Electro-oxidation of palm oil mill effluent using a boron-doped diamond anode

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Abstract. The palm oil industry produces a large amount of wastewater as palm oil mill effluent (POME) that contains high concentrations of organic compounds, which are difficult to completely remove and consequently result in the degradation of aquatic ecosystems. In this work, palmitic acid was used as a model compound of POME to study its oxidation reactions. The experiment was conducted in a flow cell system with boron-doped diamond as the anode. A voltammetric technique was used to remove palmitic acid while observing the change in chemical oxygen demand concentration to monitor the reaction. The effects of supporting electrolyte, potential, time, and flow rate on the oxidation were studied. The results indicate that degradation of palmitic acid occurs as an indirect effect of electro-oxidation at high potential in the region of oxygen evolution or formation of hydroxyl radicals. Furthermore, under optimum conditions, up to 87.91% of the palmitic acid could be electrochemically removed.

Keywords: palmitic acid, hydroxyl radicals, boron-doped diamond, electro-oxidation

1. Introduction
Indonesia is the largest palm-oil-producing country, accounting for approximately 44% of the total production in the world [1]. Continuous palm oil production produces wastewater in the form of palm oil mill effluent (POME). The direct disposal of POME to local aquatic ecosystems can cause pollution of environment. The contents of organic matter such as palmitic and oleic acids in POME were around 45% and 40%, respectively, and are hence difficult to recover [2]. According to environmental quality standards, POME must be treated and disposed of as clean water.

In the palm oil industry, the biological method is the most widely used to treat POME because several organic compounds in POME can be degraded by microorganisms, which results in less sludge and requires less energy [1]. However, the biological method has some disadvantages such as long treatment times (45–60 days), large area requirements, color removal inefficiency, unstable fluctuations of chemical and physical composition, harmful biogases discharged to the atmosphere, and high operational costs.

Recently, advanced oxidation processes (AOPs) based on hydroxyl radicals have become the focus of research in the development of wastewater treatment technologies. AOPs have been widely applied and have been shown to eliminate hazardous and toxic pollutants successfully, converting them into biodegradable compounds that can be treated by conventional methods [3]. Electrochemical oxidation is a technology based on hydroxyl radical (•OH) discharge, which is more environmentally compatible, energy efficient, versatile, and low cost than other technologies. The most attractive...
The electrode used for electrochemical oxidation to remove organic pollutants in wastewater treatment is boron-doped diamond (BDD). BDD shows excellent characteristics such as low background current, wide potential window, biocompatibility, and high stability in strong acid solutions [4–6]; therefore, BDD can rapidly treat wastewater and oxidize organic compounds to more than 90% chemical oxygen demand (COD) [7,8].

In this research, voltammetric studies of palmitic acid at BDD electrode were carried out, and application of the BDD electrode in wastewater treatment was evaluated using palmitic acid as a model compound of POME.

2. Experimental

The model compound of POME was prepared by dissolving 10 mg of palmitic acid in a mixed solution of ethanol and water (1:1). The mixture was heated at 80 °C while stirring at 500 rpm until the volume of the remaining mixture was reduced to half.

Furthermore, a thin layer of BDD was deposited by chemical vapor deposition using a hot filament on a low-resistivity p-Si substrate (p-Si/BDD). The filament and substrate were kept at around 2500 and 830 °C, respectively, and then the reactive gas containing 1% CH in H. was introduced at a flow rate of 5 L/min in the presence of trimethoxy boron to produce 1000 ppm B/C ratio. The formed thin layer of polycrystalline BDD was characterized by cyclic voltammetry using a three-electrode cell. The electrode system comprised a BDD disc 1 cm in diameter as the working electrode, a Pt spiral as the counter electrode, and an Ag/AgCl reference electrode. Cyclic voltammetry was performed in a solution of palmitic acid containing 0.1 M NaSO4 as the supporting electrolyte. A galvanostatic method was used to perform the electrolysis of palmitic acid in a continuous two-electrode cell, with the BDD electrode as the working electrode and a Pt plate as the counter electrode; the diameter of each electrode was 1 cm (figure 1). Palmitic acid solution (20 mL) was added into the container and continuously circulated through the electro-oxidation cell using a peristaltic pump at a rate of 16–46 mL/min. The potential applied to the cell was in the range of 2000–10,000 mV, and the electrolysis time ranged from 0 to 240 min. NaSO4 (0.1 M) was used as the supporting electrolyte for the electro-oxidation process. The reduction of palmitic acid in the electrolysis process was evaluated and quantified as COD using a potassium dichromate method [9].

3. Results and discussion

3.1. Cyclic voltammetry measurements of the BDD electrode in palmitic acid solution

Figure 2a shows the indirect oxidation of palmitic acid on the surface of BDD by cyclic voltammetry, which occurs in the oxygen evolution area at potentials between +1.626 and +2.0 V (E vs. Ag/AgCl). The oxidation current slightly decreased, before becoming constant at the sixth cycle. The deactivation percentage after the sixth cycle was 27.5% (table 1), indicating that the surface of the BDD electrode was contaminated by a thin layer of intermediate substances produced from the indirect oxidation of palmitic acid.

**Figure 1.** Schematic illustration of a continuous cell: 1, DC current source; 2, continuous-type electrolysis cell; 3, peristaltic; 4, BDD and platinum electrodes 1 cm in diameter; 5, sample container; 6, hot plate and stirrer.
more hydroxyl radicals were produced. degradation after is the average limiting current density for the electro.
take shows the instantaneous current efficiency (ICE) galvanostatic 3.2.1. Electro-oxidation of palmitic acid by BDD

3.2.1. Effect of potential. The electrolysis of palmitic acid solution in 0.1 M NaSO₄ was performed galvanostatically (I = 1 A). Figure 3 shows the evolution of COD with different potentials. The inset shows the instantaneous current efficiency (ICE) during electro-oxidation at various potentials, which takes place under mass transfer control.

On the basis of our calculations, the value of the mass transfer constant was $2 \times 10^{-4}$ m/s, and thus the average limiting current density for the electro-oxidation of palmitic acid was 0.0448 A/cm², which is lower than the applied current density, (1 A). Under this condition, the electrolysis was controlled by mass transfer and COD removal occurred at high potential (10,000 mV), yielding around 82.63 % degradation after one hour of electrolysis. At this potential, charge was transferred to the electrode and more hydroxyl radicals were produced.

Table 1. Peak potential, current density, and deactivation percentage of the peak oxidation of palmitic acid, measured by cyclic voltammetry for different numbers of cycles with a limit potential of $+2.0\, \text{V} (E \text{ vs. Ag/AgCl})$.

| $E_{\text{pc}}$ (V) vs. Ag/AgCl | Cycle | Current density ($\times 10^{-1}$ A) | Deactivation (%) |
|-------------------------------|-------|-------------------------------------|------------------|
| 1.994                         | 1     | 9.61                                |                  |
|                               | 2     | 8.67                                |                  |
|                               | 3     | 8.24                                |                  |
|                               | 4     | 7.32                                |                  |
|                               | 5     | 7.093                               |                  |
|                               | 6     | 6.97                                | 27.5             |

Figure 2. Cyclic voltammograms obtained with the BDD electrode for palmitic acid (a) in 0.1 M NaSO₄ as the supporting electrolyte; showing 1-cycle and 6-cycle, and (b) in different supporting electrolytes. Each concentration of the electrolyte was 0.1 M. Scan rate was 100 mV/s).

Table 1 shows the deactivation percentage of the BDD surface during the electrolysis of palmitic acid solution with 0.1 M NaSO₄ as the supporting electrolyte. The oxidation of palmitic acid in this potential region around 2 V occurred through the formation of hydroxyl radical intermediates. The results clearly indicate that the BDD electrode is very stable and can consistently produce active hydroxyl radicals that play a role in palmitic acid decomposition.

In the case of wastewater treatment, the supporting electrolyte is important for improving the conductivity and compatibility of the electrochemical process. A good supporting electrolyte provides low electrochemical potential (high conductivity) and leads to a rapid reaction that destroys organic pollutants in wastewater. Therefore, the energy consumption for wastewater treatment will be reduced drastically NaSO₄ was reported to exhibit high peak currents for oxygen evolution, resulting in more hydroxyl radicals being produced by the BDD electrode [10].

Figure 2b shows the cyclic voltammograms of the electrolysis of palmitic acid using the BDD electrode in the presence of different supporting electrolytes. The cyclic voltammograms are similar, but there is a slight increase in the peak current when using H₂SO₄ and NaSO₄ as the supporting electrolytes.
Figure 3. Effect of potential during the electro-oxidation of palmitic acid by BDD (supporting electrolyte: 0.1 M Na$_2$SO$_4$; flow rate: 16 mL/min; electro-oxidation time: 1 h). Inset shows the dependence of ICE on the electrolysis time.

Figure 4. Effect of time on the electro-oxidation of palmitic acid by BDD (supporting electrolyte: 0.1 M Na$_2$SO$_4$; flow rate: 16 mL/min; applied potential: 10 V).

Hydroxyl radicals are formed on the surface of BDD as a result of the reaction with water and they are responsible for palmitic acid degradation. Palmitic acid near the surface of the BDD electrode undergoes an oxidation reaction, wherein carbon dioxide is produced. The presence of the supporting electrolyte Na$_2$SO$_4$ in the electrolysis process leads to the production of another oxidant, i.e., peroxo disulfate, which increases the rate of the oxidation reaction of palmitic acid, and consequently, the COD value decreases [10].

3.2.2. Effect of time. Figure 4 shows the profile of COD as a function of electrolysis time. The COD value decreased exponentially up to 1 h and became steady after 2–4 h of electrolysis. The profile confirmed that the electro-oxidation of palmitic acid was controlled by a secondary reaction, i.e., the oxygen evolution reaction. Part of the current (energy) was used for side reactions, which was confirmed by the decreasing ICE curve, in the Inset of figure 3 [11].

From these results, it is concluded that the electro-oxidation of palmitic acid by BDD takes place under the control of mass transfer and can be achieved within 1 h by electrolysis.
3.2.3. Effect of flow rate. The interaction between the electrode surface and the solution in a flow electrolysis system is different from that in a bulk system; hence, the oxidation product will also be different. In a flow electrolysis system, the diffusion layer is thinner than that in a bulk system, which leads to inter-radical or intermediate reactions [12].

Figure 5 shows the profile of COD as a function of the flow rate of palmitic acid solution in the electro-oxidation cell. Increasing the flow rate caused decreases in the COD removal efficiency. This is probably because, at high flow rate, the interaction of water with the surface of the BDD electrode decreases so the production of hydroxyl radicals (•OH) will also decrease. Under this condition, the hydroxyl radical tends to react with other hydroxyl radicals or intermediates to produce oxidant species weaker than the hydroxyl radical (•OH), such as peroxide, ozone, and organic radical (•R), which will prevent the formation of new hydroxyl radicals.

4. Conclusions
The cyclic voltammetry study showed that indirect oxidation of palmitic acid occurred at a potential of around 1.626 V (E vs. Ag/AgCl), i.e., in the region of oxygen evolution or formation of hydroxyl radicals (•OH). The electro-oxidation of palmitic acid by a BDD electrode was controlled by mass transfer at high-applied potential.

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