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Treatment of Biodiesel Wastewater by Electrocoagulation Process

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Abstract

The objective of this research was to determine the optimum conditions for biodiesel wastewater treatment using an electrocoagulation process. Wastewater samples were obtained from a small-scale, commercial biodiesel production plant that employs an alkali-catalyzed tranesterification process. The wastewater was characterized by the high contents of alkali and high oil content of 6,020 mg/L. Tested operational conditions included types of electrode, current density, retention time and initial pH. The tested electrode materials for electrocoagulation were aluminum (Al), iron (Fe) and graphite (C). Five tested pairs of anode and cathode materials included Fe-Fe, Fe-C, Al-Al, Al-C, and C-C. Results show that the optimum conditions were achieved by using the electrodes of Al-C, applying the current density of 8.32 mA/cm^2 to the wastewater with an initial pH value of 6 for 25 min. The removal efficiency was found to be 97.8% for grease & oil (G&O), 96.9% for SS and 55.4% for COD. Moreover, the small amount of produced sludge was readily to remove from the treated wastewater.

Keywords: biodiesel wastewater; electrocoagulation; grease & oil removal; electrode materials

1. Introduction

Due to a great increase of the world energy demand as well as limited energy resources, many researchers have been developing use of biofuels as alternative fuels. Biofuels can be classified into 5 types; namely, biodiesel, bioalcohols, ethanol fuel, biogas, and syngas. Among these, biodiesel can only be used for diesel engine. The global production and consumption of biodiesel grew on average by 32% per year during 2000 to 2005. In Thailand, biodiesel is one of the most promising alternative fuels for a transportation sector because the availability and low cost of the biodiesel production from palm oil. In general, biodiesel can be produced with several approaches, such as transesterification using alkali catalysis, acid catalysis, enzymes and supercritical methanol, ultrasonic irradiation, and thermal decomposition of oil with alkali catalysis (Suehara *et al*., 2005). The Alkali-catalyzed transesterification is widely used in commercial production since this method produces a high conversion of oil (triglycerides) to biodiesel (methyl esters) by a simple chemical reaction in a short time. In the final process of biodiesel production, water is usually introduced into the produced biodiesel in order to remove the impurities. The washing step is repeated for 2-5 times dependent on the quantity of impurity in the methyl ester. Therefore, a large amount of wastewater is generated by approximately of 20-120 L/100 L of biodiesel fuel being produced. The generated wastewater is strong basic (alkaline), contains a high content of hexane-extracted oil, but a less nitrogen and phosphorus content; thus, it is unfavorable for the growth of microorganisms (Suehara *et al*., 2005). In Thailand community-scale biodiesel plant with the capacity of 2,000 L/day produce wastewater with concentrations of COD, G&O, methanol and glycerol for 63,200, 3,160, 11,000 and 1,370 mg/L, respectively (Phukingngam *et al*., 2008). However, most of the previous works on biodiesel were mainly focused on technical processes of the production, while its environmental management aspect has been usually neglected.

An electrocoagulation (EC) process has been attracted a great attention on treatment of industrial wastewaters because of the versatility and environmental compatibility. This technique has several advantages as compared to conventional methods in terms of use of simple equipment, ease of operation, less treatment time, reduction or absence of chemicals addition (Savas *et al*., 2007). Moreover, an EC process provides rapid sedimentation of electrogenerated flocs and a less amount of sludge production (Chavalparit and Teangvannakan, 2008). It has been used to effectively treat numerous wastewaters including leachate from solid wastes, municipal wastewater, industrial wastewaters such as dying wastewater, olive oil wastewater and wastewater containing organic species such as phenol (Feng, 2004).

The electrochemical reactions with electrode metals (M) can be summarized as follows:

At an anode: $M_{(s)} \longrightarrow M_{(aq)}^{3+} + 3e^-$ (1)
At a cathode: $3H_2O + 3e^- \longrightarrow 3/2H_2(g) + 3OH^-$ (2)
In the solution: $M_{(aq)}^{3+} + 3H_2O \longrightarrow M(OH)_3 + 3H^+$ (3)

$M_{(aq)}^{3+}$ and OH^- ions, which are produced via the reactions (1) and (2), respectively, can react to form various monomeric species, depending on a pH range, and then they are finally transformed into $M(OH)_3$ according to complex precipitation kinetics. Freshly formed amorphous $M(OH)_3$ (sweep flocs) has large surface areas that are beneficial for rapid adsorption of soluble organic compounds and trapping of colloidal particles. Consequently, these flocs can be removed by sedimentation or by floatation using H_2 bubbles, which is produced at the cathode. Many researchers have been studied on different types of wastewaters using either iron or aluminum as anodes and cathode (Mohamed and Nadji, 2008; Mouedhen *et al.*, 2008; Ivonne *et al.*, 2008; Tezcan *et al.*, 2006; Xinhua and Xiangfeng, 2004). Yet, few studies have employed the combination of aluminum (or iron) and graphite electrodes in the same reactor.

Thus, this research was aimed to determine the optimum conditions for treatment of biodiesel wastewater using an electrocoagulation process. Five pairs of anode and cathode materials, including Fe-Fe, Fe-C, Al-Al, Al-C, and C-C, were tested with different operational conditions for the performance of an EC process.

2. Materials and methods

2.1. Lab bench-scale reactor

Electrocoagulation experiments were conducted in a 1-L monopolar batch reactor. A schematic diagram of the experimental setup is shown in Fig. 1.

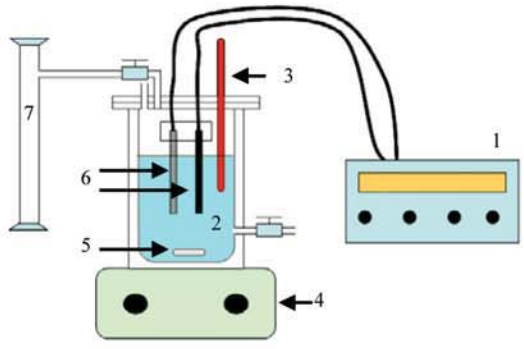

Figure 1. Experimental setup of the EC reactor: 1. DC power supply 2. Electrolyte 3. Thermometer 4. Stirrer Plate 5. Magnetic bar 6. Electrodes 7. Collected gas set.

Table 1. Characteristics of the biodiesel wastewater

Characteristics	Value
Chemical oxygen demand (COD) (mg/L)	30,980
Grease and oil (mg/L)	6,020
Glycerol (mg/L)	1,360
Methanol (mg/L)	10,667
SS (mg/L)	340
Conductivity (μS/cm)	350
pH	8.9

The reactor was connected in parallel to a digital DC power supply. A direct current was imposed by a stabilized DC power supply (Max. 60 V). The types of electrodes, levels of current density, retention time periods, and initial pH levels were varied to obtain the optimal treatment conditions. The current density levels were varied from 3.5 to 11 mA/cm^2 and reaction time periods were tested for 10 to 40 min. Initial pH of wastewater was varied from 4 to 9. The treated wastewater was allowed to settle for 30 min before collecting a sample. The sample was then analyzed for pH, COD, TSS, and G&O following the Standard Methods for Examination of Water and Wastewater. Glycerol and methanol were determined with High Performance Liquid Chromatography (HPLC, LC-3A; Shimadzu) and gas chromatography (GC, GC-7AG; Shimadzu). At the end of each trial, the electrode was cleaned, dried and then weighed to estimate weight loss of the anode and cathode. The produced sludge was analyzed by Fourier Transform Infrared (FTIR) Spectroscopy (Spectrum one; Perkin Elmer)

2.2. Materials

The tested wastewater was taken from a small–scale, commercial biodiesel production plant, which employs an alkali-catalyzed tranesterification process. This plant uses frying oil waste and crude palm oil as feedstock. Characteristics of the biodiesel wastewater are shown in Table 1. The tested electrodes were aluminum (Al), iron (Fe) and graphite (C). Five sets of different anode and cathode materials, including Fe-Fe, Fe-C, Al-Al, Al-C, and C-C, were examined. The electrodes had a flat and rectangular shape with an area of 50 cm^2.

3. Results and Discussion

Biodiesel wastewater was characterized by the high contents of COD and G&O due to the contamination of oil feed stock, soap, methanol and glycerol. Because the transesterification of triglycerides with alcohol is reversible, the excess amount of alcohol is required to shift the equilibrium in order to produce the products. Therefore,

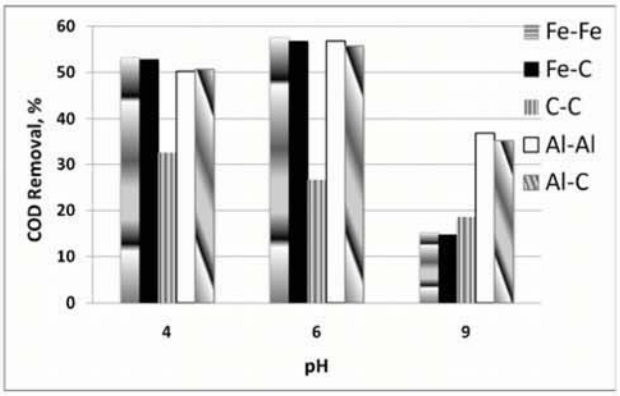

Figure 2. Effect of initial pH and electrode material on COD remove, i = 9.07 mA/cm^2, t = 30 min

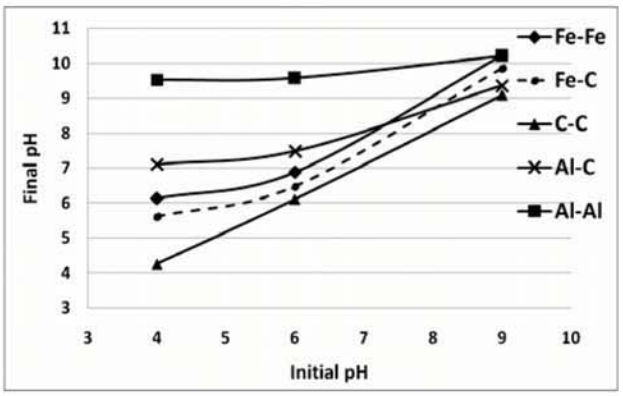

Figure 4. Effect of initial pH and electrode material on Final pH, i = 9.07 mA/cm^2, t = 30 min

methanol concentration in the wastewater was significantly as high as 10,667 mg/L. However, methanol and glycerol are easily biodegradable and could be removed effectively by conventional biological treatment

Another important contaminant in the wastewater is the residual oil and soap. Its measured concentration by a hexane extraction method was 6,020 mg/L. The widely-used alkali catalysts in transesterification include sodium hydroxide and potassium hydroxide. Since the final pH value of the wastewater was high, soap is formed by a saponification reaction with residual oil feedstock. This could inhibit the cell growth for any biological treatment. Thus, appropriate primary treatment of G&O in this wastewater is necessary in order to reduce any impact on the secondary biological treatment.

3.1. Optimum pH and electrode materials

To determine the effect of electrodes materials and initial pH on the removal efficiency of COD, SS and O&G, five pairs of different anode and cathode materials, including Fe-Fe, Fe-C, Al-Al, Al-C, and C-C, were examined using biodiesel wastewater with initial pH values of 4, 6 and 9.

Since pH of the raw wastewater was alkaline (pH=8.9), it was adjusted to desired pH using H_2SO_4. In each batch experiment, current density and reaction time were set constant at 9.07 mA/cm^2 for 30 min. The maximum COD and G&O removal efficiency was achieved using Fe or Al as anodes at the pH-adjusted acidic wastewater (4-6) as shown in Figs. 2-3. The electrode materials of Fe-Fe, Fe-C, Al-Al and Al-C also yielded the similar removal efficiency as using the same treatment conditions (pH 4-6). Yet, the graphite anode showed the lowest efficiency. This can be explained that the metallic hydroxides, $M(OH)_3$, which is generated by the electrode reaction, are formed as coagulant onto which colloidal particles can adsorb. The adsorbed particles are then removed by floatation with H_2 bubbles generated at the cathode (Mouedhen et al., 2008). As seen in Fig. 3, the Al-C and Al-Al electrodes were effective in removal of G&O for alkali wastewater (>90%).

As shown in Figs.2-5, the removal efficiency of COD and G&O were also dependent on the initial pH For the metal anodes, the maximum removal efficiency of COD was achieved at the initial pH of 4-6, while the efficiency was decreased dramatically as the pH value was increased to 9. These could be due to the formation of metal

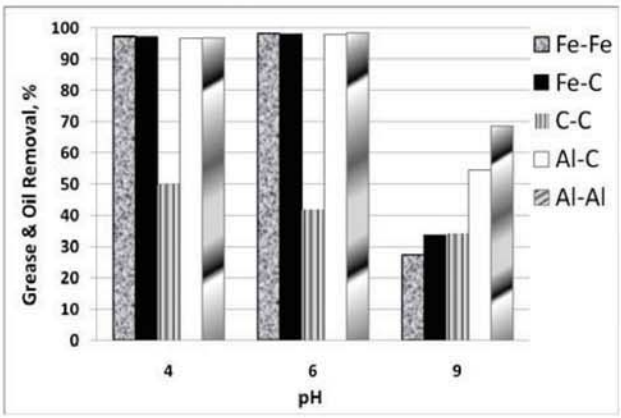

Figure 3. Effect of initial pH and electrode material on G&O remove, i = 9.07 mA/cm^2, t = 30 min

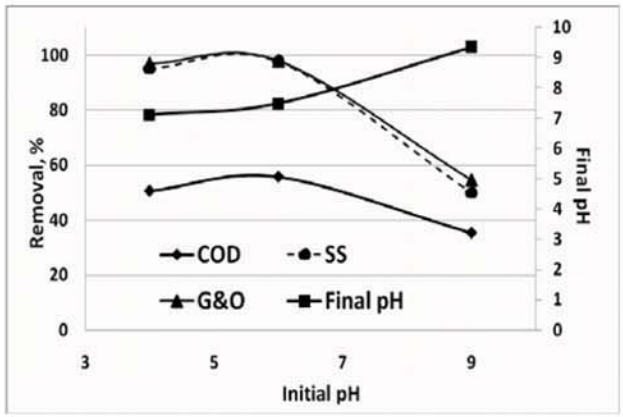

Figure 5. Effect of initial pH when used Al-C electrodes on COD, SS, G&O removal and final pH, i = 9.07 mA/cm^2, t = 30 min

Table 2. Weight loss of the electrodes at various treatment conditions

Electrode (anode-cathode)	Initial pH	Final pH	Weight loss (mg.)	Energy used (kWh/ m^3)
Fe-Fe	6	6.88	398.9	8.2
Fe-C	6	6.49	365.1	8.1
Al-C	6	7.49	164.5	8.3
Al-Al	6	9.58	342.3	9.2

hydroxide species The pH range of 4-9.5, the predominant aluminum hydroxide species is $Al(OH)_3$, while $Al(OH)_4$ is formed when the pH greater than 10 (Ivonne *et al.*, 2008). The later species is less reactive; thus, the initial high pH condition is likely to provide less effectiveness of flocculation. Moreover, the H_2 bubble production rate was increased with decreasing the initial pH. For the graphite anode and cathode, the highest removal efficiency was obtained at the initial pH of 4 as a result from the floatation by H_2 bubbles.

Analysis of energy used in the EC treatment process was calculated as the following:

$$E = V*i*t / Vol.$$

where E is the energy used for the EC treatment process (kWh/m^3 of wastewater), V is the voltage level (Volt.), i is the current density (mA/cm^2), t is the reaction time (h.), and Vol. is the volume of wastewater (m^3). The treatment conditions using the Al-C electrodes and the pH-adjusted value of 6 yielded the lowest electrode loss, energy consumption and treatment cost as shown in Table 2.

3.2. Effect of current density

It is known that the current density can affect the coagulant dosage rate and bubble generation rate, which in turn affects the treatment efficiency. Al and graphite were selected as an anode and cathode, respectively, for the next experiments to examine the effect of current density. It was varied from 3.5 to 11 mA/cm^2. The initial pH of 6 and reaction time of 30 min were maintained constant. Results show that COD and G&O concentrations were decreased as increasing the current density. Fig. 6 shows the variation of the COD removal efficiency as a function of the current density. The highest removal efficiency was achieved by applying the current density of 8.32 mA/cm^2. The G&O, SS and COD were removed by 97.8%, 97.5% and 55.7%, respectively. It is noted that the remove efficiency was remained constant when applying the current density greater than 8.32 mA/cm^2. An increased current density produces the higher quantity of coagulant (Al^{3+}) released from the aluminum anode. Simultaneous, the hydrogen gas rate at the cathode is also increased. The mixing of contaminants and coagulant taken place between the two electrodes can result in coagulation and then floatation of the sludge formed by the hydrogen gas (Vik *et al.*, 1984). Furthermore, the increased current density raises a final pH value of the treated wastewater as shown in Fig. 6. The application of the current density beyond 8.32 mA/cm^2 resulted in an increase of the treated-wastewater pH of up to 9. Therefore, the removal efficiency of G&O, COD and SS were not increased.

As seen in Fig. 7, the remove rate increased with an increase of the reaction time period. The applied current density of 8.32 mA/cm^2 produced the fastest removal rate for G&O and COD within 10 min. The removal efficiency measured at the reaction time of 10 min was 88.34% for G&O and 50% for COD and it was achieved 97.8% and 55.4% within 25 min.

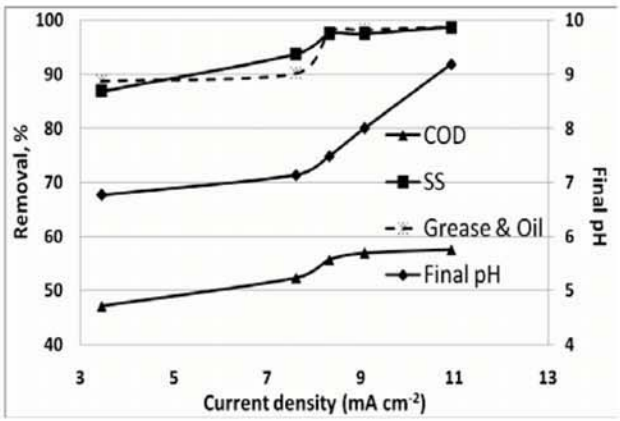

Figure 6. Effect of current density on removal efficiency and final pH, Al-C electrodes, pH 6 , t = 30 min.

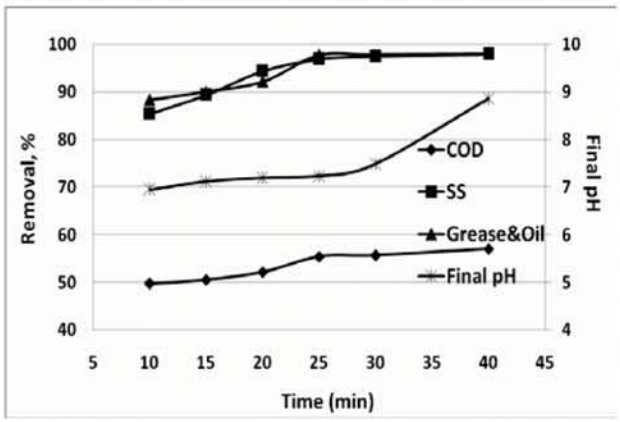

Figure 7. Effect of the reaction time on removal efficiency and final pH, Al-C electrodes, pH 6, i = 8.32 mA/cm^2

3.3. Sludge characteristics

The EC-generated sludge was dried at 103°C. The sludge production rate was found to be 1,180 mg/L of the treated wastewater at the optimum conditions. The sludge amount is significantly less than conventional-treatment sludge. The FTIR results show that the sludge composition was mostly comprised of a functional group of ester including Methyl Linoleate, Ethyl Palmitate, Ethyl Myristate, Butyl Stearate and Methyl Eliaidate. These constituents were left from the transesterification.

This study demonstrates that electrocoagulation treatment can be used to remove G&O from biodiesel wastewater effectively but it is less effective for removal of glycerol and methanol. At the optimum condition, the removal efficiency was achieved by 3.5% for glycerol and 16.9% for methanol.

4. Conclusions

Electrocoagulation treatment is an efficient method for primary treatment of biodiesel production wastewater. Results from testing on the five sets of electrodes show that the optimum conditions can be achieved using an aluminum anode and graphite cathode with the current density of 8.32 mA/cm^2 and the retention time of 25 min at the initial pH value of 6. The removal efficiency for COD, SS, and G&O were 55.7%, 97.5% and 97.8%, respectively. The sludge production was less as compared with that from conventional methods. The sludge was also easy to remove from the treated wastewater. The aluminum electrode consumption was 147.45 mg/L of wastewater, and the approximate power requirement was 6.92 kWh/m^3 of wastewater.

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