and 86% of total annual production was exported (representing 40% of total global exports) [1]. The palm oil industries are a major contributor to country’s gross domestic product (GDP). Among various types of wastes produced by Palm oil industries, palm oil mill effluent (POME) is the largest waste generated from palm oil processing [2]. POME has brownish dark color, acidic pH ranging 3.5–4.2 and highly contains organic components including COD (51,000 mg/L), BOD (25,000 mg/L), TSS (18,000 mg/L) [3] and NH₃-N (220 mg/L) [4]. It also consists of 4–5% solids, 0.5–1% residual oil and about 95% water. The dark brown colour was described as polymerisation of tannins and low molecular weight phenolic compounds in extraction of oil in plant-based wastewater [5].

The high amount POME must be treated efficiently before discharged to the environment. Un-treated POME released to the environment can cause harm to soil and aquatic ecosystems [6]. The most common method to treat POME in Malaysia is using conventional open ponding system. This system has been applied by more than 85% of palm oil industries [7]. Due to its low-cost system in terms of labour compared to other treatments, open ponding system becomes a choice. Even some studies reported that open ponding system can reduce organic contents in POME, however the result sometimes does not pass the standard regulatory discharge limit specifically in removal of tannin-lignin [8].
Moreover, open ponding system has disadvantages on required large surface, long retention time, greenhouse gasses emission and foul smell [9].

Besides conventional methods, electrochemical technology offers an alternative to treat POME. It is a simple method and effective to treat wastewater containing organic and inorganic pollutants [10]. The electrochemical treatment has several advantages including no chemical requirement, easy operation and no sludge formation [11]. In general, there are three possible mechanisms of electrochemical process including electrocoagulation, electro-oxidation also called anodic oxidation and electro-flotation [12]. Most of the studies are devoted for anodic oxidation because it combines simplicity and high efficacy favoring the oxidative destruction of organic contents in water by the direct reaction of •OH formed at the anode surface by oxidation of water via reaction below [13]:

\[ M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \]

In anodic oxidation, the performance of oxidation ability depends on selected anode. Several electrode materials have been studied such as Al [14], Fe [15], Steel wool [16] and BDD [17]. However, little study has been carried out on the anodic oxidation of POME because the high COD resulted in high energy consumption [18] and study about electrode materials is limited. Therefore this study aims to investigate the performance of graphite as electrode material on POME treatment for COD and color removal. In addition, the effect of several indicators including voltage, electrolysis time and electrolyte support was carried out to find the optimized condition for the treatment.

2. Materials and Methods

2.1 Electrochemical Reactor and Operational Condition

The reactor consists of a DC power supply (GPD-X3035 GW Instrument Co.Ltd, Taiwan), a glass reactor (250 mL) with a graphite rod (diameter: 10 mm) [19] as anode and cathode. The distance is 2 cm between anode and cathode. Both anode and cathode were connected to the DC power supply. The diagram of the electrochemical reactor is shown in Figure 1. The electrode was connected to the Copper wire on cylinder glass by using silver paint and epoxy glue as cover [20].

![Figure 1. Diagram of Electrochemical Reactor](image)

These experiments were carried out by using laboratory electrolysis cell which includes DC power supply, electrochemical glass reactor, 150 mL of POME sample and amount of electrolyte (NaCl). The electrolytic cell will be constant stirring (150 rpm) at room temperature. A magnetic stirrer was used to keep homogenize the solution. The treated sample will be taken at regular time intervals [21]. The treatment with different operating conditions as described in Table 1.

| Operating Parameters | Unit |
|----------------------|------|

Table 1. Operating conditions [22]
2.2 Analytical Methods

Raw samples and treated of palm oil mill effluent were analyzed according to water quality standard methods (APHA/AWWA/SEF, 2012). There are including pH, color, Chemical Oxygen Demand (COD) and Ammonia-Nitrogen content (NH\textsubscript{3}-N). The measurement of pH was conducted by using a pH electrode (OHAUS Starter 3100, US). The color intensities, COD and NH\textsubscript{3}-N were evaluated using spectrophotometric analysis (DR 6000 HACH Spectrophotometer). Total oil and grease concentration will be analyzed using the gravimetric method according to the standard method (5520C) [23].

3. Results and Discussion

3.1 Characteristic of Palm Oil Mill Effluent

The POME sample was collected from POMTEC, Negeri Sembilan, Malaysia. The sample was collected from raw pome at the cooling pond. The result of analysis as represents in Table 2. The sample has high COD amount, acidic pH and dark brown color. POME has similar impurities with olive oil wastewater [24]. POME contains 95-96% of water, 0.6-0.7 % oil and the rest are solid [25].

Table 2. Analysis Raw Sample of POME

| No. | Parameter (Unit) | Description |
|-----|------------------|-------------|
| 1.  | pH               | 4           |
| 2.  | COD (mg/L)       | 39,900      |
| 3.  | Ammoniacal-Nitrogen (mg/L) | 65         |
| 4.  | Color            | Dark brown  |

3.2 Effects of Voltage

The applied voltage was studied from 5, 10, 15 and 20 V compared with untreated POME. Figure 2 shows the effect of COD removal efficiency with different voltage for 3 hours. The COD removal was increased with an increasing voltage applied. This is based on Faraday’s law below, which means ion produced in surface area (m) directly proportional to the voltage or current density.

\[ m = \frac{Mjt}{ZF} \]

where Z is the number of electrons involved in oxidation-reduction. M is atomic weight of anode material; F is Faraday’s constant (96,486 C mol\textsuperscript{-1}); j is current density; t is time [26].
Table 3. Electric potential based on energy consumption

| Voltage (V) | Specific Energy Consumption (kWh kg\(^{-1}\) COD\(_{removed}\)) |
|------------|-------------------------------------------------------------|
| 5          | 2.11                                                        |
| 10         | 2.78                                                        |
| 15         | 6.11                                                        |
| 20         | 10.40                                                       |

The highest removal of COD was obtained at 20 V which the initial amount of COD was 39,900 mg/L reduced to 18,200 mg/L. At this stage, the corrosion did not occur on graphite. Based on table 3, energy consumption is directly proportional to electrical power. Even though at 20 V has highest energy consumption among other voltage, the removal of COD from other voltage is still lower than this stage. However, this number is categorized lower than energy consumption of sunflower oil refinery wastewater treatment which spends 25.12 kWh m\(^{-3}\) for 4 hours of electrolysis time. Therefore, the 20 V was selected for further investigation.

The specific energy consumption is calculated as follows [27].

\[
SEC = \frac{U \times I \times t}{(COD_x - COD_y) \times V}
\]

Where SEC is the specific energy consumption (kWh/kg of COD\(_{removed}\)); \(U\) is applied voltage; \(I\) is current intensity; \(t\) is retention time; \(COD_x\) is chemical oxygen demand before treatment; \(COD_y\) is chemical oxygen demand after treatment; and \(V\) is the volume of treated wastewater.

Figure 2. Effect of voltage on COD removal (pH 4, electrolysis time 3 hours)

3.3 Effects of Electrolysis Time

Figure 3 shows the effect of electrolysis time on COD reduction at 20 V. The COD value was decreased to 2 hours and become slightly steady for 3 hours. It can be reported that mass transport is high due to the forced convection. On the early stage of electrolysis, the hydrogen was produced at both electrodes signed by the presence of gas bubble [28]. Both electrodes build up more ions [29]. Following the early stage then the removal of COD was increased by the time because of the oxidation of organic matter. The color was starting to degrade at 2 hours and completely remove at 3 hours. Besides, the highest COD removal was at 3 hours up until 54%. Previous study reported that POME treatment using Al as electrode materials could remove 42.94% COD for 8 hours at 4 V [30]. Even though the power supply was lower which only uses 4 V, however it takes long electrolysis time. Long electrolysis time can cause
electrode passivation which affects the performance of electrolysis [31]. The COD removal was less than 50% which is not meet requirement for final discharge. Another study on olive oil mill wastewater treatment (OOMW) reported that using Fe and Al as electrode material could remove COD until 60% for 2 hours at 15 V [32]. In addition, Al also has limitation on its behavior that easy to corrosion [33]. Therefore, it can be considered that graphite as an electrode material is more effective than traditional material (Fe and Al).

![Figure 3. Effect of electrolysis time on COD reduction (pH 4, voltage 20 V)](image)

3.4 Effects of Electrolyte Support

In this experiment, NaCl was used as electrolyte support. The concentration was varied from 6.6, 13.3, 20 and 26.6 g/L. Figure 4 shows the effect of NaCl on COD removal at 20 V for 3 hours. NaCl was chosen because chloride ions reduce the undesirable effect of other anions significantly [34]. It also has several advantages including low cost, high solubility and strong oxidizing properties of active chlorine production. Compare to sulfate and nitrate, chloride was the best-supporting electrolyte for electrochemical treatment of refractory organic pollutants [35] The highest removal efficiency occur in additional of 26.6 g/L NaCl that reduced COD from 39,900 mg/L to 11,300 mg/L.

The previous study on POME treatment was using NaNO₃ as electrolyte support with concentration 8.5 g/L. The result shows that the removal of COD was increased to 72%. This is because the NaNO₃ does not interfere with the electrochemical reaction [36]. It is also beneficial for subsequent biological treatment as nitrogen source of microorganisms [37]. Therefore it can be considered that it is only slightly different on performance between NaCl and NaNO₃. On the other hand, POME treatment using boron-doped diamond (BDD) as electrode material and 0.1 M Na₂SO₄ as electrolyte support could enhance the COD removal until 82.63% for 1 hour at 10 V [38]. This is due to the production of peroxodisulfate ion which increases the rate of oxidation [39].
4. Conclusion
The electrochemical treatment of POME has been carried using graphite as electrode materials. The performance of electrolysis shows that COD could be removed up until 71% and complete removal of color at optimum condition. Using graphite as an electrode was found efficient compared to other traditional materials and capable to reduce the time POME treatment compared to conventional methods. The specific energy consumption reaches 106.5 kWh kg\(^{-1}\) COD\(_{removed}\) at optimum condition. Improvement on electrolysis performance and specific energy consumption should be carried out in the future.

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