Comparative study on the removal of COD from POME by electrocoagulation and electro-Fenton methods: Process optimization

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Abstract. This research focuses on the Chemical Oxygen Demand (COD) treatment in palm oil mill effluent by electrocoagulation and electro-Fenton methods to solve it. Initially, the aqueous solution precipitates in acid condition at pH of about two. This study focuses on the palm oil mill effluent degradation by Fe electrodes in a simple batch reactor. This work is conducted by using different parameters such as voltage, electrolyte concentration of NaCl, volume of H_2O_2 and operation time. The processing of data resulted is by using response surface method coupled with Box-Behnken design. The electrocoagulation method results in the optimum COD reduction of 94.53% from operating time of 39.28 minutes, 20 volts, and without electrolyte concentration. For electro-Fenton process, experiment points out that voltage 15.78 volts, electrolyte concentration 0.06 M and H_2O_2 volume 14.79 ml with time 35.92 minutes yield 99.56% degradation. The result concluded that the electro-Fenton process was more effective to degrade COD of the palm-oil-mill effluent compared to electrocoagulation process.
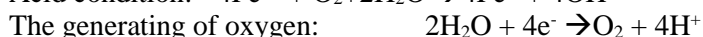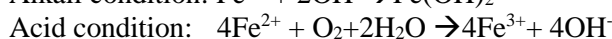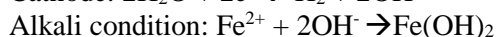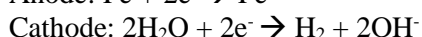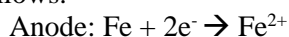
1. Introduction

The increased production of palm oil has increased the income of the Indonesian economy, particularly in the industrial field. However, although the benefit of the economic improvement, the impact on the environment emerged are the functional conversion to forest, greenhouse gas production, water, biodiversity, emissions, environmentally friendly process technology, and waste both solid and liquid [1]. Wastewater in particular, in every ton of fruit, will produce 0.65 ton of waste from the process. Palm-oil-mill effluent (POME) is a brownish liquid containing a large amount of water, oil, suspended solids, dissolved solids, and sand. The untreated POME contained some colloidal suspension of 95-96% water, 0.6-0.7% oil, and 4-5% total solids, including 2-4% suspended solids [2]. It has a pH in the range of 3.45 – 4.6, COD concentration of 30,000 – 80,000 mg/l with BOD concentration of 15,000 – 40,000 mg/l, total suspended solid of 1,500 – 50,000 mg/l, and total solid of 16,000 – 95,000 mg/l [2]. One of the popular processes of palm oil wastewater is the pond system (pond). The pond system consists of a sand-and-oil trap, a cooling pond, an acidification pond, an anaerobic pond, a facultative pond, and an aerobic pond. The sand-and-oil trap is a part of wastewater pre-treatment. An aerobic pond has a depth of 1.0 – 1.5 m, whereas the anaerobic pond ranges five to

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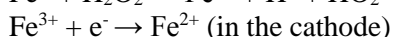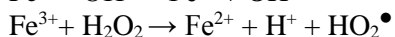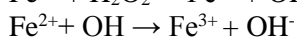[3]   To whom any correspondence should be addressed.

seven meters. The anaerobic pond could process large amounts of the solid with low-cost need. However, pond system requires a long residence time, large area, huge cost to prepare the pool, and microbes used to produce methane gas that increases the greenhouse effect [3].

Another alternative to overcome problems arising from pond system is to combine this system with other treatment systems. The treatment system used is electrocoagulation and electro-Fenton. Electrocoagulation is a coagulant production method of the in-situ process by applying an electric current through a cathode and an anode that releases metallic ions into solution. The cathode releases hydrogen recovered as an energy source or reactants for other industrial applications. In electrocoagulation, the proper anode material reduces the electrolyte to generate active coagulant species in its original place. Floc formed has a large surface area that can adsorb dissolved organic compounds and captures colloidal particles contained in solution [4]. Metal ions produced further produce hydroxide, poly hydroxide, and metal poly hydroxide compounds that have high affinity against opposite charged ions in solution [5]. In the process of electrocoagulation (EC) stages to degrade or to decrease the pollutant concentration are 1) the dissolving of anode ions in the solution, 2) the generating of OH^- ions and H_2 at the cathode, 3) electrolytic reactions at the electrode surface, 4) adsorption of coagulant in colloidal pollutants and 5), colloid removal by sedimentation or flotation [6]. After the use of the iron electrode, oxidation simplicity and reaction mechanisms that occur are as follows.

Anode: $Fe + 2e^- \rightarrow Fe^{2+}$

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Alkali condition: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Acid condition: $4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$

The generating of oxygen: $2H_2O + 4e^- \rightarrow O_2 + 4H^+$

The electro-Fenton process requires H_2O_2 addition from the outside and an anode to generate Fe. In electro-Fenton, the processes of electrocoagulation and Fenton combine to increase the organic compound degradation in the wastewater. The electro-Fenton process occurs based on the work of the dissolved anode (Fe). Anodes will give Fe^{2+} ions into the solution, and cathode assists water reduction occurs simultaneously. The efficiency of the Fenton reaction mainly depends on H_2O_2 concentrations, the ratio of Fe^{2+}/H_2O_2, pH, and reaction time. Hydrogen peroxide is useful to give conditions for the Fenton reaction. Besides, Fe^{2+} could continue to regenerate in the cathode depending on the setup of the electrolytic cell [7]. The process uses the iron catalyst both in the form of ferrous (Fe^{2+}) and ferry (Fe^{3+}) salts. Several parameters influence the process of electro-Fenton (EF) such as pH, Fe/H_2O_2 ratio, existence of other anions and the chelating agent [8]. The following chemical reactions occur in the process.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$

$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (in the cathode)

The electro-chemical process had many applications such as the olive mill wastewater processing, cannery [8], surfactants, food processing, semiconductor, mechanical polishing, liquid organic fertilizer [7], electroplating, livestock [9], textile wastewater [10], palm oil mill effluent [11, 12], winery wastewater [13], pulp and paper wastewater.

The purpose of the research is to get the organic compound reduction in wastewater degradation derived from the value of COD analyzed. In this research, the COD reduction process takes place by combining pond system with electrocoagulation and electro-Fenton. The process variables on electrocoagulation process include voltage, operation time, and the electrolyte concentration. For the electro-Fenton process, operation parameters are voltages, operating time, electrolyte concentration and the volume of H_2O_2. Response Surface Methodology (RSM) processes the data by Box-Behnken Design (BBD) to get the optimum condition and related process variables.

2. Experimental procedure and methodology

Wastewater was taken from local palm oil mill (PT Syaukath Seujahtera, Bireuen Regency, Indonesia). The liquid wastewater was from the anaerobic pond I. This wastewater contained significant amounts of organic compounds, had a brown color, and smells bad. The wastewater was then put into a jerry can, and placed in a refrigerator at a temperature of 4°C. The wastewater characteristic after H_2SO_4 addition, such as pH, COD, TSS and TDS were 2; 7,000-11000 mg/L (diluted by 10 times until 700-1100 ppm) ; 4,720 mg/l and 1011 mg/l, respectively. COD in the pond was less than the COD in fat pit that was usually in the range of 30,000 – 80,000 mg/l because the pond was the fourth stage in the wastewater treatment of oil palm factory.

2.1. Materials and research procedure

The main equipment consisted of a reactor, electrodes, and power supply. Reactors EC and EF were made of glass with a size of 14 cm × 12 cm × 15 cm. Electrodes used consisted of two pairs of iron plates with a size of 15 cm × 10 cm × 1.0 cm. The electrode was connected to a DC-power supply (Sanfix 30 A and 30 V). Chemicals used were NaCl, acetone (Merck), and H_2O_2 (technical grade). Research stages were begun by cleaning electrode every time before and after one run. Electrodes were sanded by using sandpaper to make the surface of the electrode slippery and shiny. Cleaning was continued by washing electrode by using acetone and followed by a rinse with aqua distillate.

The next stage was putting wastewater of 1.3 L into a glass reactor. A certain amount of NaCl and H_2O_2 was added to a reactor by BBD design. NaCl and H_2O_2 were added then the electric current was applied to the electrodes. During the research took place, wastewater was stirred continuously by the stirrer speed of 100 rpm. The voltage was adjusted by BBD. All runs were carried out in the room temperature of 28°C. After the run had been completed, wastewater was filtered by using the membrane with a pore size of 0.45 micrometer then the filtrate was collected 100 ml for COD analysis. The electrode was cleaned back by using the stages mentioned above.

2.2. Experimental design

The Box-Behnken Design was useful for adjusting response surface, where a formula referred to a combination of 2^k block factorial with a simple design (Tables 1 – 3). The result of the design was typically very efficient to get the number of experiments conducted. By using RSM, it could be determined the relation between dependent process variables and the result. To find the electrocoagulation variable relation, the dependent variables were set as operation times (A; 15 – 45 minutes), voltage (B; 10 – 20 volt), and electrolyte concentration (C; 0.0 – 1.0 M). In electro-Fenton process, the dependent variables included operation times (A; 15 – 45 minutes), voltage (B; 10 – 20 volts), electrolyte concentration (C; 0.0 – 1.0 M), and volume of H_2O_2 (D; 5 – 15 ml).

Based on the one-factor at an experiment, variables were identified to get strong effects on COD removal. Table 1 shows Box-Behnken design of the research of 17 trials for electrocoagulation and 29 trials for electro-Fenton process. As shown in Table 1, the factors were designed as A, B, C and D. All factors were prescribed into three levels, namely +1, 0, -1 for high, intermediate and low value, respectively.

Table 1. Input variable and code factor of response surface method of Box-Behnken design.

Code Factor	Variable	-1	0	1
For electrocoagulation and electro-Fenton				
A	Time (minute)	15	30	45
B	Voltage (V)	10	15	20
C	Electrolyte concentration (ppm)	0	0.5	1
For electro-Fenton				
D	Volume of H_2O_2 (ml)	5	10	15

Analysis of variance (ANOVA) was carried out as a parametric test to distinguish the average value of more than two data groups by comparing their variances and determining responses to their variables. For predicting the optimum condition, thus the best COD removal had been based on all variables. Based on the relationship between the significant variable and the percentage of COD reduction as response obtained, thus it was obtained a polynomial equation to predict response. The polynomial equation quality was expressed by R^2 coefficient. The function of desirability or Derringer function was the most important and most used multi-criteria method in the analytic procedure optimization.

Chemical oxygen demand was determined by referring to SNI.6989.2:2009 for organic and inorganic compound oxidized by $Cr_2O_7^{2-}$ in closed reflux methods by using UV-VIS spectrophotometer model V-630. The oxidant determination in the sample was by visible light 420 nm.

Based on these results, the percentage of COD reduction was calculated from Equation 1.

$$COD_{reduction}(\%) = \frac{COD_0 - COD_t}{COD_0} \times 100 \qquad (1)$$

COD_0 was initial COD, and COD_t was the remaining COD after electrocoagulation.

2.3. Energy consumption
In this study, the energy consumption of electrocoagulation and electro-Fenton referred to the optimum condition. The energy consumption calculation was as follows.

$$\text{Energy consumption} \left(\frac{kWh}{mg\,COD}\right) = \frac{I \times v \times t}{\Delta COD \times V} \qquad (2)$$

Where I was a current intensity (A), v was voltage (V), t was the time of electrocoagulation, V was the volume of solution (L), and ΔCOD was the experimental COD reduction in solution [14, 15].

3. Result and Discussion

3.1. Response analysis by Box-Behnken Design
The research applies the processes of electrocoagulation and electro-Fenton to degrade the COD in palm oil mill effluent. The run of the data uses the Box-Behnken design with three levels based on dependent variables for electrocoagulation process such as operation time, voltage, and electrolyte concentration. For the electro-Fenton process, the dependent variables include time, voltage, electrolyte concentration, and volume of H_2O_2. Response variables investigated are the value of COD reduction after finishing the process (Table 2). It gives the COD removal predicted by a quadratic model along with values observed. The agreement between the predicted and experimental data is strong, with a low difference in COD removal.

Experimental data of the electrocoagulation show that the highest COD reduction of POME by electrocoagulation is in 45 minutes, the voltage of 20 V, and with NaCl concentration of 0.5 M. Such conditions result in the percentage of COD reduction of 95.01%. The predicted data of this run for electrocoagulation experimental was 95.86% (Table 2). On the other hand, the lowest COD of 76.85% for 15-minute duration, the voltage of 10 V, and electrolyte concentration of 0.5 M. The predicted data of this run was 76.00%. By electro-Fenton (Table 3), the highest COD reduction in the experiment and predicted data was 99.3% and 99.7%, respectively, at the time of 45 minutes, the voltage of 15 V with the electrolyte concentration of NaCl 0.5 M and the volume of H_2O_2 15 ml. Meanwhile, the lowest COD reduction in electro-Fenton for the experiment and predicted data was 91.00% and 92.20%, respectvely, in 15 minutes of electrolysis time, 15 voltage, 0.5 M NaCl solution concentration and 10 ml volume of H_2O_2. The high COD reduction occurs because of relatively short contact time, relatively short voltage and the H_2O_2 addition. The electro-Fenton uses peroxide that could produce

hydroxyl radical. A radical could degrade organic compounds into other simple compounds in wastewater [16].

Table 2. Box-Behnken design with percentage of COD reduction after treatment by electrocoagulation

Run	Time (minute)	Voltage (V)	NaCl Concentration (M)	Actual COD Reduction (%)	Predicted COD Reduction (%)
1	**45**	**20**	**0.5**	**95.01**	**95.86**
2	30	20	1.0	92.50	91.69
3	30	15	0.5	88.50	87.91
4	**15**	**10**	**0.5**	**76.85**	**76.00**
5	15	15	1.0	77.03	78.05
6	30	10	0.0	83.20	84.01
7	45	10	0.5	86.64	86.85
8	45	15	0.0	91.25	90.23
9	45	15	1.0	91.25	91.22
10	15	20	0.5	81.59	81.38
11	30	20	0.0	91.27	91.44
12	30	15	0.5	87.75	87.91
13	30	15	0.5	88.08	87.91
14	15	15	0.0	78.05	78.08
15	30	15	0.5	86.46	87.91
16	30	10	1.0	84.90	84.73
17	30	15	0.5	88.78	87.91

Table 3. Box-Behnken design with percentage of COD reduction after treatment by electro-Fenton.

Run	Time (minute)	Voltage (V)	NaCl Concentration (M)	H_2O_2 Volume (mL)	Actual COD Reduction (%)	Predicted COD Reduction (%)
1	15	15	0.5	5	91.70	92.04
2	45	15	0.0	10	99.30	98.71
3	**45**	**15**	**0.5**	**15**	**99.30**	**99.97**
4	30	15	0.0	5	96.08	96.01
5	45	10	0.5	10	96.73	96.88
6	15	15	0.5	15	92.05	93.15
7	30	10	0.5	15	98.50	97.38
8	30	10	0.5	5	93.34	93.10
9	30	20	0.5	15	98.70	98.41
10	45	20	0.5	5	99.00	99.46
11	45	15	0.5	5	97.00	96.91
12	15	15	1.0	10	93.00	93.04
13	30	15	0.5	10	96.24	96.32
14	**15**	**10**	**0.5**	**10**	**91.00**	**92.20**
15	30	15	0.5	10	97.50	96.32
16	30	20	0.5	5	97.98	98.52
17	30	15	0.5	10	96.34	96.32
18	30	15	0.5	10	95.00	96.32
19	30	10	0.0	10	94.00	95.06
20	15	20	0.5	10	94.50	94.25
21	15	15	0.0	10	93.00	92.72
22	30	20	1.0	5	97.00	99.17

Run	Time (minute)	Voltage (V)	NaCl Concentration (M)	H$_2$O$_2$ Volume (mL)	Actual COD Reduction (%)	Predicted COD Reduction (%)
23	30	20	0.0	10	99.00	99.03
24	30	10	1.0	10	95.00	95.98
25	30	15	1.0	15	98.30	98.27
26	30	15	0.5	10	96.20	96.32
27	45	15	1.0	10	99.00	98.73
28	30	15	0.0	15	98.40	98.61
29	30	20	1.0	10	98.50	98.45

An excessive amount of peroxide in wastewater could be other pollutants in wastewater by considering its toxic and harmful properties. Because of peroxide used in electro-Fenton process, corrosion occurs more quickly to electrodes. A part of the applied current not only degrades wastewater, but also deposits electrode, thus it causes corrosion to occur more quickly to the electrode surface.

The response surface method of BBD indicates that the response from COD values is the quadratic model of the processes of electrocoagulation and electro-Fenton. Equation 3 results in the predicted data for COD reduction in electrocoagulation and Equation 4 for COD reduction in electro-Fenton process. The strong relationship between COD removal predicted by Equations 3 and 4, and the experimental results (Tables 2 and 3) show that the model accuracy and ability are good.

$$COD\,(\%) = 59.68 + 1.09\,A - 0.03\,B + 1.3\,C + 0.01\,AB + 0.03\,AC - 0.05\,BC - 0.01\,A^2 \\ + 0.01\,B^2 - 1.15\,C^2 \tag{3}$$

$$COD\,(\%) = 73.91 + 0.52\,A + 0.80\,B + 1.03\,C + 0.41\,D - 0.004\,AB - 0.01\,AC + 0.007\,AD \\ - 0.15\,BC - 0.04\,BD - 0.10\,CD - 5.32\,A^2 + 5.50\,B^2 + 2.72\,C^2 + 0.02\,D^2 \tag{4}$$

The fit checking of the model is by using the determination coefficient R^2. Based on tabulation data by the response surface method coupled with Box-Behnken design (Tables 2 and 3), both models follow statistically the quadratic model (Table 4). "Model Summary Statistics" focuses on the maximizing the "Adjusted R-Squared" and the "Predicted R-Squared" values to find model reliability. The value of R^2 that approaches one indicates the high correlation degree among observation and predicted values. Similarly, the model also indicates the higher value of *Adj*-R^2 which means that the model is more significant [17]. Based on the experimental data, data agree well with the predicted data (electrocoagulation R^2 0.9829 and the electro-Fenton R^2 0.9448). Furthermore, the R^2 values also show that each model explains 98.29% and 94.48% of the total variation in the COD removal to the operating parameters.

Table 4. Model summary statistics of electrocoagulation and electro-Fenton process.

Response	Source	Std. Deviation	R-squared	Adjusted R-square	Predicted R-square	PRESS
Percentage of COD removal by electrocoagulation	Linear	2.09	0.8819	0.8547	0.7818	104.98
	2 FI	2.31	0.8894	0.8231	0.5524	215.41
	Quadratic	**1.09**	**0.9829**	**0.9608**	**0.8237**	**84.86**
	Cubic	0.9	0.9932	0.9729	-	-
Percentage of COD removal by electro-Fenton	Linear	1.18	0.8124	0.7812	0.7147	51.05
	2 FI	1.21	0.8521	0.7699	0.5484	80.80
	Quadratic	**0.84**	**0.9447**	**0.8894**	**0.7549**	**43.86**
	Cubic	0.98	0.9679	0.8503	-1.1224	379.78

The analysis of variance (ANOVA) observed for response expresses the model reliability, as presented in Table 5. ANOVA is a comparison of the variance because of the treatment and the variance because of random errors inherent in the responses. By this comparison, it is possible to check the regression significance of variables toward responses by considering sources of experimental variance. It is important to test the significance and accuracy of the model through ANOVA.

ANOVA of Table 5 shows that the probability (*p*) values such as time, voltage, electrolyte concentration and volume of H_2O_2. It shows the significant variable determination by applying the *p-values*. As a result, such variables are significant and have a real effect on COD reduction that have a *p-value* lower than 0.05. It is because *p-value* is generally compared to a particular real standard α, usually 0.05 or 5%. Time and voltage variables have the larger interaction effect of degrading COD based on both the same *p-values* ($p < 0.05$). In electro-Fenton, significant coefficients are time, voltage, volume of H_2O_2, and interaction of voltage-volume H_2O_2. In the both processes, electrolyte concentration has a *p-value* above 0.05 which is not a significant variable and indicates that electrolyte concentration has the least interaction among other variables. In addition, the effect of the quadratic terms A^2 on the COD removal is significant.

Table 5. ANOVA results in COD removal by electrocoagulation.

Source	Electrocoagulation		Electro-Fenton	
	P-value	Remark	P-value	Remark
Model	< 0.0001	Significant	< 0.0001	Significant
A – Time	**< 0.0001**		**< 0.0001**	
B – Voltage	**< 0.0001**		**< 0.0001**	
C – Electrolyte concentration	0.5536		0.7314	
D – Volume of H_2O_2			**0.0009**	
AB	0.1384		0.4766	
AC	0.6527		0.8610	
AD			0.2656	
BC	0.8348		0.3875	
BD			**0.0194**	
CD			0.5539	
A^2	**< 0.0005**		**0.0028**	
B^2	0.5403		0.6836	
C^2	0.6043		0.059	
D^2			0.2458	
Lack of Fit	0.2512	not significant	0.6153	not significant

3.2. The effect of variables on COD efficiency

3.2.1. The interaction effect of time and voltage. The percentage of COD removal represents the effect of time (X) and voltage (Y), which was developed by using Design Expert (version 10.0.1) software. Figures of 1 and 2 show the data. To find the time effect on the COD removal, time range varies from 15 to 45 minutes. Figures 1 (a) and 2 (a) indicate that time of the process increases for electrocoagulation and electro-Fenton processes. The contours were circular and become more elongated along the time axis. So a smaller value of time and voltage increased the efficiency of COD

removal in palm oil mill effluent. Based on the data, the efficiency of COD removal increases in line with the increase in time in the range of 15 – 45 minutes. The COD removal in electrocoagulation process increases from 80% to 95% (Figures 1 (a) and (b)); likewise, in the electro-Fenton process it also increases from the value of 94% to 100%.
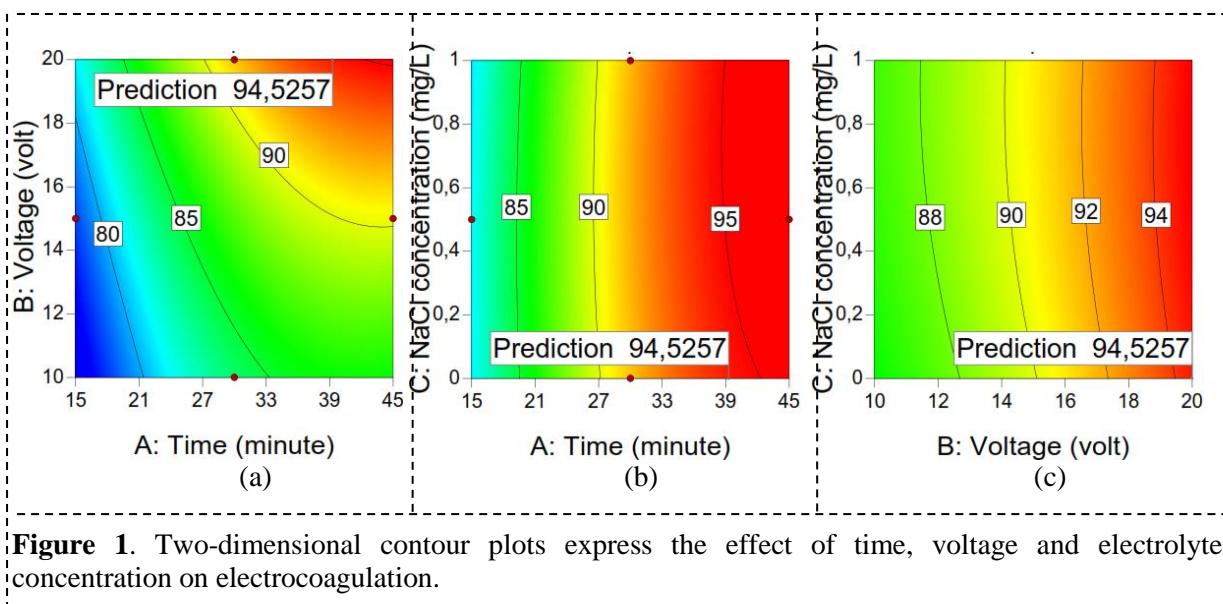

Figure 1. Two-dimensional contour plots express the effect of time, voltage and electrolyte concentration on electrocoagulation.
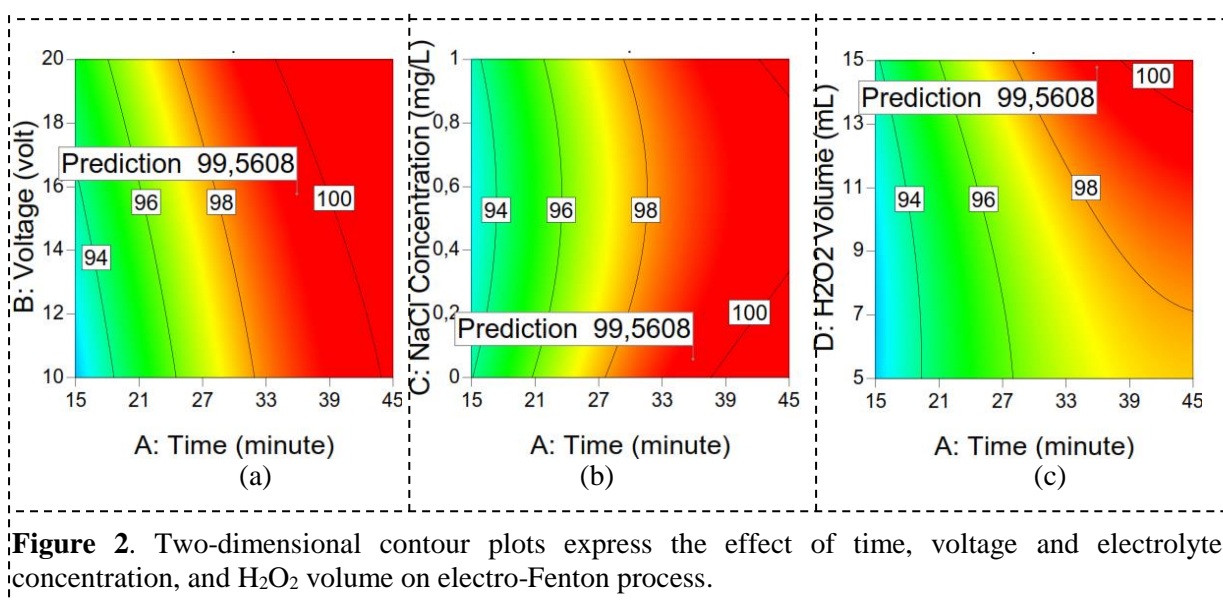

Figure 2. Two-dimensional contour plots express the effect of time, voltage and electrolyte concentration, and H_2O_2 volume on electro-Fenton process.

It indicates that longer time is more favorable in electrocoagulation and electro-Fenton processes of palm oil mill effluent. Time is a variable for controlling the rate of both processes. As a result of the change of time and voltage in the reactor, organic matter and coagulant interact and collide more effectively. The electrocoagulation generates coagulants in its original place during the time. Then, the cathode generates hydrogen bubbles during that time [18]. Pollutant and coagulant interact to form floc. This floc will form bubbles in the top of the reactor by the hydrogen existence. Some heavy flocs will sink to the bottom of the reactor.

3.2.2. The interaction effect of time and electrolyte concentration. The anion concentration on the solution could affect the passive layer stability of electrodes. In the solution, the electrolyte solution generates anions. This research uses a small concentration of the electrolyte into the reactor. This research also considers the effect of supporting electrolytes on the efficiency of an electrocoagulation system by varying the NaCl concentration from 0 to 1 mg/l (Figures 1 (a) and (b)). The electrolyte is various such as NaCl, Na_2SO_4 and others salt. The electrolyte in the research is NaCl. Some earlier works indicated that NaCl was the best electrolyte for electrocoagulation [7, 19]. Chloride ion could induce the passive layer and corrosion (pitting). As a result, anions increased electrical consumption and had a negative effect on EC efficiency [20].

Figures 1 (b) and 2 (b) show the contour plots based on variables of time (min) and electrolyte concentration (mg/L). Based on research data in Figure 1 (b), 1 (c) and 2 (b), the effect of electrolyte concentration was not significant on the removal of COD in both processes. At all level of time, the removal efficiency of palm oil mill effluent was found increased. In electrocoagulation in the range of 39 – 45 minutes and the electrolyte concentration of 0 – 1 M, COD reduction was 95% (Figure 1 (b)). At the shorter time than 39 minutes, the data fluctuated. In the range of 15 – 21 minutes, the COD removal was 85%; however, the removal increased to 90% with the increase in time until 27 minutes. Based on data and theory of electrocoagulation, the electrolyte was not so significant in removing COD in mill effluent POME treatment.

The NaCl addition does not increase conductance and current for both processes. In this research, the removal of organic compounds does not increase with the NaCl concentration addition. The complete removal got is above 39 minutes for both processes. The results of the research show that the degradation occurred efficiently without the NaCl electrolyte presence. It could be stated that the degradation became faster when NaCl electrolyte was not used in this research. It is probably because the use of NaCl causes a side reaction namely the organochloride ion formation, mainly OCl^-.

3.2.3. The interaction effect of time and H_2O_2 volume. This section explains the result of the electro-Fenton process. This process adds several oxidizing solutions. The addition aims to form the radical of hydroxyl which has standard oxidation potential of 2.8 V. This radical can oxidize several organic matters into CO_2, H_2O and inorganic ions by the specific reaction [20]. The optimum volume of H_2O_2 in removal efficiency of COD in this study is in the range of 5 – 15 ml. In 45 minutes, 15 volts, NaCl and 10 ml H_2O_2, the highest removal efficiency is 99.3% (Table 2). However, the increase in the volume of H_2O_2 causes the COD removal is slightly different. It may occur as a result of inactivity of some H_2O_2 because of the voltage applying to the electrode. The highest volume of H_2O_2 indicates the efficiency of COD removal is nearly complete. At the time reaches 45 minutes, such efficiency was almost adjacent. The COD removal efficiency in electro-Fenton depends on H_2O_2 dosage and time. The unlimited presence of the oxidizing agent forms the radical of hydroxyl more effectively to degrade the organic matter [21].

3.3. Energy Consumption
To find the efficiency of both processes, this research investigates the energy consumption/kg COD degraded in the optimum operating variables. Equation 4 indicates energy consumption of electrocoagulation for 39.28 minutes, 20 volts without NaCl is 0,1617 kWh/mg COD degraded. For the electro-Fenton process, the optimum condition in 35.92 minutes, 15.78 V, 3.9 Ampere with 14.79 ml H_2O_2 shows that energy consumption is 0,067 kWh/mg COD degraded. This shows that value of energy consumption of electro-Fenton is lower than that of electrocoagulation. However, further study is necessary to analyze the operating cost of both processes to prove the economic cost which refers to the more reliable value.

3.4. Comparison of removal efficiency for Electrocoagulation and Electro-Fenton
Response surface method of Box-Behnken Design (BBD) determines the optimum condition of this research without adding the experimental cost. BBD allows calculation of COD removal on

intermediate levels that are not experimentally investigated. A three-level BBD used in the research is to get the optimum conditions through a minimal investigation number compared to other designs. It uses constraint provided to meet the optimum condition. The experimental and predicted data show that the independent variable setting is different to the optimization by BBD for both processes. For both processes the constraint consists of NaCl concentration, electrolysis time, voltage set in their ranges and for electro-Fenton it also consists of H_2O_2 volume.

The high desirability indicates that the condition becomes optimal (closest to 1). The desirability (Derringer function) is the most important and the most current multi-criteria method used for optimizing analytic rules. This method initially refers to a construction a desirability function of each response [22]. Based on the response surface method of BBD, the optimum COD removal by electrocoagulation is 94.53% at operation time of 39.28 minutes, a voltage of 20 V, and without electrolyte. For electro-Fenton process, it is optimal at 99.56% in operating time of 35.92 minutes, a voltage of 15.78 V, electrolyte concentration of 0.06 M and H_2O_2 volume of 14.79 ml. The optimum COD removal prediction by BBD is close to the experiment data (Tables 2 and 3). Based on optimal prediction and experiment data, the electro-Fenton has the best result in removing the organic matter in palm-oil-mill-effluent treatment by comparing the removal efficiency of the COD.

4. Conclusion

This research investigates electrocoagulation and electro-Fenton performances in palm oil mill effluent treatment in a batch. The efficiency of COD removal is the main response of this research. The research uses response surface method (RSM) with Box-Behnken Design to get the experimental data interaction. As a result, the high R^2 values of COD removal of electrocoagulation and electro-Fenton are 0.98 and 0.95, respectively. ANOVA provides the R^2 values to verify that the processes are quadratic models. The largest removal of COD for electrocoagulation and electro-Fenton are 95.01% and 99.3%, respectively. In electrocoagulation, the optimum COD removal is 94.53% at operation time of 39.28 minutes, a voltage of 20 V and without electrolyte. For electro-Fenton process, it is optimal at 99.56% in operating time of 35.92 minutes, a voltage of 15.78 V, electrolyte concentration of 0.06 M and H_2O_2 volume of 14.79 ml. It is clear that the RSM gives information on interactions among those factors and helps to get optimum values of the investigated factors. Overall, both processes are successful in treating the palm oil mill effluent. This research indicates that the electro-Fenton process is the most successful process that degrades COD. Within all variables tested the COD removal is proportional to the operation time, voltage and electrolyte concentration for electrocoagulation and proportional to H_2O_2 volume for electro-Fenton process. For the application of electro-Fenton process in industries, other electrodes and response could be experimentally designed and tested by response surface method to remove organic pollutants in wastewater.

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