Palm oil has become the most popular vegetable oil in the world and is extensively used by both the food and cosmetics industries. Industrial palm oil processing is responsible for causing serious environmental threats that are associated with health risks. Palm oil mill effluent (POME) is well known for the extensive and generally irreversible damage it causes to the natural environment, including deforestation, habitat destruction, and a significant increase in greenhouse gases. Worldwide, 45 million metric tons of palm oil was produced in 2009 [1]. Approximately 1.5 m³ of water is typically used to process one ton of fresh fruit bunches (FFB). For every ton of palm oil produced, approximately 2.5 m³ of POME is generated [2].

Introduction

Palm oil has become the most popular vegetable oil in the world and is extensively used by both the food and cosmetics industries. Industrial palm oil processing is responsible for causing serious environmental threats that are associated with health risks. Palm oil mill effluent (POME) is well known for the extensive and generally irreversible damage it causes to the natural environment, including deforestation, habitat destruction, and a significant increase in greenhouse gases. Worldwide, 45 million metric tons of palm oil was produced in 2009 [1]. Approximately 1.5 m³ of water is typically used to process one ton of fresh fruit bunches (FFB). For every ton of palm oil produced, approximately 2.5 m³ of POME is generated [2].
can be described as a colloidal suspension of 95-96% water, 0.6-0.7% oil, and 4-5% total solids, including 2-4% suspended solids [3].

Open ponding systems have been employed by the majority of palm oil mills to treat POME and maintain waste disposal standards. A long retention time and large treatment area are the major weaknesses of ponding systems [4]. Currently, a combination of open lagoon technology and land application is used for the cost-effective reduction of the polluting nature of POME; additionally, this combined technique re-utilizes potential ingredients for cultivation purposes [5, 6]. Recently, different conventional techniques, including anaerobic digestion, anaerobic digestion with methane tapping, aerobic lagooning, conventional biological waste treatment, extended aerobic processes and bio-reactor systems, are also used to treat POME [2]. High operational costs, long retention times and a vast pond area are the drawbacks of the prevailing conventional methods for pre-treating POME.

Electrocoagulation (EC) is an alternative wastewater treatment that dissolves metal anodes using electricity to provide the active cations required for coagulation without increasing the salinity of the water [7]. Electrocoagulation has the capability to remove a large range of pollutants under a variety of conditions, including suspended solids, metals, petroleum products, color from dye solutions, and aquatic humus, and can be used for the de-fluoridation of water [7]. Electrocoagulation is generally known for its ease of operation and reduced production of sludge [8]. Aluminum (Al) and iron (Fe) are suitable electrode materials for the treatment using electrocoagulation [9]. It has been reported that the removal efficiency of electrocoagulation using Al electrodes is higher than that of Fe electrodes [10].

Electrocoagulation is an electrochemical technique in which iron or aluminum anodes release active coagulant ions into solution. The reactions at the anode (Al) are as follows:

\[
\text{Al} - 3e^+ \rightarrow \text{Al}^{3+}
\]

Alkaline condition:

\[
\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 + 3\text{H}^+
\]

Acidic condition:

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+
\]

The reaction at the cathode is as follows:

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{O}_2 + 2\text{OH}^-
\]

The electrolytic dissociation of water by EC generates hydroxide ions, which are known as one of the most reactive aqueous radicals, and it oxidizes organic compounds because of its high affinity [11]. The generated hydroxides or polyhydroxides have strong attractions toward dispersed particles as well as counter ions, which causes coagulation. The gases that evolve at the electrodes are also helpful in removing the suspended solids in an upward direction [12].

Response surface methodology (RSM) is a combination of mathematical and statistical techniques used for designing experiments, building models, evaluating the effects of influencing factors, and probing the optimum conditions for a specific response [13].

A number of factors can influence the efficiency of EC in treating wastewater. The important factors include the applied voltage, the retention time, the addition of supporting electrolytes, and pH. In EC, pH is a factor that varies and cannot be fixed because of the formation of metal hydroxyl ions. As a result of electrolytic dissociation, the metal ions can either react directly with an organic compound or form polymeric metal hydroxyl complexes, which can remove pollutants by adsorption and result in charge neutralization. In comparison with water, the dynamic response of pH during EC using POME has been studied in detail [14]. Three variables, including applied voltage, retention time, and the addition of sodium chloride, were selected to be optimized to treat POME and produce hydrogen using EC. Sodium chloride (NaCl) was considered as a factor to be optimized because it has been observed to be a supporting electrolyte [15].

The objective of this study was to demonstrate a method of POME treatment to reduce polluting factors and produce advantageous hydrogen gas using a small land area and a low retention time compared to the prevailing conventional systems. The RSM application was applied to establish a set of optimized values for the main influencing parameters to achieve optimal multi-factor operating conditions for the electrocoagulation of palm oil mill effluent.

Methodology

Materials and Equipment

POME was obtained from Sime Darby Plantation, Sendirian Berhad, East Mill, located on Carey Island, Malaysia, which has employed pond systems for treating POME prior to disposal. The effluent from post-aeration pond and pre-sedimentation pond were used as the experimental samples. NaCl was used to increase the conductivity of the POME and to study the effects of NaCl on the efficiency of electrocoagulation. The high-range COD reagent “Hanna Instruments USA (HI 93754C-2)” was used to determine the COD of the effluent prior to and after treatment.

A reactor with a capacity of 20 L was used for electrocoagulation and operated using a rectifier. The power supply used a working electric current range of 0-60 amps, a voltage of 0-15 volts, an ampere meter with a digital range of 0-20 amperes, and a voltmeter with a digital working range of 0-300 volts DC. Twelve aluminum plates, which were cut from a 3 mm thick commercial grade sheet (95-99%), were arranged in connection with a low voltage power supply. Of the twelve total plates, six alternate plates were connected to the positive pole of the battery to act as the anode and the other six were connected to the negative pole to act as the cathode. A 3 cm inter-electrode distance was maintained between the plates. The experimental setup, including the electrocoagulation tank equipped with electrodes, is shown in Fig. 1. Three variables, including the voltage supplied to conduct the electricity, the retention time, and NaCl as a supporting electrolyte, were optimized.
using the Box-Behnken design for the efficient removal of pollutants and the enhanced hydrogen production from POME during EC. The electrode surface was mechanically rubbed with 400 grade abrasive paper before each run. A closed container (Fig. 1) was used to perform electrocoagulation; the gas was collected using gas bags and a peristaltic pump at a rate of 1.8×10⁻³ m³/hr at room temperature. The cumulative hydrogen gas, the electrical energy supplied to the system and the amount of produced hydrogen gas were calculated using different equations, which have been described in the literature [14].

Analysis

The concentration and composition of the hydrogen gas were analyzed using a gas chromatography instrument (SRI 8610C, USA) equipped with a helium ionization detector and a packed column. The temperatures of the oven, injector, and detector were 50°C, 100°C, and 200°C, respectively. The concentrations of heavy metals (Ca, Mg, and Fe) were measured using an atomic absorption spectrometer (AAS) (AAAnalyst 800 Perkin Elmer Instrument model). A turbidity meter (Portable Microprocessor Turbidity Meter, “Hanna Instruments”) was used to measure the turbidity of the samples prior to and after electrocoagulation.

Turbidity, COD, and heavy metal concentration were taken as variables of this study. Removal efficiency (%Y) was calculated using the following equation:

\[
\%Y = \frac{Y_o - Y}{Y_o} \times 100\%
\]

...where \(Y_o\) and \(Y\) represent the initial and final values of turbidity, COD, or concentration of heavy metals, respectively.

Experimental Design

Minitab software was used to create a set of designed experiments. For the response surface method (RSM), the Box-Behnken design was used to study the effects of three variables on the efficiency of electrocoagulation: NaCl as an additive to enhance conductance, the voltage supplied and the residence time.

The experimental data were fitted to a second-order polynomial model, and the regression coefficients were obtained. The generalized second-order polynomial model used in the response \(Y\) surface analysis is shown below:

\[
Y_i = \beta_0 + \sum_{1}^{3} \beta_i X_i + \sum_{1}^{3} \beta_{ii} X_i^2 + \sum_{1}^{3} \beta_{ij} X_i X_j
\]

...where \(\beta_0, \beta_i, \beta_{ii}\) and \(\beta_{ij}\) are the regression coefficients for the intercept, linear, quadratic, and interaction terms, respectively, and \(X_i\) and \(X_j\) are the independent variables. Analysis of variance (ANOVA) was used to examine the model fitness level and was expressed in terms of \(R^2\). Additionally, the optimum values of each factor were obtained by a Minitab simulation using the optimization tool.

Results and Discussion

Removal of COD

The quadratic model regression shown in Equation 3.1 (Table 1) is well fitted with a high \(R^2\) value (87.8%). A p-value greater than 0.05 indicates that there is no dominant effect for the linear, square, or interaction factors. The contour plots of COD removal, which are based on three factors, including \(A = \text{NaCl added (g/L)}\), \(B = \text{voltage supplied (V)}\), and \(C = \text{retention time (hours)}\), are shown in Fig. 2. It is clear that the removal of COD is directly proportional to the retention time. The supplied voltage induced the current transfer to the EC system according to Ohm’s Law. NaCl increases the conductivity of wastewater by increasing the number of electrons transferred to the anode and the number of metal cations formed [16], which may enhance the flocculation/coagulation of suspended solids. In this study, NaCl was not observed to be a significant factor for the removal of COD. This result can be explained on the basis of the generation of products from the electrolytic dissociation of NaCl into Na⁺ and Cl⁻, which may lead to the production of soluble sodium salts. Because of the production of these soluble salts, NaCl may contribute to the formation of COD. Electrolytic dissolution at the anode and water
reduction at the cathode leads to the formation of complex hydroxides, which are used as flocculating/coagulating species for the suspended solids to reduce the COD [17]. Under optimized conditions, electrocoagulation was able to remove 42.94% of the COD. The efficiency of EC depends on the nature and composition of wastewater. Chavalparit and Ongwandee reported the removal of up to 55.43% of COD from biodiesel using an applied voltage of 18.2 V and a reaction time of 23.5 min [18]. Using EC with a 10 min operating time, Can et al. reported the removal of 50% of COD from textile wastewater [19]. Agustin et al. [15] reported a 30% removal of COD with maximum reduction in the turbidity of POME using electrocoagulation [15].

Removal of Turbidity

Equation 3.2 (Table 1) is the regression model for turbidity removal; the quadratic model was fitted and the $R^2$ value was high (93.1%). The small $p$-values for the linear terms ($p = 0.02$) suggested that the model is more linear in the RSM. The interaction between factors and the square terms of each factor were less important. The contour plots of turbidity (%) removal, which were based on three factors, including $A = \text{NaCl added (g/L)}$, $B = \text{voltage supplied (V)}$, and $C = \text{retention time (hours)}$, are shown in Fig. 3. Turbidity and COD have a straight relationship because the removal of COD is always associated with a lower level of turbidity. Similarly, the removal of COD and turbidity increases as the retention time, the concentration of NaCl, and the voltage supplied increase (Fig. 3). Under optimized conditions, electrocoagulation was able to remove 83.16% of the turbidity at 83.16%. The removal of turbidity was relatively dependent on the voltage supplied and the retention time. The addition of NaCl reduced the voltage required to achieve the same treatment efficiency [20]. The mechanism for the removal of pollutants from POME using EC generally involves the electrolytic dissociation of water to produce a reactive species (OH$^-$), which reacts with the anode (Al$^{3+}$) to generate Al(OH)$_3$XH$_2$O. This complex hydroxide acts as a flocculating/coagulating agent for the suspended solids. The gases produced at the electrodes are also helpful for removing the lighter particles in an upward direction.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>$\text{COD (%) } = -2.1390A+15.9125B+17.1063C-0.2118A^2+3.2417B-1.4183C-0.0463AB+0.9338AC+0.6350BC-12.3492$</td>
</tr>
<tr>
<td>3.2</td>
<td>$\text{turbidity (%) } = 13.7591A+38.4113B+33.2125C-0.3295A^2-2.5813B-1.7872C-1.0494AB+0.9375AC-1.3950BC-131.08$</td>
</tr>
<tr>
<td>3.3</td>
<td>$\text{Fe (%) } = -3.5879A+17.1400B+1.2863C+0.2998A^2+4.422B-0.0307C^2+1.1831AB-0.0659AC+0.0963BC+12.4104$</td>
</tr>
<tr>
<td>3.4</td>
<td>$\text{Mg (%) } = -1.0440A-27.1150B-11.2625C-0.0990A^2+2.3654B+0.0689C^2-0.1906AB+0.6234AC+3.7413BC+73.1921$</td>
</tr>
<tr>
<td>3.5</td>
<td>$\text{Ca (%) } = 5.5882A+18.6925B+18.6925C+9.2094C+0.2868A^2-0.9171B^2+0.6386C^2-0.5988AB+0.3178AC+1.3775BC-78.1229$</td>
</tr>
<tr>
<td>3.6</td>
<td>$\text{H}_2 (%) = 0.8699A+2.8213B+10.6700C-0.1602A^2+0.6671B^2-0.7814C^2+0.2181AB+0.0088AC-0.0050BC-28.9896$</td>
</tr>
</tbody>
</table>
Removal of Metals

Equation 3.3 (Table 1) is the regression model for Fe removal; the quadratic model was fitted and the $R^2$ value was high (94.7%). The high p-values indicate that there are no dominant effects for the linear, square, and interactive terms with regard to Fe removal. Using electrocoagulation, the contour plots of Fe (%) removal are shown in Fig. 4. The results revealed that the voltage supplied is the major factor influencing Fe removal efficiency. The highest removal efficiency can be obtained with a combination of high voltage and high NaCl concentration. Compared to COD and turbidity, NaCl concentration exerted a greater effect on the removal of Fe. This increased effect may be attributable to the Cl⁻ produced as a result of EC causing the production of FeCl₃, which is a well-known flocculant for water treatment [21]. The initial concentration of Fe in the raw POME was 47 mg/L, which is much higher than the acceptable disposal standards in Malaysia (http://www.water-treatment.com.cn/resources/discharge-standards/malaysia.htm). The most highly efficient removal of Fe obtained in this study was 29.36%, which was
achieved with a current density of 3.29 mA/cm². However, Merzouka et al. [20] reported 90-99% Fe removal using a high current density of 11.55 mA/cm². It has also been reported that the removal of Fe can be improved by increasing the voltage supplied [22].

Equation 3.4 (Table 1) is the regression model for Mg removal; the quadratic model regression was well fitted and the R² value was high (91.1%). The high p-values indicate that there are no dominant effects for the linear, square, or interaction factors. The effects of NaCl concentration, retention time, and voltage supplied are shown in Fig. 5. The voltage supplied and retention time had greater effects on Mg removal. A maximum of 30-40% of magnesium was removed with the combination of high voltage and high retention time. The initial concentration of Mg was higher in the raw POME compared to the other metals/non-metals, excluding potassium. Therefore, the exhibited removal efficiency was not as high as those of other metals/non-metals [20]. The electrocoagulation technique is usually considered an effective strategy to remove the Mg from hard water; however, time factor and electrical volt difference have a substantial impact on removal efficiency [23]. NaCl

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**Contour Plots of %Magnesium**

![Figure 5](image)

*Fig. 5. Contour plot for the removal of Mg (%) from palm oil mill effluent using electrocoagulation.*

**Contour Plots of % Calcium**

![Figure 6](image)

*Fig. 6. Contour plot for the removal of Ca (%) from palm oil mill effluent using electrocoagulation.*
concentration did not exhibit an effect on the removal of Mg, which may be attributed to the solubility of “MgCl2” in water.

Equation 3.5 (Table 1) is the regression model for Ca removal; the quadratic model was fitted with an R² value of 89.2%. Linear, interaction, and square factors have high p-values, indicating that none of these factors are dominant. Increases in retention time, voltage supplied, or NaCl concentration were found to increase the removal percentage of Ca, which is shown in Fig. 6. Under optimized conditions more than 70% of Ca can be removed; this value is much higher than those of Fe and Mg in the same electrocoagulation process. Calcium is known as a scale-forming species and is frequently processed for removal from industrial wastewater prior to disposal [24]. This study was performed using an aluminum electrode, and it has been reported that the removal of calcium using an aluminum electrode is faster than removal with an Fe electrode [25]. The substantial removal of Ca in the presence of NaCl may be attributed to the possible combination of Ca with chloride ions to produce CaCl₂, which is frequently used as a flocculant/coagulant to remove suspended solids. It can be assumed that the formation of metal chlorides may enhance the coagulation of the metals; however, the overall contribution of sodium chloride is not significant in all cases.

Hydrogen Gas Production

The regression model of the hydrogen gas produced during the electrocoagulation process is shown in Equation 3.6 (Table 1). This regression model had the lowest p-value (0.033) (<0.05) but exhibited a high R² value (91.4%), indicating that the model was well fitted. The operational cost of industrial wastewater treatment is considered to be a contributor to increasing production costs. However, the revenue-generating hydrogen production during wastewater treatment was assumed to be a cost-reducing factor. Hydrogen production was affected by the NaCl concentration, the voltage supplied, and the retention time; these effects are shown in the contour plot (Fig. 7). It is clear from the contour plot that the primary factor influencing hydrogen gas was the voltage supplied. The maximum hydrogen gas produced was >30%, with a gas flow rate of 1.8×10⁻³ m³/hr; the highest rate of hydrogen gas production was >0.54×10⁻³ m³/hr. Using a 0.02 m³ electrocoagulation reactor capacity, the maximum concentration of hydrogen gas produced was approximately 2.7×10⁻⁵ m³H₂/m³.

### Table 2. Comparison of the optimum conditions and removal efficiencies of the experiments and the Box-Behnken design optimization simulation.

<table>
<thead>
<tr>
<th></th>
<th>Box-Behnken design optimization</th>
<th>Experiment</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum Condition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl added (g/L)</td>
<td>0.04050</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>4.00000</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Retention Time (hour)</td>
<td>6.04641</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>COD removal %</td>
<td>42.9380</td>
<td>49.09</td>
<td>14.33</td>
</tr>
<tr>
<td>Turbidity Removal%</td>
<td>83.1603</td>
<td>85.82</td>
<td>3.20</td>
</tr>
<tr>
<td>Fe Removal%</td>
<td>23.6161</td>
<td>29.36</td>
<td>24.32</td>
</tr>
<tr>
<td>Mg Removal%</td>
<td>27.5621</td>
<td>32.61</td>
<td>18.31</td>
</tr>
<tr>
<td>Ca Removal%</td>
<td>47.8315</td>
<td>56.71</td>
<td>18.56</td>
</tr>
<tr>
<td>Hydrogen Produced%</td>
<td>28.8699</td>
<td>30.5</td>
<td>5.65</td>
</tr>
</tbody>
</table>

![Contour Plots of Hydrogen](image_url)

Fig. 7. Contour Plot for the production of hydrogen gas while treating palm oil mill effluent using electrocoagulation.
This study focused on the reduction of the polluting factors from POME as well as hydrogen production as a revenue-generating by-product. Other researchers have reported a complicated system while focusing on efficient hydrogen production using electrolytic techniques. Take et al. [26] reported hydrogen production using a methanol-water solution as an electrolyte and separating the cathode and anode with a membrane; that study reported hydrogen in the cathode exhaust gas in the range of 95.5 to 97.2 mol% [26].

Optimal Points

The optimal points of the simulation are shown in Table 2. The optimal conditions in the electrocoagulation system are 4 volts supplied, 6 hours of retention time, and no NaCl addition. The treatment efficiencies determined using simulations and experiments are nearly the same, with less than 25% error. Based on the results, the removal efficiency of COD and turbidity are up to 42.94% and 83.16%, respectively. The metal removal efficiencies are 23.62%, 27.56%, and 47.83% for Fe, Mg, and Ca, respectively. The efficiency of hydrogen gas produced under optimal conditions was 28.87%.

Conclusion

A closed electrocoagulation reactor system equipped with systematically arranged aluminum electrodes was established. A significant production of hydrogen gas was recorded while conducting the EC of POME for pollutant removal under optimized conditions. Compared to conventional methods of POME treatment (such as the ponding system), EC can be considered as an environmentally friendly and revenue-generating technique for such treatments. Electrocoagulation can be performed simply using a small area and low retention time compared with the conventional aerobic/anaerobic pond system. The application of the Box-Behnken design reduced the number of runs needed to optimize the operating conditions.

The quadratic model developed in this study showed a high correlation between the experimental and predicted values. Analysis of variance showed a high coefficient of determination ($R^2 = 0.998$), which indicates a satisfactory agreement of the quadratic regression model with the experimental data. The theoretical values obtained from mathematical modeling of the removal of the pollutants (COD, turbidity, and metals) and the production of hydrogen gas were in agreement with the experimental values.

Acknowledgements

The authors are thankful to Sime Darby Plantation, Sendirian Berhad, East Mill, located on Carey Island, Malaysia for providing a POME sample, and University Kebangsaan Malaysia for research funds to complete this study.

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