

Treatment of biodiesel wastewater by indirect electrooxidation: Effect of additives and process kinetics

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Abstract—Due to the presence of growth inhibitor and high impurity concentration in biodiesel wastewater, both biological and chemical processes are ineffective for treating such wastewater. In this work, biodiesel wastewater was treated by electrooxidation via Ti/RuO₂ electrodes in batch and continuous modes. Effects of the additive type, hydrogen peroxide (H₂O₂) and sodium chloride (NaCl), and concentration on the treatment efficiency, monitored in terms of the reduction in the biological oxygen demand (BOD), chemical oxygen demand (COD) and oil and grease level, were explored. The addition of NaCl gave higher treatment efficiency than H₂O₂, and both were higher than no addition, due to the continuous generation of the oxidizing chloride species. The removal of almost all the COD and oil and grease and ~95% BOD was obtained in the presence of 0.061 M NaCl at an applied current density of 4.28 mA/cm² for 7 h. In continuous operation mode, the steady state condition was reached within 11 h and the treatment efficiency decreased as the wastewater feed rate increased. By using wastewater feed rate of 2 mL/min, approximately 83.56, 61.43 and 91.72% of BOD, COD and oil and grease levels were respectively removed. The rate of pollutant removal fitted a first order reaction for both the batch and continuous operation modes.

Keywords: Biodiesel Wastewater, Indirect Electrooxidation, NaCl

INTRODUCTION

Biodiesel is recognized as an alternative fuel that can be used as a partial replacement of fossil fuel-derived diesel due not only to its sustainably renewable nature but also to its high lubricity, flash point and cetane number, low toxicity and biodegradability. In addition, it is seen as a much safer fuel than the fossil fuel-derived diesel because on combustion it emits a low level of sulfur dioxide, hydrocarbons, particulates, polycyclic aromatic hydrocarbons and carbon monoxide [1].

Biodiesel is currently commercially produced from the transesterification of vegetable oil or animal fat with alcohol in the presence of basic or acidic catalysts to free fatty acid methyl esters (FAMES) [2]. However, the biodiesel obtained from the production process is not ready to use because it contains various impurities, such as free glycerol, soap, metals, methanol, free fatty acids (FFAs), catalyst, water and glycerides, which impact negatively on the performance and durability of the diesel engine [3].

The wet washing method is typically applied to remove most of contaminants from the biodiesel, but for every 100 L of raw biodiesel this process produces ~20 L of a milky-like wastewater with

a high pH value and high levels of contaminants, measured in terms of the level of biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, total Kjeldahl nitrogen (TKN) and total dissolved solid (TDS) [4]. Discharging such wastewater without any proper treatment negatively affects the environment.

Currently, several processes have been developed to treat or improve the properties of biodiesel wastewater prior to discharging into the environment. Current biological processes are not capable of treating this biodiesel wastewater because its composition is unsuitable for microbial growth due to the presence of growth inhibitors [4]. Although a cheap two-step treatment process, comprised of chemical recovery by acid addition and then coagulation with Al₂(SO₄)₃ or poly-aluminum chloride, can enhance the removal of BOD, COD and oil and grease levels to greater than 97%, their residual levels were still higher than the acceptable values for discharging into the environment due to the high initial content of contaminants in the biodiesel wastewater [5]. The coagulation-flocculation had high efficiency to pre-treat biodiesel wastewater [6].

A novel approach was developed to enhance the efficiency of the dissolved air flotation (DAF) for biodiesel wastewater by acidification and coagulation. First, grease and oil and chemical oxygen demand (COD) removal efficiencies of biodiesel wastewater using acidification with pure hydrochloric acid and pure sulfuric acid at pH=3 and 1 day retention time were more than 80%, and 50%, respectively. Second, grease and oil and COD removal effi-

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Table 1. Properties of biodiesel wastewater discharged from biodiesel production plant using waste oil as a raw material

Properties	Thai standard	Fresh biodiesel wastewater	Acid pretreated wastewater	Treated wastewater	
				Batch	Continuous*
pH	5.5-9	9.25-10.79	2.5	2.2	2.08
BOD (mg/L)	≤60	168,000-300,000	186,000-204,000	18,000	33,000
COD (mg/L)	≤400	312,000-588,000	129,600-336,000	<1.2	30,600
Oil and grease (mg/L)	≤5	18,000-22,000	320-1840	<1.5	140
TKN (mg/L)	≤100	439-464	N/A	N/A	N/A
TDS (mg/L)	≤3,000	26,580-26,740	22,620	24,140	N/A

*Property of wastewater treated at 4.28 mA/cm² for 7 h in the presence of 61 mM NaCl at a wastewater feed rate of 2 mL/min

ciencies of biodiesel wastewater using alum, polyaluminum chloride and ferric chloride coagulants without acidification at 1.0 g/L were more than 90% and 30%. Third, DAF alone and DAF with acidification could not separate grease and oil from biodiesel wastewater. Thus, DAF with the acidification and coagulation is suggested for biodiesel wastewater treatment. The treatment of biodiesel wastewater by acidification before alum coagulation was effective to remove grease and oil of around 85-95%, which had the efficiency greater than other process of around 10% [7]. Using a continuous full scale treatment process that consisted of primary adsorption/coagulation/flocculation/sedimentation processes, followed by biological treatment with a combination of trickling filter and activated sludge systems, secondary flocculation/sedimentation processes, and finally reverse osmosis (RO), resulted in the removal of high levels of COD and salts when plane rather than spiral membranes were used [8]. Using commercial chitosan flakes as the adsorbent, greater than 93.6%, 97.6% and 95.8% of the initial BOD, COD and oil and grease levels, respectively, were removed via a physical adsorption process according to the Langmuir isotherm [9]. The adsorption process was controlled by a mixed process of diffusion and adsorption of the pollutants during the early treatment period (0-1.5 h) and then solely controlled by adsorption after 2 h [10].

Other interesting and effective processes for treating some pollutants in biodiesel wastewater is electrochemical processes due to their high efficiency, low treatment space requirement and ease of operation [11-13]. In addition, they can be applied in various different forms, such as electrooxidation, electroprecipitation, electrocoagulation, electrodeposition, electro-Fenton and electroflocculation [14-17]. The electrocoagulation process with an aluminum anode and graphite cathode was found to be effective at the removal efficiency of greater than 95% of the oil and grease and total suspended solid (TSS) levels in biodiesel wastewater, but was ineffective to remove the residual glycerol and methanol [18]. By using a monopolar batch reactor with Fe-Fe, Fe-C, Al-Al, Al-C and C-C electrodes, around 97.8, 55.7 and 97.5% of oil and grease, COD and suspended solid were, respectively, removed with less removal efficiency of methanol and glycerol of 16.9 and 3.5%, respectively [19]. The batch electrooxidation using a titanium/ruthenium oxide (Ti/RuO₂) electrode could completely remove the COD and oil and grease, and reduced the BOD levels by more than 95% in biodiesel wastewater with pseudo-first-order rate kinetics [20]. By using a combined electroflotation (pre-treatment) and electrooxidation pro-

cesses, the levels of turbidity, TSS, oils and grease, COD and methanol were removed by the electroflotation with aluminum electrodes, while the methanol and COD were more effectively removed up to 68% and 95%, respectively, by the electrooxidation process with Ti/RuO₂ anodes [21].

In the present work, the indirect electrooxidation technique was applied to treat biodiesel wastewater in both batch and continuous operation modes. The effects of the additive type, sodium chloride (NaCl) or hydrogen peroxide (H₂O₂), and concentration on the treatment efficiency were first explored in a batch operation mode and then applied in a continuous operation mode with different wastewater feed rates. The kinetic model describing the change of pollutant concentration was also explored for both the batch and continuous operation modes.

EXPERIMENTAL

Biodiesel wastewater was collected from a local biodiesel production plant that uses waste oil and methanol as the raw materials. Due to the presence of high levels of BOD, COD, oil and grease, TKN and TDS and a high pH value (Table 1), the fresh wastewater was first pretreated by the addition of concentrated H₂SO₄ (98%, Fisher) to pH 2.5 and allowed to phase separate [20]. Thereafter, the remaining aqueous phase was subjected to electrochemical treatment in an electrochemical glass reactor of 2.5 L capacity. In each experiment, 2 L wastewater was contained in the electrochemical reactor. Two commercial Ti/RuO₂ grids having a total surface area of 816.5 cm² were rearranged as a simple monopolar configuration with a distance between them of around 0.05 m. A magnetic stirrer was used to achieve a good mass transfer in the system at constant stirring rate of 250 rpm. A regulated DC power supply (ZS 3205-2X) was employed to supply a constant external current density of 4.28 mA/cm² [20]. During the treatment, the levels of BOD, COD, oil and grease in the biodiesel wastewater were analyzed at the specified time intervals according to the standard methods [22].

RESULTS AND DISCUSSION

1. Properties of the Fresh and Acid-pretreated Biodiesel Wastewater

The fresh biodiesel wastewater looked like a milky solution (Fig. 1(a)) with a high pH value of 9.25-10.79 and high levels of BOD, COD, oil and grease, TKN and TDS, which were in excess of the

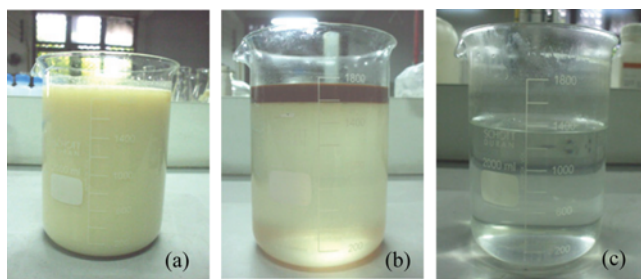


Fig. 1. Representative images of the (a) untreated fresh biodiesel wastewater, (b) acid-pretreated biodiesel wastewater and (c) acid-pretreated wastewater after electrochemical treatment at a current density of 4.28 mA/cm^2 for 7 h in the presence of 0.061 mM NaCl .

Thai government standard for discharge into the environment (Table 1). The principle contaminants in this biodiesel wastewater

were glycerin, soap, alcohol and catalyst residuals, un-reacted or residual FFAs and some biodiesel [20]. It also contained various types of some saturated/unsaturated fatty acids such as methyl caprate, methyl laurate, lauric acid, methyl azelaaldehyde, methyl palmitoleate and methyl 9-octadecenoate (Fig. 2(a)), which were the compositions present in raw material used in biodiesel production. After the acid pretreatment stage, the properties of biodiesel were improved with the COD, BOD and oil and grease levels in the remaining aqueous phase significantly reduced to approximately 13-24%, 40-74% and 87-98%, respectively, of the original levels (Table 1). Some impurities were removed by the acid pretreatment stage, leaving glycerol as the main composition in acid-pretreated biodiesel wastewater (Fig. 2(b)). This is attributed to the fast protonation of the fatty acid salts to form the less polar and water insoluble FFA [10]. In addition, some generated H^+ can also substitute the water molecule combining with biodiesel leading to the formation of the FAMES [21]. Both FFA and FAME are water-insoluble

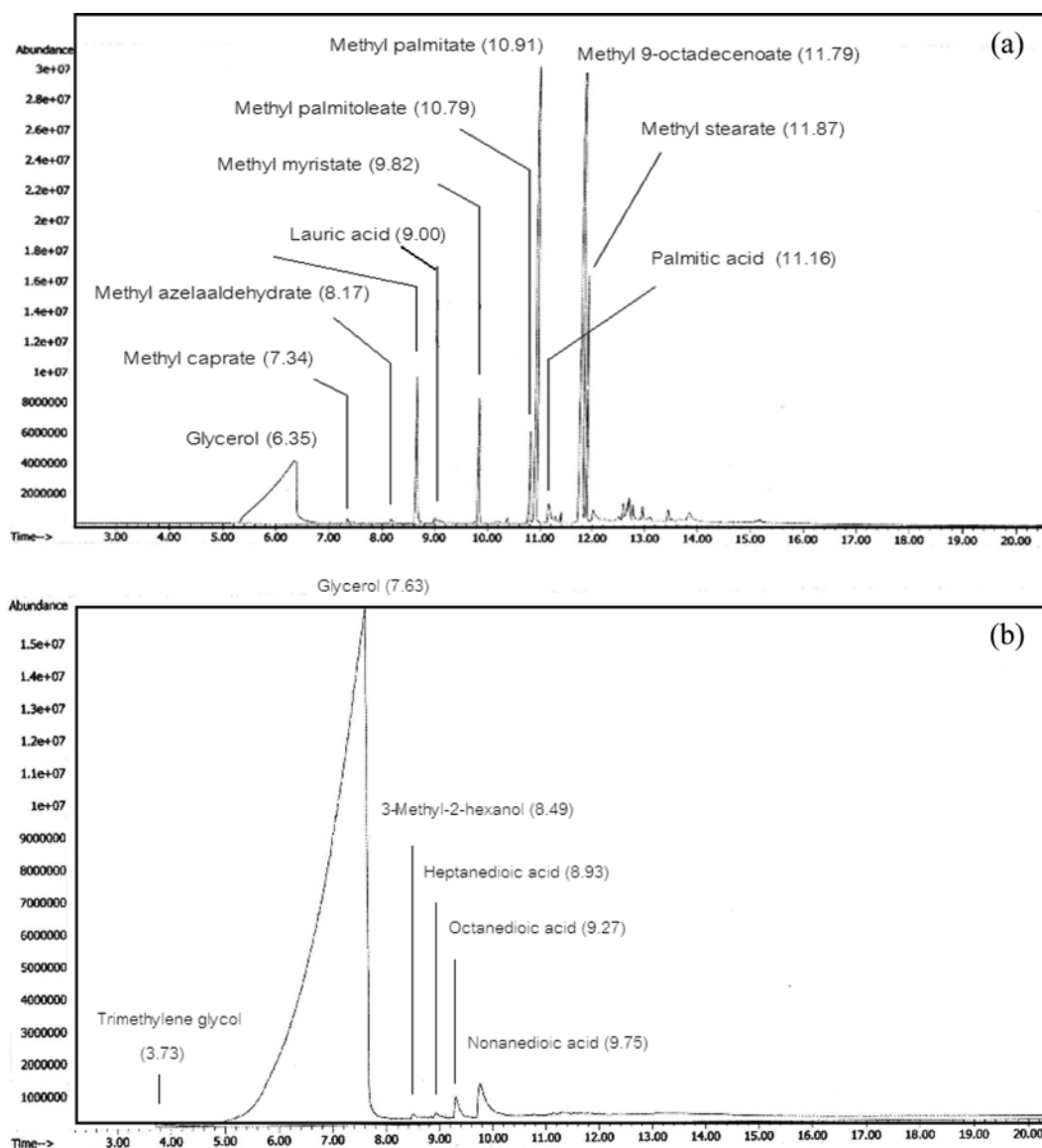


Fig. 2. GC-MS chromatogram of (a) fresh biodiesel wastewater and (b) acid-pretreated biodiesel wastewater.

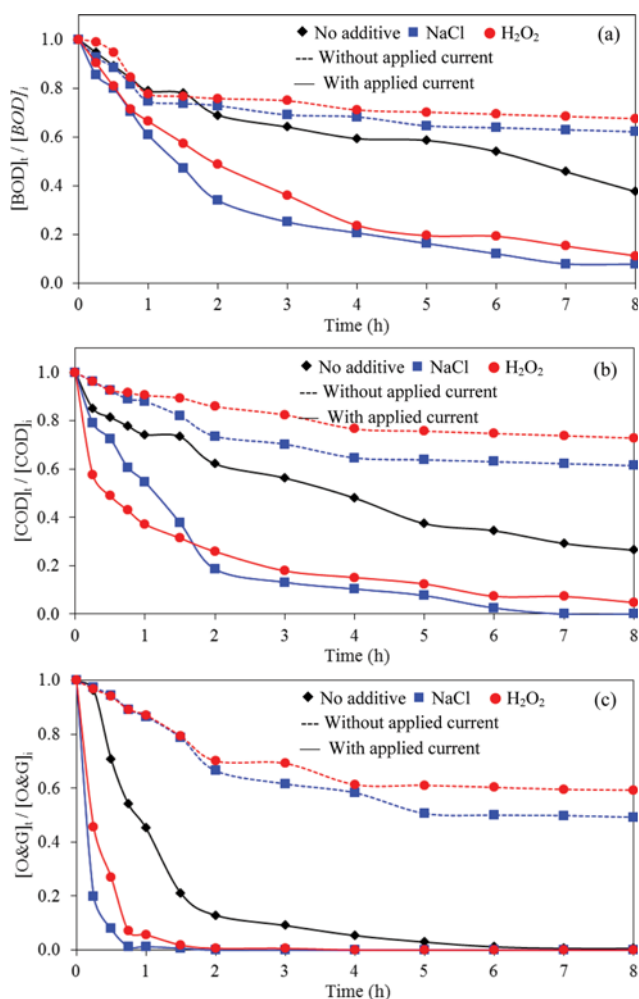


Fig. 3. The (a) BOD, (b) COD and (c) oil and grease levels as a function of time in the absence (no additive) or presence of either NaCl or H_2O_2 with and without an applied current density of 4.28 mA/cm^2 .

substances, which separate automatically as the top oil-rich phase, leaving the bottom aqueous water-rich phase with a lower level of contaminants (Fig. 1(b)).

2. Efficiency of Biodiesel Wastewater Treatment in a Batch Operation Mode

The BOD, COD and oil and grease levels in biodiesel wastewater after treatment in the presence of NaCl or H_2O_2 with or without an applied current density of 4.28 mA/cm^2 are summarized in Fig. 3. As expected, the level of BOD, COD and oil and grease decreased with the increasing time. In the absence of electricity, the addition of either NaCl or H_2O_2 reduced the level of BOD, COD and oil and grease insignificantly. Approximately 30, 24 and 39% of the BOD, COD and oil and grease levels were removed after 5 h electrolysis time in the presence of H_2O_2 , while those were 35, 36 and 49% in the presence of NaCl at the same period. In the presence of solely electricity but absence of additives, approximately 41, 63 and 97% of the BOD, COD and oil and grease levels were removed after 5 h electrolysis time. When either NaCl or H_2O_2 was added in the electrochemical treatment system, the lev-

els of pollutant were significantly reduced.

In the absence of additive, some organic pollutants can be destroyed electrochemically by direct oxidation by the electrogenerated physically adsorbed active oxygen ($\text{MO}_x(\text{OH})_z$) or by the chemisorbed active oxygen (oxygen in the oxide lattice, MO_{x+1}). The former active oxygen can cause the complete oxidation of organic pollutants, and the latter active oxygen can participate in the formation of selective oxidation products, as demonstrated in reactions (1) and (2) [16,23], respectively:



where $\text{MO}_x(\text{OH})_z$ is the hydroxyl radicals that are adsorbed on the anode surface, P is the organic pollutant and PO is the organic compound from the oxidized pollutant.

When some additives such as NaCl or H_2O_2 were added in the electrochemical system, the destruction of pollutant can precede via both adsorbed active oxygen (direct oxidation) and electrogenerated oxidants (indirect oxidation). When NaCl is present, the active chlorine/hypochlorous acid (Cl_2/HOCl) oxidizing species can be generated electrochemically due to the pH of system fluctuating between 2.0–2.2 by the oxidation of chloride ions to chlorine (Eq. (3)), and subsequent reacted in-situ with water to form hypochlorous acid (HOCl) [24,25]:



In contrast, in the presence of H_2O_2 , the bulk HO^\bullet radicals are electrochemically formed in the reduction reaction of H_2O_2 with the external supplied electricity according to Eq. (5),



All electrogenerated Cl_2 , HOCl and HO^\bullet radicals can destroy the organic compounds simultaneously with the adsorbed active oxygen ($\text{MO}_x(\text{OH})_z$ and MO_{x+1}) to either intermediate species or, if complete oxidation occurs, to carbon dioxide and water [23,26,27], resulting in a high treatment efficiency compared to that without additive.

From Fig. 3, the electrochemical system with NaCl was more effective at reducing the pollutants than that with H_2O_2 . Although the HO^\bullet has higher oxidizing power than the OCl^- [28], it is not stable and decomposes rapidly in an aqueous solution and so decreases in concentration over time. In contrast, the HOCl and Cl_2 are generated continuously in the chloride cycle [26] and so it is always available for oxidizing the pollutants and their intermediates/oxidized products in the wastewater.

Thus, the effect of the NaCl concentration on the reduction of the BOD, COD and oil and grease levels was then explored. As clearly demonstrated in Fig. 4, raising the NaCl concentration from 0 to 0.061 M significantly decreased the level of all three pollutant categories in a dose-dependent manner. This is attributed to the fact that higher NaCl concentrations lead to a higher generation of the active chloro-species, which can then readily oxidize the organic pollutants in the wastewater. However, further raising the NaCl from 0.061 to 0.092 mM did not further decrease the BOD and COD levels (Fig. 4(a) and (b)).

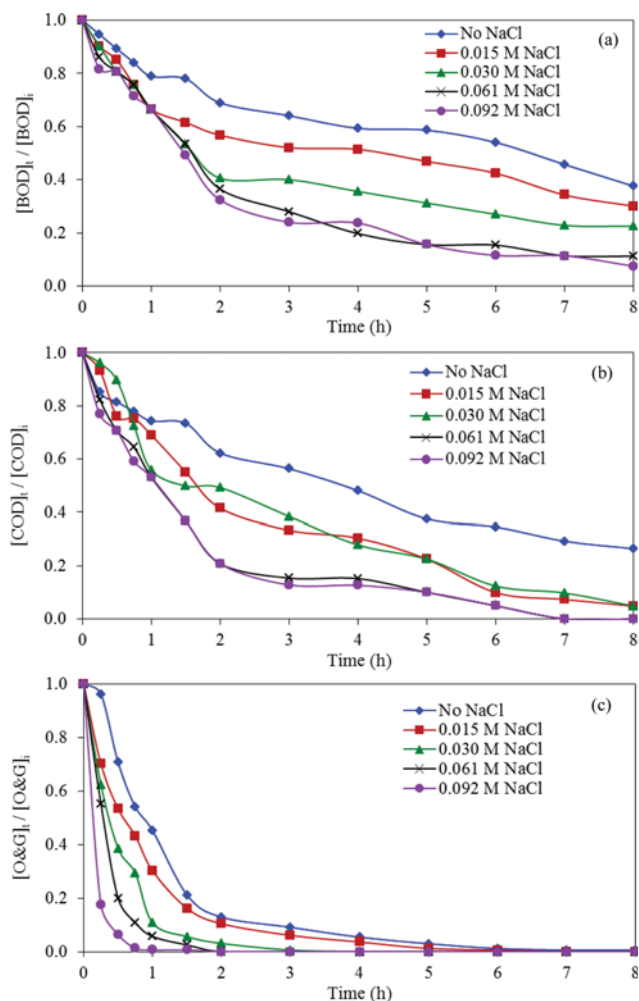


Fig. 4. Effect of the NaCl concentration on the BOD, COD and oil and grease removal at an applied current density of 4.28 mA/cm².

The appearance and properties of the biodiesel wastewater after indirect electro-oxidation in batch mode with 0.061 mM NaCl for 7 h at an applied current density of 4.28 mA/cm² are shown in Fig. 1(c) and Table 1. The levels of COD and oil and grease in the treated wastewater were markedly decreased to below the current maximum allowed levels for discharge permission by the Thai Government. However, the levels of BOD and TDS were still markedly above the Government standard, and the pH was too low. Again, that the proposed process does not remove the pollutants in the biodiesel sufficiently reflects their very high initial concentrations. Nevertheless, the obtained treated wastewater can be then treated by other methods, such as aeration ponds, to reduce the BOD and TDS levels to acceptable limits.

The rate of pollutant degradation by electrochemical technique in the presence of NaCl was then investigated. The rate of pollutant degradation was proportional to the amount of OCl⁻ species electrochemically produced in the system. Thus, it can be written as

$$\frac{d[P]}{dt} = k'[P][Cl] \quad (6)$$

where k' is the rate constant of Eq. (6); $[P]$ is the concentration of

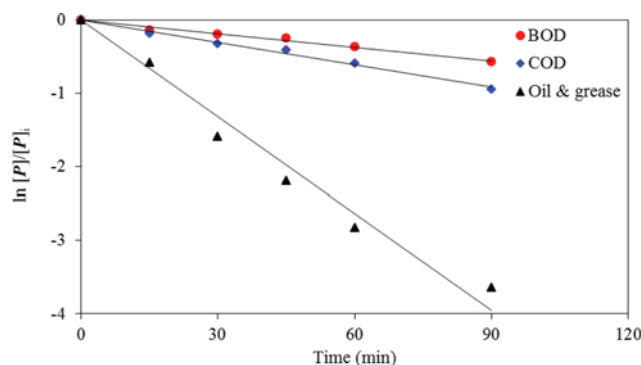


Fig. 5. Example $\ln [P]/[P]_i$ plot as a function of time.

pollutant and $[Cl]$ is the concentration of chloride species such as HOCl or Cl₂, respectively.

However, the rate of HOCl generation remained constant under a given set of experimental conditions because a constant current was applied [25]. Thus, its concentration did not limit the rate of pollutant degradation. Then, Eq. (7) can be written as

$$-\frac{d[P]}{dt} = k[P] \quad (7)$$

where k is the pseudo-first order rate constant of pollutant degradation. Integrating Eq. (7) with the boundary condition at $t=0$ that $[P]=[P]_i$ and rearrangement provided Eq. (8),

$$[P] = [P]_i e^{-kt} \quad (8)$$

Thus, a plot of $\ln [P]/[P]_i$ versus t provides a straight line with slope of $-k$, as seen for these results in Fig. 5. The pseudo-first order rate constants of BOD, COD and oil and grease during the investigated concentration ranges of NaCl were 0.004 ± 0.002 , 0.007 ± 0.003 and $0.027 \pm 0.014 \text{ min}^{-1}$, respectively. It is obviously demonstrated that the rate constant for the oil and grease degradation was significantly greater than that for BOD and COD. This suggests that the electrochemical technique was more effective at reducing the oil and grease level in biodiesel wastewater than the BOD and COD levels in both the absence and in the presence of NaCl.

3. Efficiency of Biodiesel Wastewater Treatment in a Continuous Mode

Treatment of wastewater in a batch mode would typically be more ideal for application in industry. So, a continuous operation mode was then performed at different wastewater feed rates (2–6 mL/min) in the presence of 0.061 M NaCl at a current density of 4.28 mA/cm². Electrooxidation was performed for the first 7 h in the batch mode with a constant volume of 2 L wastewater and no fresh wastewater was fed into/drawn out of the electrochemical reactor. After 7 h the operation mode was switched to continuous by feeding fresh biodiesel wastewater continuously into the reactor at the specified rate, and draining it at the same rate to maintain a constant 2 L reactor volume. During the initial 7 h batch operation, the level of all investigated pollutants (BOD, COD, oil and grease) decreased continuously (Fig. 6), and then immediately increased when switched to the continuous mode as fresh wastewater was added into the treatment reactor. Nevertheless, the system recovered itself and reached a steady state condition after about

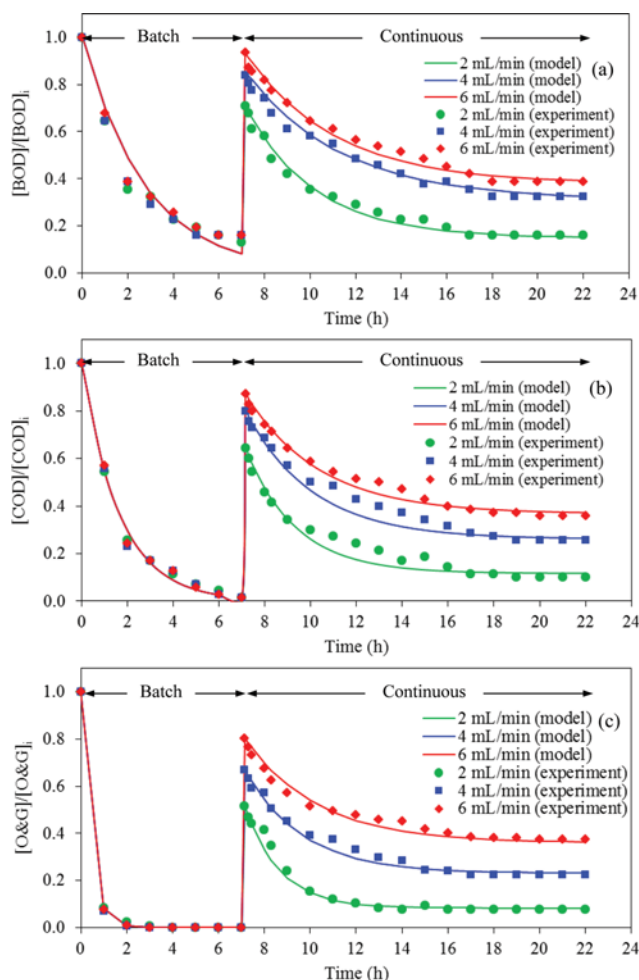


Fig. 6. The (a) BOD, (b) COD and (c) oil and grease level as a function of time after electrooxidation (4.28 mA/cm^2 with 61 mM NaCl) in a batch mode for 7 h followed by a continuous operation mode for 15 h with different wastewater feed rates.

11 h of continuous mode operation (18 h total reaction time). The reduction rate was inversely related to the flow rate, being slower with increasing flow rates due to the reduced retention time in the reactor at higher flow rates, consistent with previous work [17].

With respect to the variation in the BOD, COD and oil and grease levels as a function of the reaction time, the decrease in the level of all three investigated pollutant categories during the batch operation mode (0–7 h) can be expressed by Eq. (7). On the other hand, during the continuous mode, the concept of macroscopic balance with conservation law of component was applied [29], as shown in Eq. (9);

$$\left[\begin{array}{c} \text{Accumulation} \\ \text{rate of } P \text{ within} \\ \text{the system} \end{array} \right] = \left[\begin{array}{c} \text{Rate of } P \text{ in} \\ \text{the system} \end{array} \right] - \left[\begin{array}{c} \text{Rate of } P \text{ out} \\ \text{of the system} \end{array} \right] + \left[\begin{array}{c} \text{Rate of } P \\ \text{generated within} \\ \text{the system} \end{array} \right] - \left[\begin{array}{c} \text{Rate of } P \\ \text{consumed within} \\ \text{the system} \end{array} \right] \quad (9)$$

where the quantity P is the fundamental quantity of the BOD, COD

and oil and grease levels.

Based on a well-mixed electrochemical reactor without generation of species P , the change of pollutant concentration at an unsteady state condition can be written as Eq. (10);

$$\frac{d\{[P]V\}}{dt_C} = [P]_i F_i - [P]F - k_C [P]V \quad (10)$$

where $[P]$ is the concentration of pollutant in the reactor, which is equal to the concentration of pollutant in outlet stream for a well-mixed reactor, $[P]_i$ is the concentration of pollutant in the inlet stream, V is the volume of wastewater, t is the reaction time in the continuous experiment, F_i is the inlet feed rate of wastewater, F is the outlet feed rate of wastewater, k_C is the rate constant of pollutant reduction during the continuous operation and t_C is the treatment time during the continuous operation.

Due to the equal inlet and outlet stream of wastewater, the volume of wastewater in the reactor was constant and so Eq. (10) simplifies to Eq. (11),

$$V \frac{d[P]}{dt_C} = [P]_i F_i - [P]F - k_C [P]V \quad (11)$$

By dividing both sides by V , to obtain Eq. (12),

$$\frac{d[P]}{dt_C} = \frac{[P]_i F_i}{V} - \frac{[P]F}{V} - k_C [P] \quad (12)$$

and then solving Eq. (12) with the boundary condition of $t_C=0$, $[P]=[P]_{i,C}$, we derive Eq. (13);

$$[P] = \frac{[P]_i F_i}{VA} + \left([P]_{i,C} - \frac{[P]_i F_i}{VA} \right) e^{-At_C} \quad (13)$$

when $A=k_C+(F_i/k_C)$, and $[P]_{i,C}$ is the initial concentration of pollutant in reactor when the continuous process was initiated.

The values of all parameters in Eq. (13) are known except for k_C , and thus the trial and error concept was used to determine the value of k_C in order to get the best fit between the experimental data and model equation. These values of k_C , with a coefficient of determination (R^2) of greater than 0.9628, are plotted in Fig. 7. Interestingly, the rate constant for the pollutant removal was lower in the continuous mode than that in the batch mode, and they decreased with increasing wastewater feed rates into the reactor. This

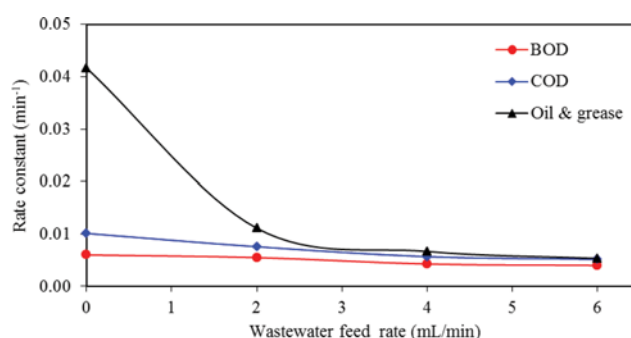


Fig. 7. Variation in the rate constant of BOD, COD and oil and grease reduction by electrooxidation (4.28 mA/cm^2 with 0.061 M NaCl) as a function of the wastewater feed rate in a continuous operation mode.

might due to the longer residence time of wastewater in the reactor at the lower feeding rate or due to the difference in the initial pollutant concentration during the shift condition from a batch to a continuous mode of operation.

The properties of the biodiesel wastewater treated by the continuous indirect electrooxidation operation mode at a 2 mL/min flow rate are summarized in Table 1. The treated wastewater still contains a high level of BOD, COD and oil and grease. Thus, a more extensive and expanded study is still required to improve the treatment efficiency, such as by increasing the surface area of the electrodes in the electrochemical reactor using monopolar parallel connections.

CONCLUSIONS

Biodiesel wastewater containing a high level of BOD, COD and oil and grease was treated by indirect electrooxidation in both a batch and continuous operation mode after an initial acid-pretreatment. The inclusion of NaCl gave a higher treatment efficiency than the inclusion of H₂O₂ due to the continuous generation of the Cl₂ and HOCl oxidizing agent in the chloride-chlorine-hypochlorite-chloride cycle. The treatment efficiency increased as the NaCl concentration increased up to 0.061 mM, but concentrations above this did not result in any further improved treatment efficiency due to the rate of pollutant degradation being limited (controlled) by the oxidation reaction of the pollutant by the oxidizing species. For the continuous operation mode, the rate constant for each pollutant removal was lower than that in the batch mode. The treatment efficiency and rate constant decreased as the wastewater feed rate increased. Overall, the indirect electrooxidation process was more effective at reducing the COD and oil and grease levels than the BOD levels.

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