

Article

High performance electrocoagulation process in treating palm oil mill effluent using high current intensity application☆

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ABSTRACT

Electrocoagulation process using high current intensity to treat palm oil mill effluent (POME) was investigated in this study. Various operating parameters such as electrolysis time, inter-electrode distance and initial pH were carried out to determine the efficient process condition on the removal of chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solids (SS). The highest treatment was achieved at 50 min with the removal efficiencies for COD, BOD and SS obtained as 85%, 83%, and 84%, respectively. More than 50 min treatment showed the fluctuated trends of removal efficiencies which can be considered insignificant. The application of higher current resulted in higher removals of organics while the gas bubbles also assisted in removing the pollutant particles by floatation. In an inter-electrode distance study, the removal efficiency decreased when inter-electrode distance was either higher or lower than 10 mm due to the increase of solution resistance and the decrease of anode active surface area. In initial pH study, it was found that high removal efficiencies were achieved in slightly acidic POME sample rather than in neutral or basic condition. An electrocoagulation process by using the optimum operating parameters was able to remove COD, BOD and SS up to 95%, 94% and 96% respectively. The experimental results confirm that application of high current intensity in electrocoagulation provided high treatment efficiency at a reduced reaction time.

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1. Introduction

Palm oil industry in this country has grown by leaps and bounds over the last few decades making Malaysia one of the largest crude palm oil producers in the world. However, the increasing production and processing of oil palm and its derivatives have generated considerable wastes, termed as palm oil mill effluent (POME) that adversely affects human and aquatic life [1]. Every year, this country alone generates approximately 43.29 million cubic metres of POME [2]. This excessive industrial wastewater must be treated well to reach the discharge standard in order to protect the environment. Various studies have been performed for the treatment and disposal method for POME such as ponding system, aerobic and anaerobic methods [3]. Not only for POME treatment, but also this biological treatment is a conventionally practiced method to treat most kinds of wastewater [4]. For example, different microorganisms and techniques have been tested to valorize olive mill wastewater, which is the wastewater that has pollutant concentration similar to POME [5]. However, these biological treatment methods require a proper maintenance as well as periodic monitoring

since the processes solely rely on microorganisms to degrade the high molecular weight fraction of wastewater [6]. Moreover, these methods need a particular attention and commitment by expert and are also time-consuming. Besides that, these biological treatments also take a longer hydraulic retention time and need a huge investment in land for pond and digesters [7]. Thereby, it is necessary to find other method or technique as an alternative to the conventional treatment system in order to comply with the requirements and regulations of safe wastewater discharge [8]. The alternative method must include various factors such as more convenient to operate, short retention time, ease of installation, energy efficiency, cost effective, widely applicable on the various pollutant ranges, less labour and less maintenance.

An advanced electrochemistry-coagulation process, known as electrocoagulation is an alternative treatment method to remove the pollutant from wastewater. Electrocoagulation method has potential to treat POME as it is a stand-alone portable treatment with the ability to remove a wide range of pollutants. This treatment method was tested successfully for treating phenolic wastewater [9], olive mill wastewater [10], sewage [11], drilling fluids wastewater [12], tannery wastewater [13], poultry slaughterhouse wastewater [14], textile wastewater [15], chicken industry wastewater [16], removal of lead [17] and phosphate recovery from sludge anaerobic supernatant [18]. Other than low management cost, this method is also safe and natural environmentally

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friendly. With its ability and efficiency in treating so many types of wastewater which had been acknowledged by many researchers, it is the possible best solution as an alternative way to treat POME in terms of treatment efficiency in a short period of time.

To the best of our knowledge, limited study has been reported on electrocoagulation for POME treatment. The study reported by Nasution *et al.* [19], showed that the optimal time for POME treatment by electrocoagulation was 6 h with a COD removal efficiency of 42.94%. Another researcher, Agustin *et al.* [20] reported that they were able to remove about 30.44% of COD in 6 h. Although the processing period is rather shorter than conventional POME treatment, it is still considered long due to the lack of condition in operating parameters that should be paid attention to. This was not only applied for POME treatment, but also for the other wastewater treatments especially for the wastewaters that have high concentration of pollutant. For example, most researchers have studied the electrocoagulation process in terms of current intensity/density by using low current condition. The problems with the use of low current intensity are that it takes a relatively long treatment period as well as less efficient on removing complex composition in highly polluted wastewater, which resulted in COD and BOD readings that are still high after treatment. The researchers were generally using an initial current intensity of less than 5 A to treat wastewater for example treatment on olive mill wastewater [21], tannery [22], paper mill effluent [23] and paper industry [24] which either achieved the COD removal of less than 80% or took a long time to treat even though the wastewater sample was less than $10000 \text{ mg} \cdot \text{L}^{-1}$ of COD. In the present study, high intensity of more than 10 A current was introduced to remove high COD level ($<20000 \text{ mg} \cdot \text{L}^{-1}$) of organics in the raw POME. This study also identifies the optimum point of highest treatment in each operating parameter such as time, inter-electrode distance and pH by using one factor at one time (OFAT) study.

2. Materials and Methods

2.1. Sample preparation

Raw POME wastewater used in this study was obtained from the first effluent pit at Kilang Sawit Lepar Hilir 3, Gambang, Kuantan, Pahang. The sample was characterised to identify the concentration of COD, BOD, SS and pH and then was stored in the freezer with temperature below than -20°C to prevent any of bacteria activity such as degradation of plant dry matter, breaking down lipids, degradation and decomposition of fatty acid of the sample. The sample used the experiment is raw without other dilution or modification except for experiment to determine the effect of pH. Table 1 presents the main characteristic of POME sample.

Table 1
Main characteristic of POME sample

Parameter	Concentration
Biochemical oxygen demand (BOD)	15600 ± 100
Chemical oxygen demand (COD)	25500 ± 100
pH	4.6 ± 0.1
Total carbohydrate	10000 ± 100
Total nitrogen	800 ± 50
Ammonium-nitrogen	20 ± 10
Total phosphorus	90 ± 1
Phosphorus	14 ± 1
Oil and grease	2000 ± 50
Total solid	20000 ± 300
Suspended solid(SS)	12300 ± 200
Total volatile solid	17500 ± 200
Conductivity/ $\mu\text{S} \cdot \text{cm}^{-1}$	158 ± 4

Note: All values are in $\text{mg} \cdot \text{L}^{-1}$ except pH and conductivity.

2.2. Experimental setup and analysis

Electrocoagulation tests were carried out in batch-scale that are shown in Fig. 1. The criteria of electrode design for electrochemical cell have successfully been determined by selecting 4 pieces of steel wool in vertical electrode orientation with monopolar series arrangement which were dipped into a 1000 ml beaker (served as a reactor) that can hold 700 ml of POME sample. The criteria of electrode design were selected due to the highest performance from the previous study [25]. The bottom of the reactor was allowed for easy stirring to maintain the homogeneity of the sample by using a stirrer (Brand: IKA, EUROSTAR power control visc, P1) at $80 \text{ r} \cdot \text{min}^{-1}$. The current intensity was controlled by a precision digital direct current power supply, DC Power Supply (EDU-LABS TPR-3030D; $30 \text{ V}/30 \text{ A}$). A DR 5000 spectrophotometer (HACH) was used to measure COD using the 8000 and 10212 methods, US EPA. A Sension6 DO meter (HACH) was used to measure dissolve oxygen (DO) for a 5-day BOD test using the 5210 B method, APHA. The DR 5000 spectrophotometer (HACH) was used to measure SS using the 8006 photometric method. A field emission scanning electron microscope with energy dispersive X-ray (FESEM-EDX, JEOL; JSM-7800F, USA) was used to analyse the morphology and identify the element of floc sample.

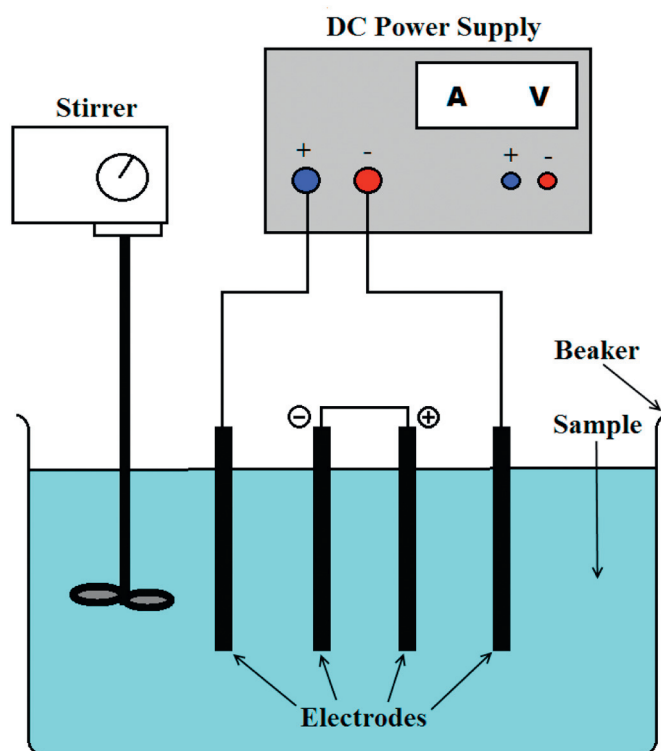


Fig. 1. Schematic diagram of the experimental setup.

2.3. Procedure to determine the effect of operating parameters

All experiments were conducted in batches and triplicates. At the end of each experimental run, the sample was transferred into a glass vial and kept undisturbed for at least 10 min in order to allow the flocs that formed during the electrocoagulation process to settle down. After that, the supernatant sample was collected to perform the analysis. These experiments have been carried out to determine the effect of operating parameters such as electrolysis/electrocoagulation time, current intensity, wastewater initial pH and inter-electrode distance on the percentage of COD, BOD, and SS removals. These experiments were run by using OFAT study in which one of the operating

parameters was varied, while other parameters were constant except for electrolysis time. The electrolysis time was conducted for 60 min for current intensity, wastewater initial pH and inter-electrode distance experiments to give a comprehensive overview of the results.

2.3.1. Procedure to determine the effect of electrolysis time

The electrolysis was operated in 120 min, while the other operating parameters such as current intensity, inter-electrode distance and initial pH were kept constant at 10 A, 15 mm and 4.6 (raw POME pH) respectively.

2.3.2. Procedure to determine the effect of current intensity

Six different amounts of current intensities such as 1 A, 5 A, 10 A, 15 A, 20 A and 25 A were applied. The sample was taken every 5 min of time interval in 60 min for analysis. The pH of the raw sample has not been altered and the inter-electrode distance was constant at 20 mm. These experiments were done in order to observe the practical influence of applied current on the electrocoagulation process and to demonstrate the difference between low and high current intensity on the treatment.

2.3.3. Procedure to determine the effect of inter-electrode distance

The experiment was carried out for 60 min with 5 min of time interval by applying 15 A of current intensity. Seven different inter-electrode distances were operated which were 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, 30 mm and 35 mm. This study was done to find out whether the treatment is efficient in low or high electrode distance.

2.3.4. Procedure to determine the effect of pH

The pH of the solution was altered using HCl and NaOH. The experiment was carried out for 60 min with 10 min of time interval by applying 15 A of current intensity at 20 mm of inter-electrode distance. Eight experiments were operated with different initial pH values which were 2, 3, 4, 5, 6, 7, 8 and 9. It was done to determine the optimal point of pH value that gives the best effect on treatment.

2.3.5. Procedure to find the effect of optimum operating parameters

The optimum point for every operating parameter from OFAT study was applied in one experiment to find the effect on POME treatment. The floc obtained from the study was analysed by using FESEM–EDX to determine the floc morphology and elemental identification.

3. Results and Discussions

3.1. Effect of electrolysis time

The variation of COD, BOD and SS removals with treatment time was exhibited in three distinct zones as depicted in Fig. 2. From the figure, it has been observed that in the first 40 min (Zone I), the treatment efficiencies for COD, BOD and SS removals were highly achieved at 74%, 73% and 77% respectively with the rates of removals of $472 \text{ mg COD} \cdot \text{min}^{-1}$, $285 \text{ mg BOD} \cdot \text{min}^{-1}$, and $237 \text{ mg SS} \cdot \text{min}^{-1}$. The rapid and high treatment occurred due to the fact that the amount of coagulants produced into the solution increased when the electrocoagulation time increased which is in accordance with Faraday's law. According to Faraday's law (Eq. (1)), the amount of Fe^{2+} ions released from anode depends on electrolysis time and current intensity.

$$m = itM/nF \quad (1)$$

where m , mass of iron dissolution (g); i , current density (A); t , time (s); M , molecular weight of Fe ($M = 56$); n , number of electrons involved in the oxidation reaction ($n = 2$); F , Faraday's constant, $96\,500 \text{ C} \cdot \text{mol}^{-1}$.

These removals corresponded to the critical generation of metal ions, which in turn, rapidly formed floc and resulted in high pollutant removal. Moreover, in the first 40 min, there are still plenty of contaminants that needed to be treated which turn the rates of removals become high.

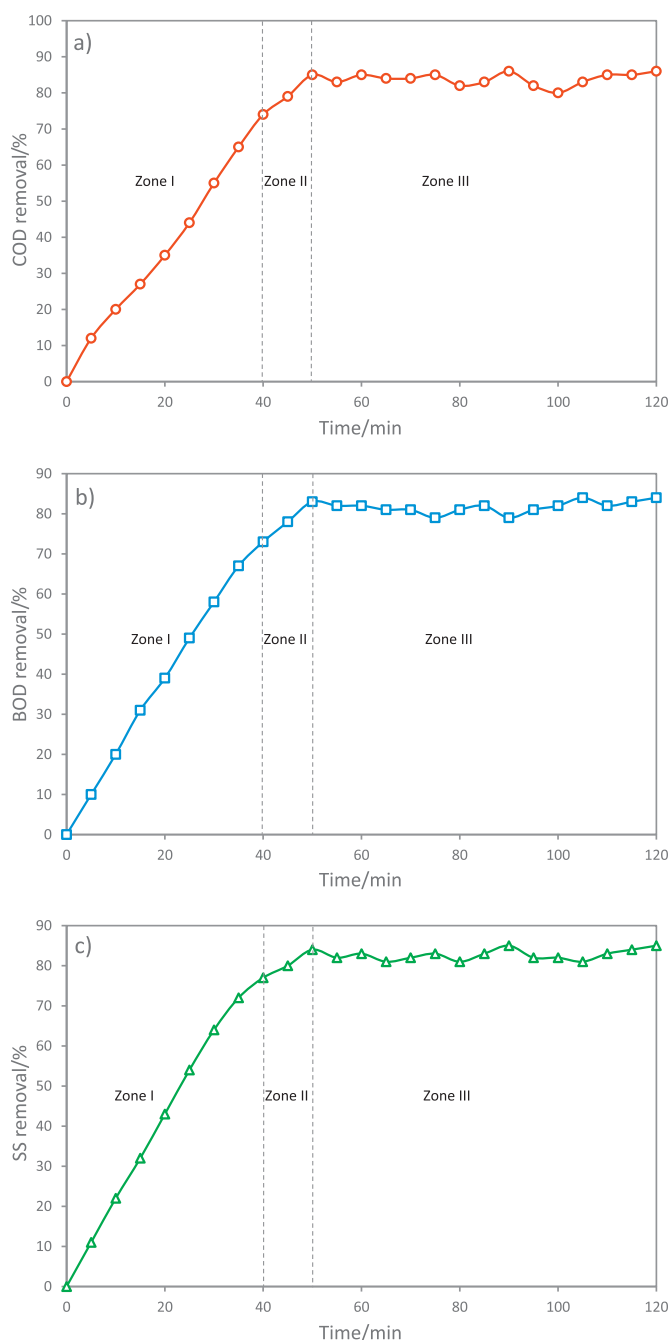


Fig. 2. Effect of electrolysis time on (a) COD removal, (b) BOD removal and (c) SS removals.

When the treatment entering Zone II that is from 40 min to 50 min the COD, BOD and SS removal rates at 50 min were found to slow down as $281 \text{ mg COD} \cdot \text{min}^{-1}$, $156 \text{ mg BOD} \cdot \text{min}^{-1}$ and $86 \text{ mg SS} \cdot \text{min}^{-1}$, respectively. The removal percentage of the same was calculated as 85%, 83%, and 84%, respectively. The rate of removals slowed down because of the electrode passivation occurrence. Holt *et al.* [26] stated that electrode passivation happens when the electrolysis process was operated in a long period of time and this is recognized as detrimental to the electrocoagulation performance. Electrode passivation will also depend on the electrode material used. While, the treatment in Zone III which is from 50 min to 120 min, the addition of metal ions and coagulant by the electrocoagulation process has no longer given much effect on the treatment. As can be seen from the figure, the treatment efficiencies for COD, BOD and SS were achieved at 86%, 84% and 85%, respectively and the removal pattern during this period fluctuated. The rates of removals

in this zone were found to be $4 \text{ mg COD} \cdot \text{min}^{-1}$, $2 \text{ mg BOD} \cdot \text{min}^{-1}$ and $2 \text{ mg SS} \cdot \text{min}^{-1}$ which could be considered as insignificant. From the overall observation, 50 min is chosen as the best electrolysis time due to the highest removal efficiencies of COD, BOD and SS and has been selected to be used in the effect of optimum parameters study. While 60 min of electrolysis time was applied to all effect of operating parameters experiments in this study to clearly observe their effects.

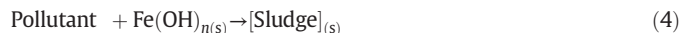
3.2. Effect of current intensity

In the electrocoagulation process, the most important parameter for controlling the coagulant dosing rate and reaction rate into the medium sample is current intensity. Therefore a few experiments have been conducted to determine the effect of current intensity on the treatment of POME. Fig. 3 shows the relationship between removal efficiencies of COD, BOD, SS and electrolysis time for the current intensity of 1 A, 5 A, 10 A, 15 A, 20 A and 25 A. From the figure, it was found that by applying 1 A, 5 A, 10 A, 15 A, 20 A and 25 A of current intensities, the processes were able to remove 45%, 59%, 78%, 83%, 92% and 90% of COD; 46%, 59%, 74%, 85%, 91% and 92% of BOD; and 42%, 58%, 76%, 84%, 94% and 93% of SS respectively in 60 min of the process. These increments indicate that the percentage of COD, BOD and SS was increased with the increase of current intensity. This could be attributed to the fact of applied current intensity in which the anodic dissolution for steel wool was initiated and created hydroxo-cationic complexes or iron hydroxide, resulting in COD, BOD and SS removals. Once the iron hydroxide is produced, it removes pollutants by surface complexation and electrostatic attraction [27]. In surface complexation, it is assumed that the pollutant can act as a ligand to bind a hydrous iron moiety with precipitation and adsorption mechanism [28].

Coagulation and precipitation:



Adsorption:



According to Faraday's law, the applied current intensity determines the production rate of a metal cation (Fe^{2+} and Fe^{3+}) released to the solution by the cathode. Moreover, the iron hydroxide formed during reaction contains apparent positive and negative charges which attract opposite charged polluting species as charge neutralization which could contribute to reduce the stability of suspended entities and then become flocs. Furthermore, the metal cations could also precipitate in the form of polymerized amorphous hydroxides that promote the pollution removal through a non-specific mechanism which is usually denoted as sweep coagulation or sweep flocculation [29]. As these sweep flocs exhibit a large interfacial area, they could favor first the rapid adsorption of soluble and insoluble pollutants, and colloids or suspended solids might also be simply embedded into the growing precipitate [30]. However, the application of 10 A and above shows a significant removal compared to those below 10 A. These indicate that more tendency of sweep coagulation occurs when the higher current intensity was applied, rather than adsorption and charge neutralization. The mechanism of sweep coagulation is illustrated in Fig. 4. The sweep coagulation can happen when a relatively large amount of coagulants are added to the solution sample and form

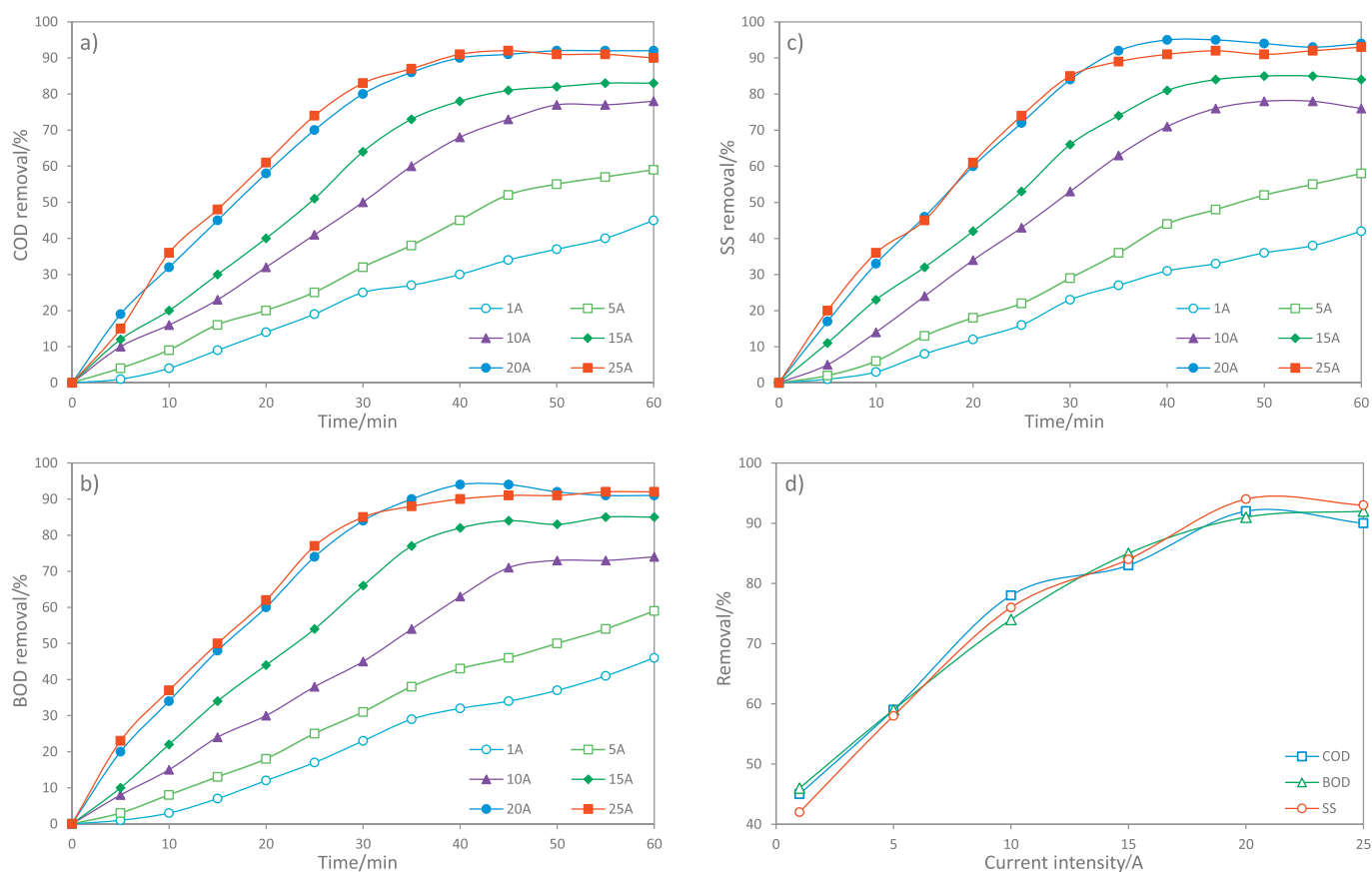


Fig. 3. Effect of current intensity on percentage of (a) COD removal, (b) BOD removal, (c) SS removal of raw POME in 60 min with 20 mm of inter-electrode distance and (d) percentage of COD, BOD and SS removal against current intensity at 60 min of electrocoagulation process.

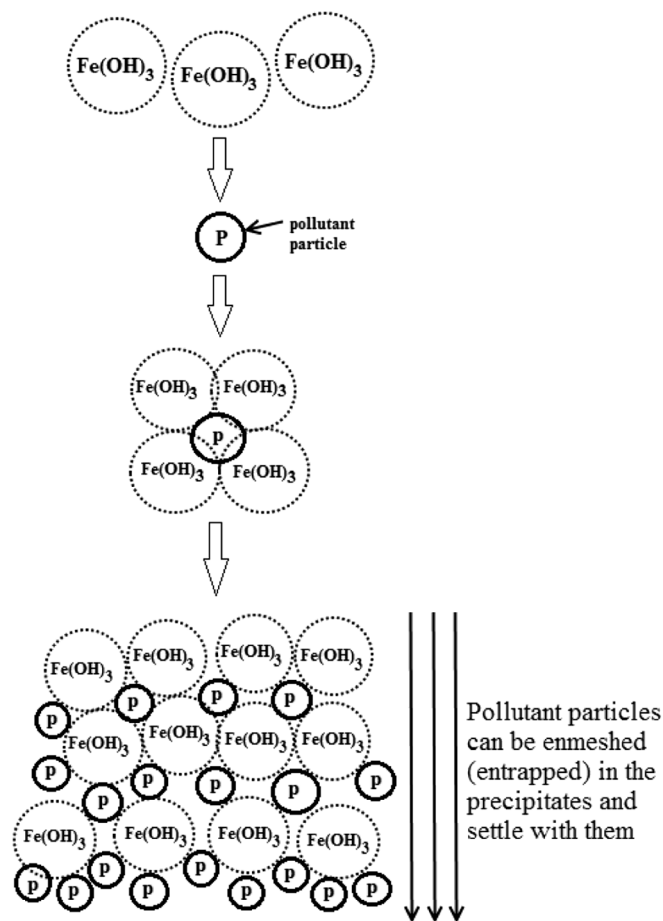
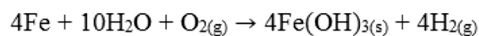


Fig. 4. Sweep coagulation mechanism in electrocoagulation process.

flocs and precipitates that can enmesh (entrap) more pollutants and settle with them. The produced floc is primarily responsible for the pollution abatement and hence the higher the dissolution of metal ion, the higher the removal efficiency [31].

In the electrocoagulation process, the gas bubble had a strong contribution to the treatment effectivity. The liberated H_2 gas bubble serves as an excellent floatation agent and carries the suspended particle to the surface [32]. Gas bubble generation rate increases and the bubble size decreases with increasing current intensity. An increase in the gas bubble density with a reduction in their size enhances the upward flux, resulting in higher pollutant removal by floatation [33]. The removal of pollutant by gas bubbles was showed in Fig. 5(a). Besides acting as a floatation agent, the gas bubble also served as an oxidizing agent towards the pollutant by a direct or indirect oxidation process. O_2 gas produced at anode was able to oxidize organic pollution [32]. When sufficient voltage is developed across the electrodes, direct oxidation takes place near the anode due to the release of electrons by the organic compounds in order to maintain the flow of current, whereas indirect oxidation occurs due to the strong oxidants that form during the reaction [34].

Although theoretically increasing the current intensity will increase pollutant removal, increasing the current intensity beyond 20 A did not show any significant improvement in the percentage of COD, BOD and SS removals. As explained, the rate of gas bubble production increases with the increase of current intensity, yet more gas bubble production also will somewhat decrease the specific area of the electrode which makes it vulnerable and did not perform on its full potential. This can be logically explained by finding that the performance of using 25 A of current intensity was not much different from the performance of

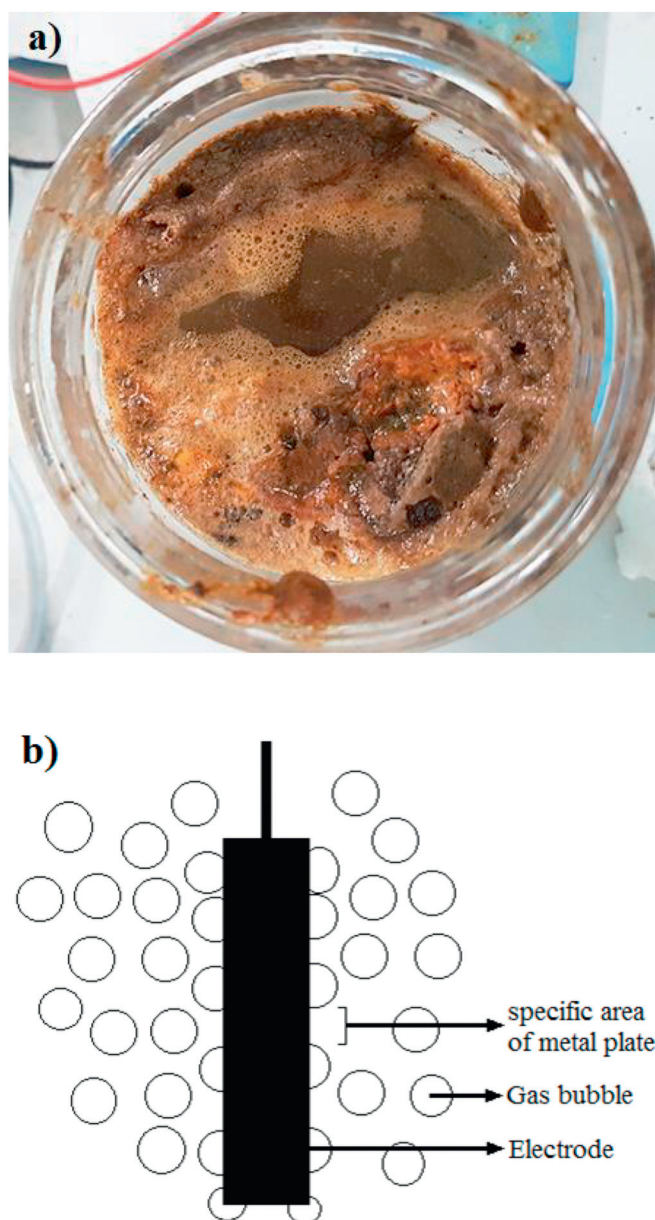


Fig. 5. Pollutant removal by gas bubble (a) after electrocoagulation process, (b) during electrocoagulation process.

using 20 A. This phenomenon is illustrated in Fig. 5(b). Among the current intensities applied in this experiment, 20 A was chosen as the best due to the highest treatment efficiency and has been selected to be used in the effect of optimum parameters study.

3.3. Effect of inter-electrode distance

The distance between anode and cathode is one of the parameters that influence the treatability of POME wastewater by the electrocoagulation process. Therefore an experiment had been made to determine the effect of inter-electrode distance on the treatment of POME. The removal efficiencies with all investigated inter-electrode distances were compared. Fig. 6(a), (b) and (c) shows the removal efficiencies of COD, BOD and SS with time for 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, 30 mm and 35 mm of inter-electrode distances. From the figure, it was found that increasing the inter-electrode distance more than 10 mm resulted in the decrease of the percentage of COD, BOD and SS removals. The gap

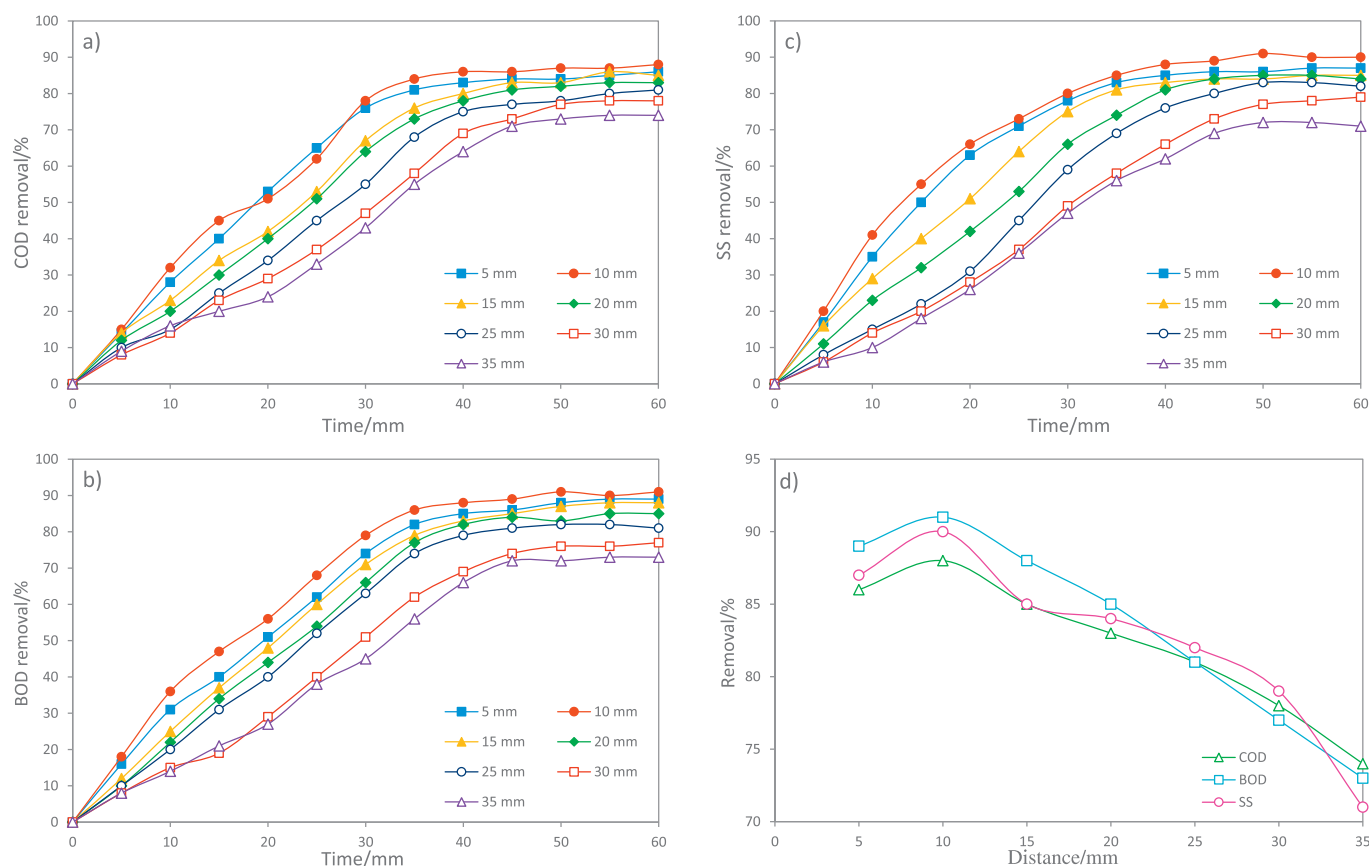


Fig. 6. Effect of inter-electrode distance on percentage of (a) COD removal, (b) BOD removal, (c) SS removal of raw POME in 60 min using 15 A and (d) percentage of COD, BOD and SS removal against inter-electrode distance at 60 min of electrocoagulation process.

between anodes and cathodes of 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, 30 mm and 35 mm could be able to remove 86%, 88%, 85%, 83%, 81%, 78% and 74% of COD; 89%, 91%, 88%, 85%, 81%, 77% and 73% of BOD; and 87%, 90%, 85%, 84%, 82%, 79% and 71% of SS respectively in 60 min of treatment. The decrease of treatment efficiency at inter-electrode distances of 15 mm and above was due to the weak molecule interactions with both oxidants and coagulants and this was in agreement with Naje *et al.* [35]. The interaction of oxidants and coagulants in the process was related to the conductivity of the sample substance. The disruption or resistance will adversely affect the interaction of oxidants and coagulants in the process. The solution resistance or IR-drop is proportional to the distance between the electrodes, current intensity, disproportional to surface area (A) of the cathode and specific conductivity of the solution [36]. In this case, since the current intensity, surface area of the cathode and the specific conductivity of the solution were constant, and the distances between anodes and cathodes were increased, therefore the solution resistance or IR-drop increased [37]. Hence, the effectiveness of the treatment could be improved by minimizing the distance between the electrodes which indirectly minimizes the IR-drop.

Even though the trend of the treatment efficiency seems to decrease with the increase of inter-electrode distances from 10 mm to 35 mm, the decreasing phenomena were also observed with the decrease of inter-electrode distance to 5 mm. The possible reason for this phenomenon was because the conductivity of POME is relatively high. Fadali *et al.* [38] stated that, if the wastewater conductivity is high, it is recommended to have a bigger space between electrodes. This could be explained by the fact that with the inter-electrode distance of 5 mm, the gaps between the anodes and cathodes were too close for easy solid and fluid transfer, resulting in accumulated solid particles and bubbles and obstructed between the anodes and cathodes. This

circumstance insulates the surface area of electrodes and caused a consequent higher electrical resistance [39].

On the other hand, increase in the treatment efficiency occurred at 10 mm of inter-electrode distance from 5 mm, this probably happened due to the electrostatic effect [40]. Electrostatic attraction is the attraction between atoms of opposite charge that holds the atoms together as ionic bonds. Any electrical charge created at the surrounding medium is called electric field. This electric field applies a force to any charged particle. Electrostatic force depends on the size of the structures and distance between electrodes. For that reason, in this particular case the further the distance, the slower the movement of ion. In this circumstance, it was a great opportunity to generate aggregate flakes which then these flakes are able to absorb more pollutants [40]. Overall, it can be concluded that 10 mm of inter-electrode distance is the most effective on the treatment and has been selected to be performed in the effect of optimum parameters study.

3.4. Effect of pH

It has been established that the initial pH has a considerable influence on the performance of the electrocoagulation process [27,37,41,42]. In order to examine its effect, the POME sample was adjusted to the desired pH by using sodium hydroxide (NaOH) and hydrochloric acid (HCl). It is proven that, the pH will modify the surface charge of particles and affect the speciation of iron species, thus it will have a significant influence on the process mechanism and consequently influence the removal of colloidal dispersed organics from the solution [27]. Since iron hydroxide is amphoteric, the pH became a sensitive factor for the formation of iron hydroxide flocs. Fig. 7(a), (b) and (c) shows the effect of pH on the treatment performance with time. It was found that 2, 3, 4, 5, 6, 7, 8 and 9 of pH

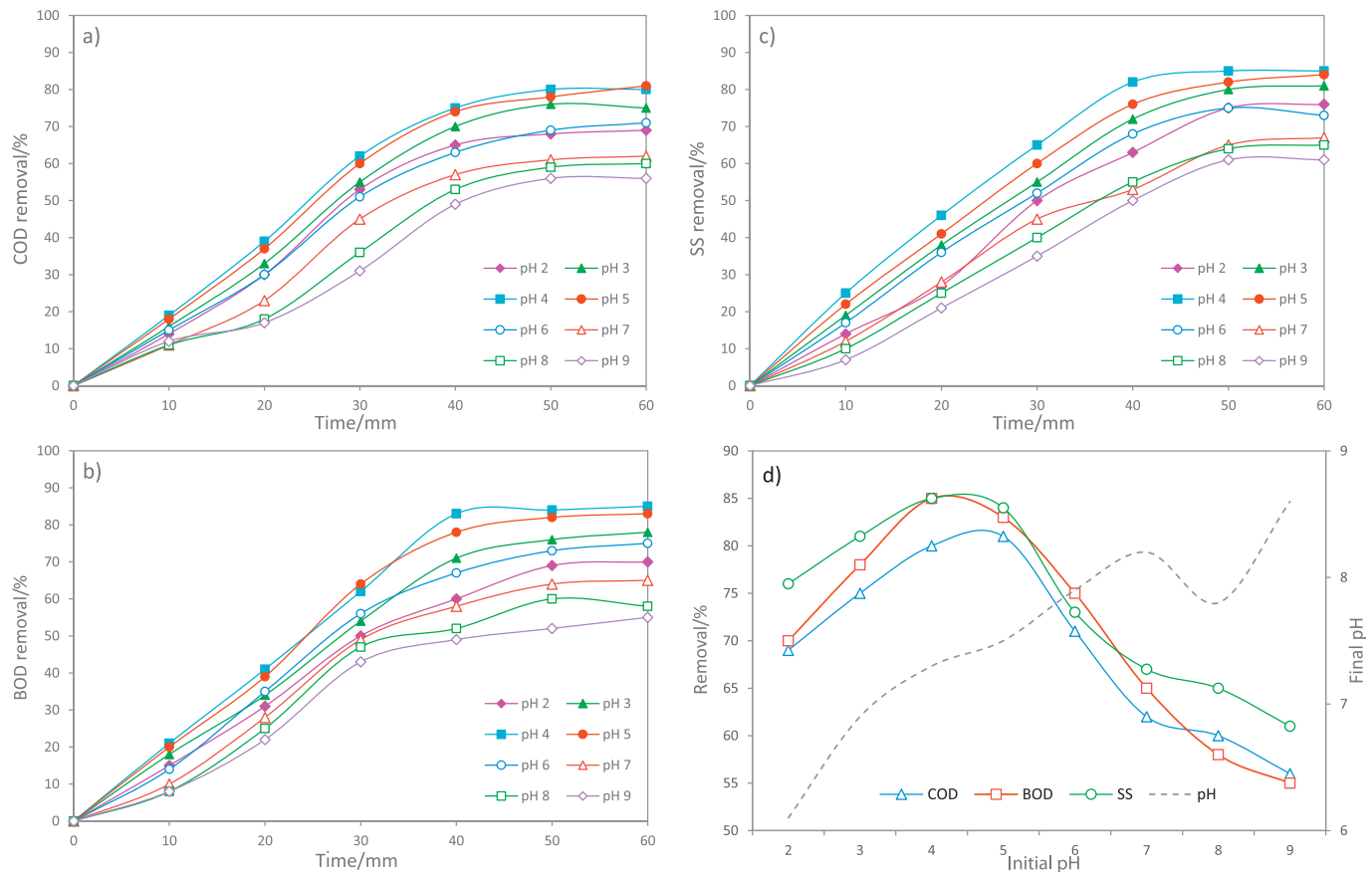


Fig. 7. Effect of initial pH of POME on percentage of (a) COD removal; (b) BOD removal; (c) SS removal in 60 min using 15 A of applied current intensity 20 mm of electrode distance; and (d) percentage of COD, BOD and SS removal and final pH against initial pH at 60 min of electrocoagulation process.

levels were able to treat 69%, 75%, 80%, 81%, 71%, 62%, 60% and 56% of COD; 70%, 78%, 85%, 83%, 75%, 65%, 58% and 55% of BOD; and 76%, 81%, 85%, 84%, 73%, 67%, 65% and 61% of SS, respectively in 60 min of treatment. This results showed that the high treatment efficiencies were attained in a relatively acidic medium (3–6 pH value), due to the electro-generation of Ferric ions. Ferric ions electro-generated from monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, namely, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^{+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}$, depending on pH range and these complex species have a pronounced tendency to polymerize at pH 3.5–7.0 [43]. Moreover, these compounds remain in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [44].

The effluent treated with iron electrodes as sacrificial anodes initially appeared as greenish and then turned yellow and turbid. This green and yellow color must have resulted from Fe^{2+} and Fe^{3+} ions generated during the electrocoagulation process. Fe^{2+} is the common ion generated *in situ* of electrolysis of iron electrode. It has the relatively high solubility at acidic or neutral conditions and can be oxidized easily into Fe^{3+} by dissolved oxygen in the water. This Fe^{3+} exists in yellow fine particles of $\text{Fe}(\text{OH})_3$ [42]. The oxidation of Fe^{2+} to Fe^{3+} is called rust. In the following Eqs. (6) to (11), a complete sketch of formation of green rust is reiterated [45]:

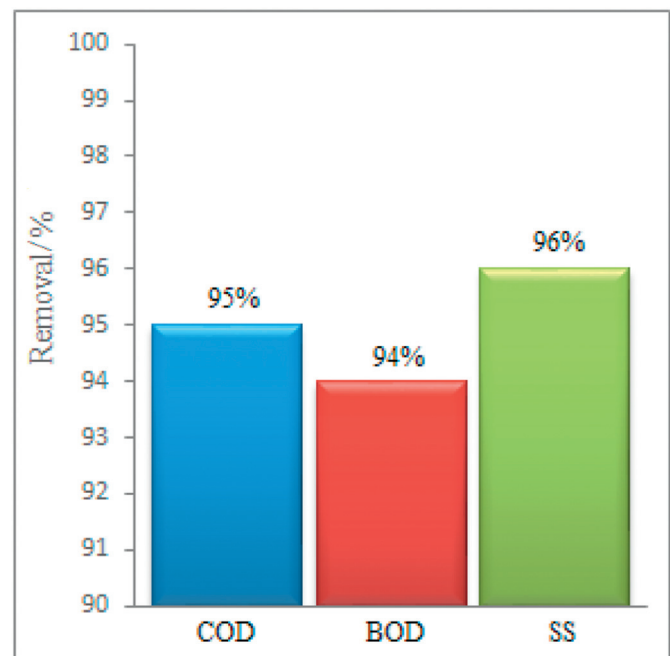
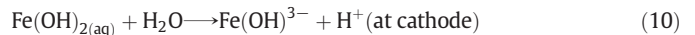
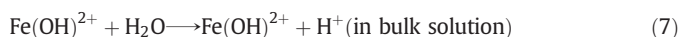
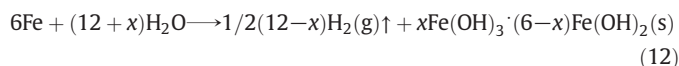


Fig. 8. Percentage of COD, BOD and SS removals after electrocoagulation process at optimum operating parameters.

In general, hydrogen gas and green rust are formed at the cathode as shown below.



According to Moreno *et al.* [45], if pH conditions are too acidic or alkaline for the bulk solution, the electrocoagulation process will not lead to green rust formation and the removal efficiencies of pollutants will be small, especially for amphoteric metals. These metal hydroxide flocs have a large surface area, which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from the aqueous medium by sedimentation or flotation [22]. The removal efficiency decreased due to the formation of soluble ion, $\text{Fe}(\text{OH})_4^-$ which is dominant at a high pH [46] and $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$, when pH is too low [47] which are unsuitable for floc formation.

As shown in Fig. 7(d), a pH increase occurs in every experimental run. The initial pH of 2, 3, 4, 5, 6 and 7 abruptly increased to the final pH of 6.1, 6.9, 7.3, 7.5, 7.9 and 8.2 respectively in 60 min of the process. This situation is described by Vik *et al.* [48], who stated that the increase of pH was due to the hydrogen evolution that happened at cathode. However, this statement has been disputed by Chen *et al.* [49], who ascribed that the increasing pH was actually due to the release of CO_2 from wastewater owing to H_2 bubble disturbance. Indeed, CO_2 is oversaturated in wastewater at low pH and can be released during H_2 evolution which consequently increases the pH value. Moreover, some anions such as NO_3^- , HCO_3^- , SO_4^{2-} and Cl^- that are present in wastewater can as well replace the hydroxide in $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ and release OH^- which is also one of the factors of pH increase. On the other hand, the initial pH of 8 and 9 showed a slight decrease to the final pH of 7.8 and 8.6 respectively. This is because at basic condition, any metal cation such as Ca^{2+} and Mg^{2+} that is present in wastewater could co-precipitate with $\text{Fe}(\text{OH})_2$ in the form of hydroxide and result in a pH decrease. The optimum initial pH range was 4 which resulted in a

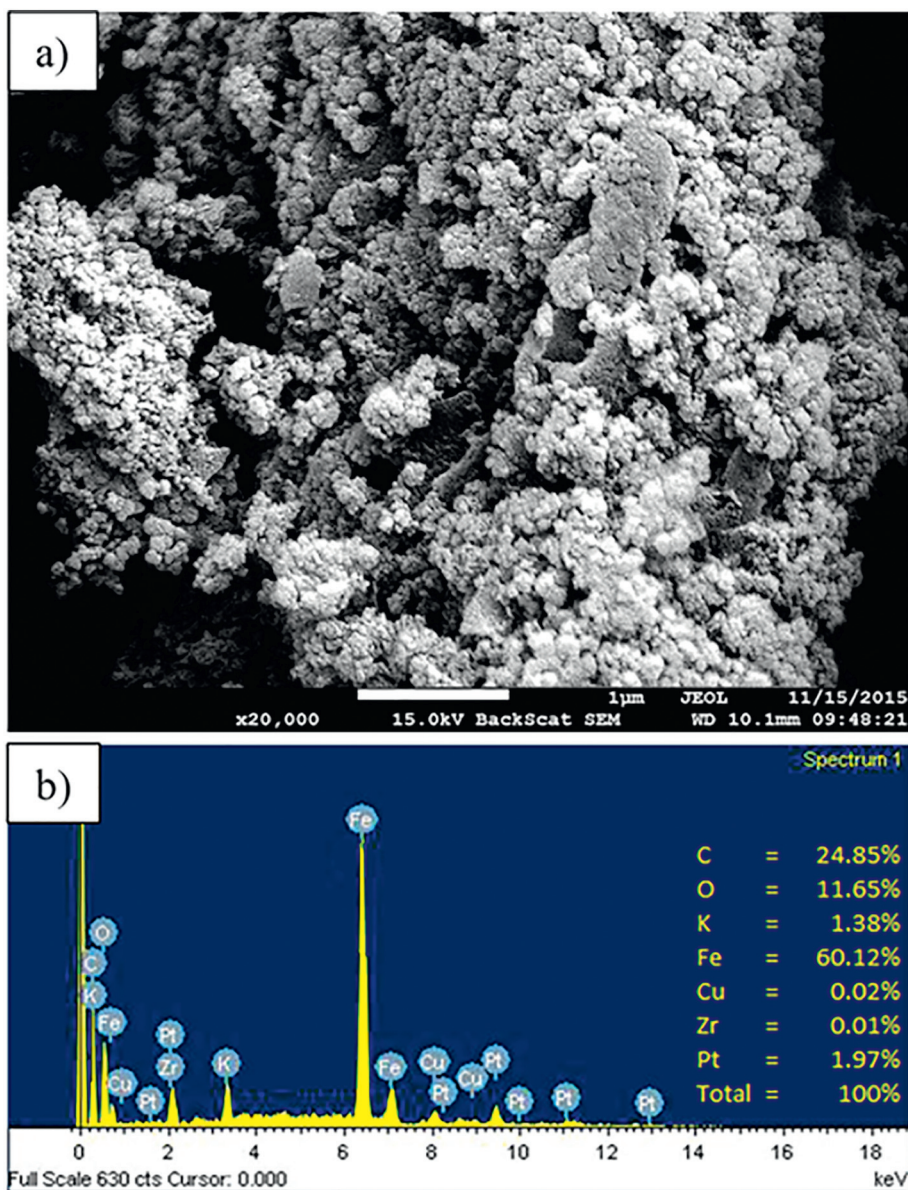


Fig. 9. Analysis of POME floc after electrocoagulation process at optimum operating parameters by using (a) FESEM (20000× magnification); and (b) EDX.

pH value of 7.3 at the end of the process that is nearly neutral and was suitable for discharge.

3.5. Effect of optimum operating parameters

The optimum parameters from OFAT study were found to be 50 min for electrolysis time, 20 A for current intensity, 10 mm for inter-electrode distance and 4 for initial pH. An experiment to determine this effect was conducted and the result was shown in Fig. 8. The electrocoagulation process by applying the optimum operating parameters has removed COD, BOD and SS up to 95%, 94% and 96% respectively. A FESEM analysis was performed to evaluate the structural features of the floc that was generated during the electrocoagulation process. Fig. 9(a) shows the FESEM image of the floc. From the figure, the agglomeration of coagulant–pollutant particles can be seen clearly in a single floc. It looks like the coagulant was more than 10 times smaller than 1 μm and seems as a bunch of coagulants were trying to bind and wrap the pollutant particle. Meanwhile, Fig. 9(b) shows the elemental analysis performed by EDX. The peaks indicate that carbon, oxygen, potassium, iron, copper, zirconium and platinum are present in the floc. This analysis confirms that once the colloidal matter is destabilized, it can be separated from the wastewater.

4. Conclusions

In this study, the treatment of POME by using the electrocoagulation process with high current intensity was investigated. Operating parameters such as electrolysis time, current intensity, inter-electrode distance and initial pH have a great influence on the removals of COD, BOD and SS. The experimental results from electrolysis time study have shown that the removal rates were high in the first 40 min and decreased afterward. From the current intensity study, an application of higher current resulted in higher removal. Gas bubbles that generated along with the electrocoagulation process also helped to remove the pollutant by floatation. However, the more gas bubbles produced resulted in lessening the active specific area of the electrode and will cause the treatment performance to reduce. In inter-electrode distance study, the removal efficiency decreased when the inter-electrode distance was either higher or lower than 10 mm. This was due to the increase of solution resistance and the decrease of active surface area of the electrodes because of accumulation of solid particles. In initial pH study, it was found that high removal efficiency was achieved in slightly acidic POME sample rather than in neutral or basic condition. An electrocoagulation process by using the optimum operating parameters was able to remove COD, BOD and SS up to 95%, 94% and 96% respectively. It can be concluded from this study that highly removals of COD, BOD and SS can be achieved by using high current intensity in the electrocoagulation process.

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