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Treatment of palm oil mill effluent by electrocoagulation with presence of hydrogen peroxide as oxidizing agent and polialuminum chloride as coagulant-aid

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ABSTRACT

The purposes of this study were to investigate the effects of operating parameters, such as electrode material, current density, percentage of hydrogen peroxide and amount of polialuminum chloride (PAC) on chemical oxygen demand (COD) removal of palm oil mill effluent (POME). The current density was varied between 30–80 mA cm^{-2}, PAC (1–3 g L^{-1}) as coagulant-aid and 1 and 2% of hydrogen peroxide as an oxidizing agent. As for the performance of electrode type, iron was more effective than aluminum. It appeared that the removal of COD increased with the increased of current density. When PAC and H_2O_2 increased, the percent of COD removal was increasing as well. The overall results demonstrate that electrocoagulation is very efficient and able to achieve more than 70% COD removal in 180 min at current density 30–80 mA cm^{-2} reliant upon the concentration of H_2O_2 and PAC.

1. Introduction

Palm oil industry is one of the largest international agro-based industries. A number of operating processes are involved in order to extract palm oil from the fruit of *E. guineensis* such as sterilization, stripping, digestion, pressing, classification, purification, and vacuum drying [1]. This industries are of fundamental economic importance for Malaysia over the last three decades. However, this important industrial activity generates an enormous amount of environmental pollution in term of POME [2]. POME is characterized as a thick liquid, brownish in colour, rich in organic matter and unpleasant odour [3]. This highly polluted wastewater if not treated properly then discharge to the waterbody, it definitely will cause considerable environmental harms due to its high chemical oxygen demand (COD) of 50,000 mgL^{-1}, biological oxygen demand (BOD) of 25,000 mg L^{-1}, oil and grease (O & G) of 8,000 mg L^{-1}, suspended solids (SS) of 20,000 mg L^{-1}, and total solid of 40,000 mg L^{-1}[4].

Several different techniques have been reported in the literature regarding on treatment of POME such as: anaerobic digestion [5–8], aerobic oxidation based on an activated sludge process [9], anaerobic and aerobic digest ions [10], chemical flocculation and coagulation [11,12], membrane anaerobic system [13], up-flow anaerobic sludge fixed film (UASFF) reactor [14], immobilized up-flow anaerobic sludge blanket (UASB) reactor [15] and adsorption [16]. Although aforementioned treatment technique can be applied as the efficient methods, either they took a long period or needed a large amount of substance, both ways are less effective in treating this type of wastewater where it requires a short time treatment and an environmental compatibility with less chemical effect.

Recent study has demonstrated that electrocoagulation method deals an interesting option to conventional techniques in wastewater treatment, especially from sewage [17], textile [18,19], dye [20–24], tannery [25], olive mill [26], and paper industry [27]. In this process, electrode metal species generates metal ion upon the application of a direct current then hydrolysed in the electrochemical cell to produce metal hydroxide according to reaction (1)–(7).

At the cathode:

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \tag{1}$$

By using iron as electrode.

At the anode:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2}$$

In the solution (with dissolved oxygen):

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$$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2 \quad (3)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (4)$$

$$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3 \quad (5)$$

By using aluminum as electrode.
At the anode:

$$Al \rightarrow Al^{3+} + 3e^- \quad (6)$$

In the solution (with dissolved oxygen):

$$Al^{3+} + 3OH^- \leftrightarrow Al(OH)^3 \quad (7)$$

This technique has some advantages such as less retention time, rapid sedimentation of electrogenerated flocs, less sludge production, absence or less of additional chemicals, simple equipment and easy to operate. However, by dealing with POME wastewater which contain high concentration of COD, the needs of additional application have to be done to enhance this treatment process. The study of hybrid treatment of POME by using electrocoagulation-chemical coagulation-oxidizing agent has not yet been studied. This study determined the treatability of POME by electrocoagulation method using two types of electrodes (iron and aluminum) accompanying with additional application of hydrogen peroxide as oxidizing agent and PAC as coagulant aid that would be practicable in use for small and medium size facilities.

2. Materials and methods

Fresh POME was collected from the receiving tank of an oil palm mill in Kilang Sawit Lepar Hilir 3 Pahang, Malaysia which be kept at 4–8 °C prior to use. The POME was fully characterized, as shown in Table 1.

A schematic diagram of the experimental set-up is depicted in Fig. 1. The electrochemical unit consists of an electrocoagulation cell, a D.C power supply and the electrodes (aluminum and iron). There are two monopolar electrodes having same dimension (120 mmx100 mmx2 mm) as an anode and a cathode which spacing of 10 mm between each other. The total effective electrode was 1.652×10^{-2} m^2. In order to maintain an unchanged composition and avoid the association of the flocs in the solution, the stirrer was turned on and set at 80 rpm. The Reynolds number of the fluid solution is 2149.33. All the electrodes were washed with dilute HCl before every experiments conducted. At the beginning of each experiments, 1000 mL of POME wastewater was fed into the electrocoagulation cell and a certain amount of current was applied to the circuit for 240 min. The amount of current densities that have been applied to the system were 30, 40, 50, 60, 70 and 80 mA cm^{-2} with initial voltage of 6 V. Every experiment was performed at the room temperature. Experimentalsampleswere takenat specific intervalsofeach run for COD measurement.

Table 1
Characteristics of POME.

Parameter	Concentration
Biochemical oxygen demand (BOD)	15,600
Chemical oxygen demand (COD)	25,000
pH	3.6
Total carbohydrate	10,000
Total nitrogen	800
Ammonium–nitrogen	20
Total phosphorus	90
Phosphorus	14
Oil and grease	2000
Total solid	20,000
Volatile suspended solids	4500

All values are in mgL^{-1} except for pH

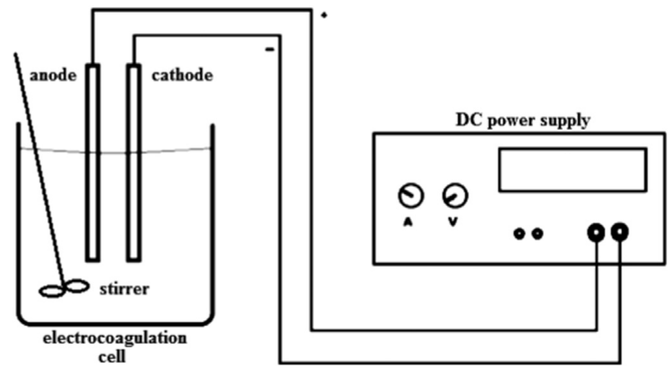

Fig. 1. A schematic diagram of the experimental set-up.

The reagent grade of chemicals was used without further purification in every experiment. PAC was used as additional coagulant and hydrogen peroxide (H_2O_2) as the oxidation agent. There was unnecessary to apply any electrolyte supportive since the conductivity of POME (15.68 mS cm^{-1}) was already high. The pH value was determined by a pH meter (Hanna, HI2211-02). The COD values were measured by a colorimetric method using Hach DR5000 spectrophotometer after sample's digestion using Hach COD Digestion Reagent. The system's current was provided by a regulated DC power supply (EDU-LABS TPR-3030D; 30V/30A) and was determined by a multimeter (Uni-T, UT203 multimeter).

3. Result and discussion

Preliminary experiments show that the removal's percentage of COD was 86.67% in 180 min of electrolysis. The percentage of COD removal can be deliberated as the core performance benchmark in this study. A number of experimental runs were conducted to determine the appropriate operating conditions, such as electrode material, EM (aluminum or steel); current density, i (Am^{-2}); the concentration of hydroxides [H_2O_2] % and coagulant-aid [PAC], (gL^{-1}). COD removal efficiency RE_{COD} (%) was evaluated in order to monitor the performance of the system. The COD removal efficiency was determined as:

$$RE_{COD}(\%)=\frac{COD_0 - COD_t}{COD_0}\times100\% \quad (8)$$

where COD_0 is the initial amount of COD (mgL^{-1}) and COD_t is amount of COD (mgL^{-1}) at the specific time.

Electrode assembles as the heart of the EC process and for that reason, it is very concern to find the suitable material selection. Iron and aluminum are the material that most commonly used in EC process as they are economic, readily available, and proven to treat wastewater effectively. In that case, the two materials were used in this study. The comparison of COD removal efficiency between iron and aluminum electrodes under the same conditions was showed in Fig. 2. By using iron electrode, COD removal efficiency reach its optimum level of 86.67% in just 180 min of electrolysis time as compared to the 81.11% in 210 min by using aluminum electrode. In the first 90 min, the graph shows more than half of COD concentration reduce for both type of electrode used, which the removal efficiency of 66.19% and 53.02% for iron and aluminum electrodes, respectively In electrocoagulation process, the dissolution of aluminum and iron electrodes, form a range of coagulant species which are metal hydroxides or polymeric metal hydroxides, that can destabilize and aggregate the suspended particles or precipitates to become flocs and absorb dissolve organic particles [28]. The metal hydroxide flocs can also remove wastewater through enmeshment or sweep coagulation [29]. In this case, even though both of the materials are rather effective, iron electrode showed a better performance than aluminum. The observa-

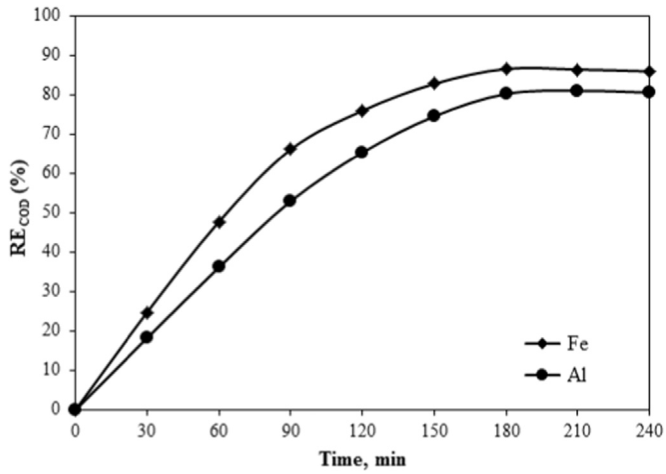

Fig. 2. The variation of final COD removal efficiency for different electrode materials. i=70 mA cm^{-2}, [PAC]=0 gL^{-1} and [H_2O_2]=0%.

tions of the structure of the iron sludge and aluminum sludge after electrocoagulation, using the SEM analysis, are shown in Fig. 3. The SEM images show that the size of the particles in the iron sludge was smaller than that of the particles in the aluminum sludge. Since the particle size is small, the area occupied by the flocs is larger, and this increases the possibility of pollutants being attached to the flocs. This is also match with [30], which the authors observed that iron electrodes were more successful than aluminum electrodes in terms of durability and cost.

In order to determine the effect of current density, the application of six different current densities (30, 40, 50, 60, 70, 80 mA cm^{-2}) were operated in 240 min Fig. 4 shows the COD removal efficiency during the treatment with variation of current densities. At the final operation, the increment of current density from 30 to 80 mA cm^{-2} resulted in increment of COD removal efficiency from 72.86% to 88.25%. This can be explained by as the current density increase, the efficiency of ion production in anode and cathode also increase, leading to the percentage of removal for COD to increase. In this process, coagulant Fe^{3+} was produced in situ by electrochemically sacrificing of iron anode and the dosage was determined by charge loading.

PAC as a coagulant-aid was used in this study in order to enhance the removal efficiency. Fig. 5 shows the COD removal efficiency of POME in 240 min by different coagulant-aid dosages. The figure shows that a higher COD removal efficiency was achieved when the electrocoagulation process was conducted simultaneously with coagulant-aid. Furthermore, it was observed that the formation of flocs when coagulant-aid was added enhanced their surface area which at the same time increase their settling ability. Additional coagulants can change the properties of pollutant's surface charge to endorse agglomeration and enmeshment of fine particles to become larger flocs which can be easily removed by sedimentation or filtration.

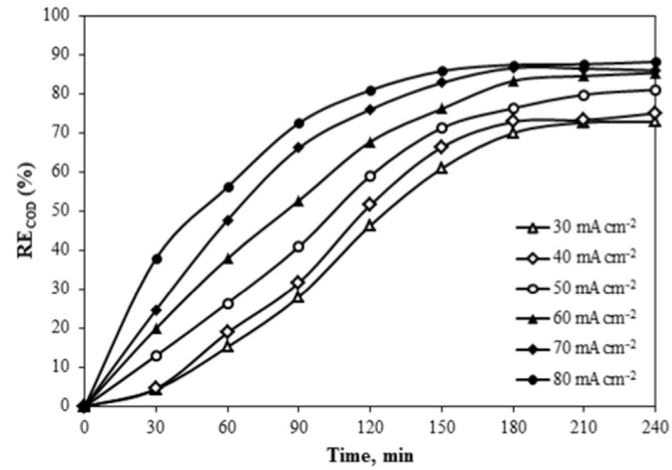

Fig. 4. The variation of final COD removal efficiency for different current densities. EM = Iron, [PAC] =0 gL^{-1} and [H_2O_2] =0%.

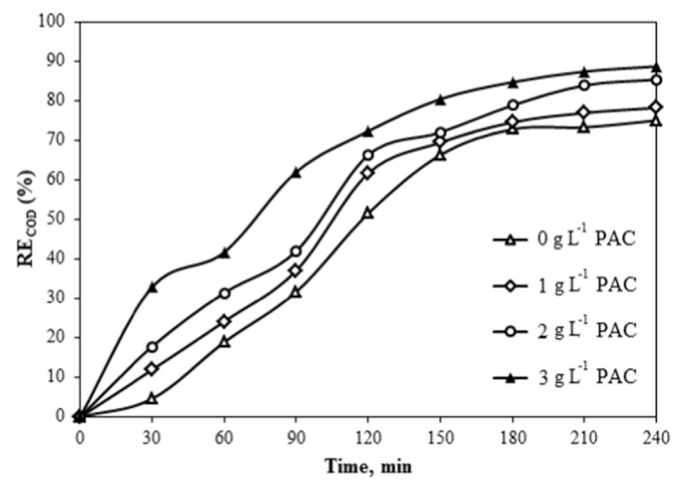

Fig. 5. The variation of final COD concentrations for different concentrations. EM=Iron, i=40 mA cm^{-2}.

An amount of H_2O_2 as oxidizing agent was added in the electrolysis of POME for electro-Fenton system and produce hydroxyl radical (•OH) generated by H_2O_2 reduction (Eq.(5)) with ferrous ion (Fe^{2+}) produced via iron oxidation at the anode (Eq.(2)).

$$H_2O_2 + Fe^{2+} \rightarrow \bullet OH + OH^- + Fe^{3+} \quad (9)$$

Hydroxyl radical (•OH) has strong oxidizing potential and has ability to oxidize organic pollutants. Thus, in order to increase COD removal efficiency, this feature was used to assist electrocoagulation process by adding1% and 2% of H_2O_2. Fig. 6 shows the removal efficiency of COD versus time at different H_2O_2 concentrations.

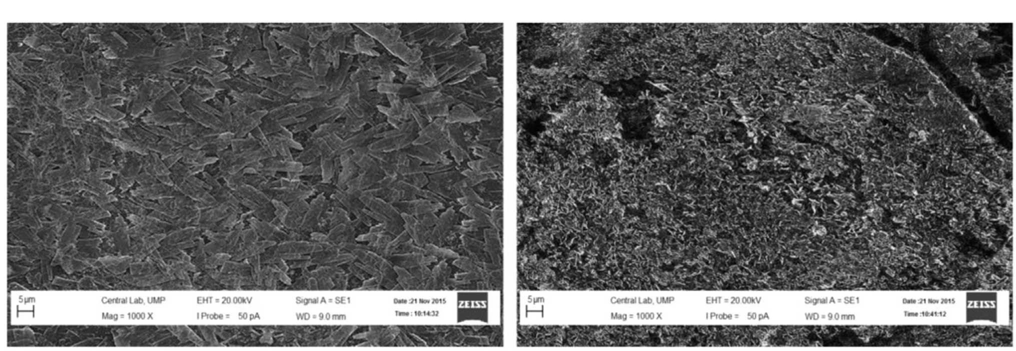

Fig. 3. SEM image of the sludge produced by electrocoagulation process using a) aluminum plate and b) iron plate with 1000X magnification.

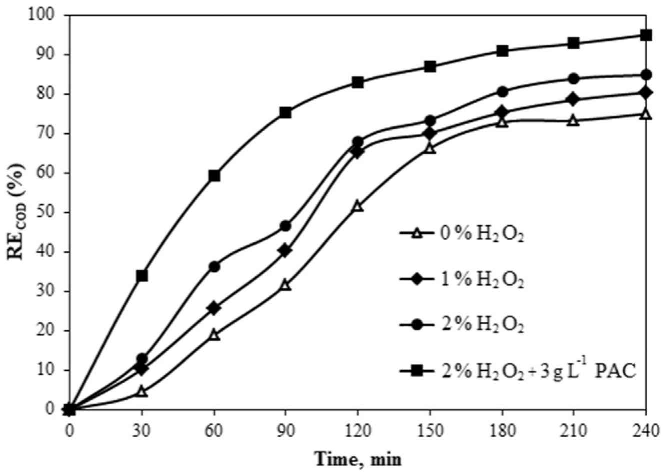

Fig. 6. The variation of final COD concentrations for different concentrations of H_2O_2 and PAC. EM = Iron, i=40 mA cm^{-2}.

Removal efficiencies of 75.08, 80.48, 84.92% for 0, 1, 2% H_2O_2, respectively were obtained after 240 min of electrolysis. Moreover, 95.08% COD removal efficiency was achieved by adding 2% H_2O_2 plus 3 g L^{-1} PAC to the electrocoagulation process. Therefore, the results show that the presence of coagulant-aid and oxidant together with electrocoagulation is very effective for treating this type of wastewater.

4. Conclusion

Through investigation has been carried out in this study, electrocoagulation using iron electrode rather than aluminum is a feasible process for treatment of POME due to better removal efficiency. Treatment efficiency seen to increase with an increase in current density. The best current density for this process was recorded at 80 mA cm^{-2}. The highest removal efficiency have been obtained in electrocoagulation process by adding 2% H_2O_2+3 g L^{-1} PAC. Indeed, the reported results showed that electrocoagulation process is more effective and significant with presence of H_2O_2 as oxidation agent and PAC as additional coagulant.

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