Kinetics and thermodynamics of biodiesel wastewater treatment by using ozonation process

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ABSTRACT

Biodiesel wastewaters contain high amounts of oil, methanol, soap and glycerin. These wastewaters pollutant concentrations as chemical oxygen demand (COD), total organic carbon (TOC), glycerin and MeOH are fluctuating in the ranges of 250,000–450,000 mg/L, 54,000–110,000 mg/L, 800–1,500 mg/L, and 6,000–15,000 mg/L, respectively. Biodiesel wastewaters lead to blockage of oil drainage systems and reduction of biological activity in biological treatment systems. The purpose of this study was to treat wastewater by ozonation after the electrocoagulation process as pre-treatment. In the ozonation process, the initial wastewater pH value was 13.9, ozone dose was 1.5g/L h, reaction time was 7 h and reaction temperature was 45°C. As a result of 7 h of ozonation, 98.64% of COD, 97.48% of TOC and 99.37% of MeOH removal efficiencies achieved. With these results, biodiesel waste water can be discharge to into the receiving environment according to standards.

Keywords: Ozonation process; Biodiesel wastewater; Methanol

1. Introduction

87% of the energy needs of the entire world today are met by fossil fuels such as petroleum, natural gas and coal; however, the lifespan of the remaining petroleum reserves of the world was determined as 53.8 years [1]. This show lifespan determined for fossil fuels, high prices and aims to recover from environmental effects have given rise to the need for production of renewable and clean fuels and increased the number of studies on this issue [2]. While biodiesel is similar as a fuel to petroleum-based diesel fuel, it does not contain petroleum. However, petroleum-based diesel and biodiesel may be blended in varying ratios and used in vehicles with diesel engines without needing much replacement or any replacement at all. As opposed to the case in fossil fuels, biodiesel is biodegradable, non-toxic and more environment-friendly, and it attracts attention by these characteristics [3–6].

Biodiesel is an alternative type of fuel that is produced by a transesterification reaction between renewable resources such as plant and animal oils, used cooking oils, waste treatment sludges and even algae and short-chain alcohols like methanol or ethanol in the presence of a catalyst [6–10].

Biodiesel wastewater comes from the washing procedure that is applied with the purpose of removing impurities such as soap, free glycerin, free fatty acids and methanol in biodiesel at the stage of production [11]. The substances that disrupt the purity and quality of the fuel may create significant damages on injection systems by reducing the performance of diesel engines and may increase the emissions of aldehyde and acrolein [12,13]. Production of each 1 L of biodiesel corresponds to creation of 0.2–1.2 L of

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biodiesel wastewater [14] and the increased fuel cost that is dependent on the need for removing the high pollution carried by this wastewater is one of the most significant problems about production of biodiesel [12]. This is why various treatment methods were tried in the form of one-step and two-step methods in the literature with the aim of treating biodiesel wastewater. The treatment processes that were tested in the literature may be listed as solvent extraction [15], coagulation-flocculation [12,16], electrocoagulation (EC) [14,17], adsorption [18], chemical recovery and EC [19] and aerobic-anaerobic biological treatment [20–23]. Ozone is a strong oxidant (redox potential: 2.07 V) and it reacts with organic and inorganic substances in aqueous solutions with its special dipole structure [24]. Ozone reacts with organic substances in two ways as directly in aqueous solutions and indirectly via the hydroxyl radicals that occur by its disintegration. Hydroxyl radicals have better oxidant properties (redox potential: 2.33 V) in comparison to ozone, and they oxidize pollutants in the water up to the stage of mineralization without [24–26]. While under pH 4 the direct reactions occur, above pH 10 indirect oxidation exists. Around pH 7 both ways (direct and indirect) can be remarkable in ground and surface waters. According to contamination content of wastewaters even at pH 2 the indirect oxidations can be significant. While an ozonation process is designed, direct and indirect reactions should be taken in consideration [27]. It was observed that the mechanism of the ozonation process varies at high pH values, and hydroxyl radicals form as a result of a complex chain reaction [28]. Bicarbonate, carbonate and humic substances are broken down by a closed chain reaction of ozone and hydroxide ion, and $^{\bullet}$OH and radical-radical couple reaction processes. Moreover, it is also possible for the macro and/or micro pollutants to react with $^{\bullet}$OH radicals [24].

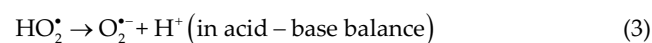The complete reaction of ozone can specified as direct and indirect reactions expressed as follows:

Direct reactions:

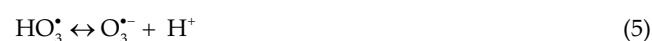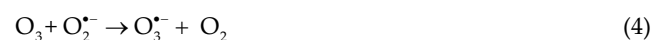Ozonation of wastewater at low pH level direct oxidation occurs;

$$O_3 + R \rightarrow Products \tag{1}$$

İndirect reactions:

At high pH levels indirect oxidation reactions consist and OH anions reacts with O_3 and formation of superoxide anion ($O_2^{\bullet-}$) and hydroperoxyl radical ($HO_2^{\bullet}$) take a place.

$$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{\bullet-} \tag{2}$$

$$HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+ \left(\text{in acid}-\text{base balance}\right) \tag{3}$$

Ozone anion $O_3^{\bullet-}$ generation by the superoxide anion and ozone reaction. And rapid degradation to $OH^{\bullet}$ with $HO_3^{\bullet}$ occurs.

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \tag{4}$$

$$HO_3^{\bullet} \leftrightarrow O_3^{\bullet-} + H^+ \tag{5}$$

$$HO_3^{\bullet} \leftrightarrow OH^{\bullet} + O_2 \tag{6}$$

The $OH^{\bullet}$ can react with ozone in the following way

$$OH^{\bullet} + O_3 \rightarrow HO_4^{\bullet} \tag{7}$$

$$HO_4^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \tag{8}$$

The total reactions (Eq. 2–8) shows that two $OH^{\bullet}$ are formed by three O_3 molecules.

$$3O_3 + H_2O \rightarrow 2 OH^{\bullet} + 4O_2 \tag{9}$$

The reactions of $OH^{\bullet}$ with organic matters can assumed as

$$H_2R + OH^{\bullet} \rightarrow HR^{\bullet} + H_2O \tag{10}$$

$$OH^{\bullet} + H_2R \rightarrow HRO_2^{\bullet} \tag{11}$$

$$HRO_2^{\bullet} \rightarrow R + HO_2^{\bullet} \tag{12}$$

$$HRO_2^{\bullet} \rightarrow RO + OH^{\bullet} \tag{13}$$

Furthermore $OH^{\bullet}$ can react with some organic and inorganic matters to produce secondary radicals. That cause the inhibition of $HO_2^{\bullet}/O_2^{\bullet-}$ formation mechanism [27].

The literature studies about the wastewater treatment with ozone oxidation can be summarized as follows: domestic wastewater [29,30], hospital wastewater [31], industrial textile wastewater [32], industrial wastewater [33], removal of natural organic substances [34], Organophosphate (methylparathion) [35] and yeast wastewater [36]. Formation of calcium oxalate, calcium carbonates and ferrous hydroxide are the most common operational problems in waste water treatment by ozonation. The precipitated CaC_2O_4, $CaCO_3$ and $Fe(OH)_3$ leads to the clogging of the reactor valves and pipes as well as the failure of the pumps [27]. While there are various studies on this topic in the literature, ozone oxidation, which is an advanced treatment method, has not been studies for this type of wastewater. This study treated biodiesel wastewater in two steps and aimed to make it suitable for discharge standards. The water that was treated by EC in the first step was treated in the second step by exposure to advanced oxidation with ozone. The pH, ozone dose, time and temperature parameters were examined separately in the electrocoagulated biodiesel wastewater (ECBW) and the optimum conditions for removal of parameters of MeOH, total organic carbon (TOC) and chemical oxygen demand (COD) were determined. In the time- and temperature-dependent trials with the determined optimum conditions, treatment of ECBW with ozone was investigated in terms of kinetics and thermodynamics.

2. Materials and methods

2.1. Chemical analysis

The COD and TOC analyses were made by using Standard Methods For The Examination of Water and Wastewater, 23rd ed., [37]. COD analysis was made based on 5220 D and TOC analysis was made based on 5310 B using

an HACH (Germany) IL 550 TOC/TN model device [37]. The pH was adjusted by solutions of NaOH or H_2SO_4. MeOH analysis was conducted using the spectrophotometer model SHIMADZU (Japan) UV/Vis 1700. The methanol analysis involved the reactants of 10% (m/v) sodium nitroprusside (m/v), 10% (m/v) potassium ferricyanide and 5% (m/v) sodium hydroxide solutions by 100 ml each. The solutions were filled up to 600 mL by distilled water and the chromogenic indicator (SNP) was obtained. MERCK (Germany)-branded methanol (MeOH) (Gas Chromatography Grade) was used in the stock solution. For MeOH analysis, 6 mL of SNP is added onto 1 mL of the specimen, and the samples are prepared by shaking for 1 min. They are left for 45 min at room temperature, and their absorbance's are read at a wavelength of 481 nm [38]. Ozone is produced by air flow under high electrical current. Ozone production was achieved with an ozone generator with the brand SABO (Turkey) and model SL-10 which has a maximum capacity of 15 g/L h.

2.2. Characterization of biodiesel wastewater

In order to minimize the variation in the characteristics of biodiesel wastewater, the wastewater to be used in the experiments was produced in the laboratory of the Department of Environmental Engineering at Sakarya University. In order to facilitate methyl ester production in 1 L of oil, 200 mL MeOH and 4.9 g KOH were used. MeOH solution was added onto the oil which was brought to 40°C, and the reaction was facilitated by mixing for 1 h at 55°C. The glycerine layer that occurred was left for a night for it to precipitate. 1 L of oil was topped up with water by half its volume, and biodiesel and biodiesel wastewater were produced by conducting a washing procedure for 7–8 h with the help of an air pump and air stone [39]. Table 1 shows the components of raw biodiesel wastewater.

2.3. EC of biodiesel wastewater

Metallic hydroxide flocs produced by EC process for the wastewater treatment. Soluble or colloidal contaminants are absorbed on the formed coagulants and then eliminated by sedimentation. The effected operational factors for EC process can be listed as pH, electric current density and the application time [40].

The experimental system employed that was similar to ones used in our previous study [41]. EC experiments were conducted in a 250 ml bipolar batch reactor. Reactor system consists of a D.C. power supply (30 V–5A) and iron flat rectangular shapes electrodes. Four electrodes were placed in parallel and vertically with a separation distance of 7.5 mm and the gaps between the electrodes were kept constant in all experiments. Each electrode dimensions were 6 cm × 12 cm × 0.15 cm and total effective area was 288 cm^2.

Because of the high pollution load of raw biodiesel wastewater and high amount of oil in water, it is difficult to treat with oxidation processes without pre-treatment. Even though high removal efficiencies have been obtained with the EC process, COD values decreased to 24,000–18,800 mg/L [41,42]. And discharge standards cannot be achieved. For this reason, it was pre-treated with EC process before ozonation process. For the EC process, the initial pH of the biodiesel wastewater was determined as 6, with a NaCl concentration of 0.5 g/L for conductivity, a current density of 0.7 mA/cm^2 and optimum electrolysis time of 2 min [42]. EC removes all fatty acid methyl esters. So, these do not contribute to the oxidation process as pollution load. After EC, the ECBW was treated by ozonation, which is an advanced oxidation process. The contents of the ECBW are shown in Table 2.

2.4. Ozonation of biodiesel wastewater

Ozone is a very strong oxidant thus direct and indirect oxidation can be occur in the ozonation process depend on pH levels [43]. When it is dissolved in water, it reacts with organic substances via direct oxidation as molecular ozone or indirect oxidation by forming hydroxyl radicals [44].

ECBW treatment studies conducted by used a high voltage corona discharge with the capacity of 15 g/L h. The total reactor volume was 250 ml. There was an ozone entry system. For effective homogenization the waste water and ozone was mixed by magnetic stirrer. After ozonation, potential residual ozone eliminated by aeration the sample for 5 min extra. The process follow diagram as shown in Fig. 1. The ozonation process effected by several factors as pH, ozone dose, reaction time and temperature that used in this study.

2.5. Thermodynamic and kinetic examination

Gibbs free energy levels were calculated in the temperature experiments. Kinetic modelling suggests that removal rates could be a second-order model. Second-order rate constants and a linear pseudo-second-order equation

Table 1
Characterization of biodiesel wastewater

Parameter	Value
pH	10.35
Oil-Gres (mg/L)	20,300
COD (mg/L)	389,000
TOC (mg/L)	77,000
TN (mg/L)	0
BOD_5 (mg/L)	210,400
TSS (mg/L)	12,800
MeOH (mg/L)	21,100

Table 2
Characterization of electrocoagulated biodiesel wastewater

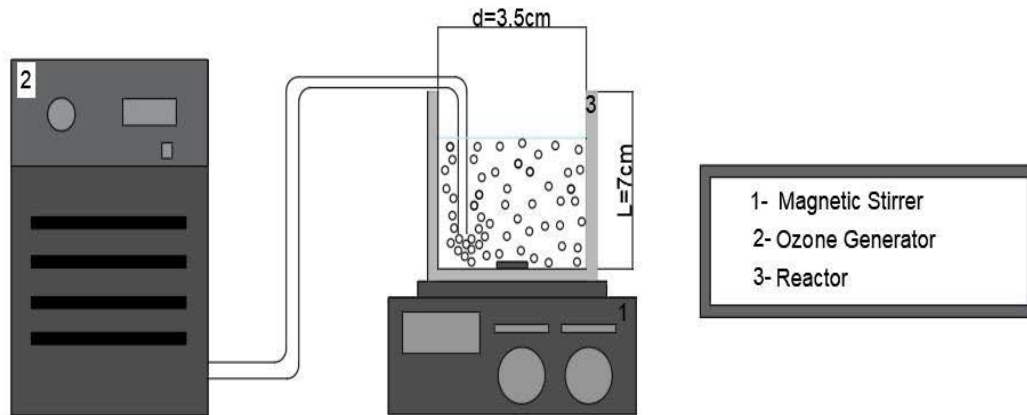| Parameter	Value
pH	7.8
Oil-Gres (mg/L)	25
COD (mg/L)	13,030
TOC (mg/L)	3,528
BOD_5 (mg/L)	222
TSS (mg/L)	107
MeOH (mg/L)	6375

Fig. 1. The ozonation reactor system.

were found suitable. The linear pseudo-second-order rate constants are given as follows [44]:

$$\frac{t}{c} = \frac{1}{k_2 C_e^2} + \frac{1}{C_e} t \tag{14}$$

where k_2 = Oxidation rate constant (L/mol h); c = Concentration of matter removed at time t (M); C_e = Concentration coefficient.

Speed constants are expressed as a function of temperature. As the kinetic parameters of the oxidation process are dependent on temperature, they can be calculated by the Arrhenius equation (Eq. (15)). Gibbs free energy in the oxidation process is calculated by Eq. (16) below [45].

$$k = A \times \exp\left(-\frac{E_a}{RT}\right) \tag{15}$$

$$\Delta G^\circ = -RT \ln k \tag{16}$$

3. Results and discussion

3.1. Effect of initial pH

Ozonation of ECBW adjusted to different pH levels was used to investigate the effect of pH on ozone's efficiency to for the removal COD, TOC, and methanol (MeOH). Formation of hydroxyl radicals do not occur at low pH level (under pH 3), therefore ozone and water pollutants are not decayed. Under acidic pH levels production of radicals except for hydroxyls is accelerated the efficiency of ozonation process [43].

All experimental studies to obtain pH effect have been done by using 2 h, of 0.3 g/L h O_3 and 25°C. Since, ozone molecules join reactions indirectly at high pH values, depend on wastewater type removal efficiencies at high pH values are generally high. As the results of experiments, a linear relationship was observed between COD, TOC, and MeOH removal efficiency and pH increase as seen in Fig. 2. Similarly a study showed that the removal efficiency by the ozonation process for phenol removal from water increasing with high pH values (pH 13), and decreasing at low pH
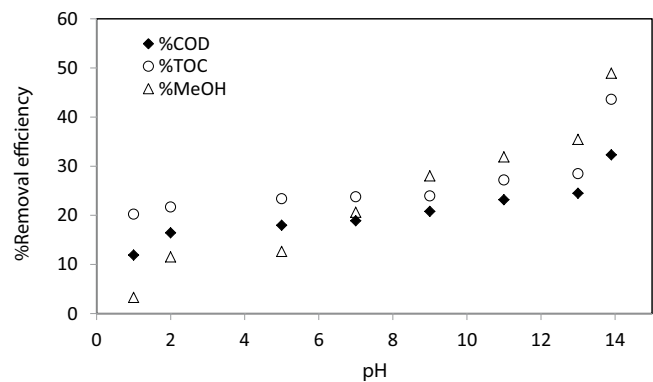

Fig. 2. The effect of pH on the COD, TOC and MeOH removal efficiency ($C_{0,COD}$ = 13,030 mg/L; $C_{0,TOC}$ = 3,528 mg/L; $C_{0,MeOH}$ = 6,375mg/L; ozone dose = 0.3 g/L h; t = 2 h; T = 25°C; agitation speed = 120 rpm).

2.5 [46]. And the other one was applied ozonation to dairy wastewater as advanced oxidation process and pH 12 level was determined as more efficient for COD removal [33]. pH adjustment studies carried on pH 1,2, 5, 7, 9, 11, 13, and 13.9 and the highest treatment performance was achieved at pH 13.9. The COD removal efficiencies for pH 1 and pH 13.9 respectively were found as 11.9% and 32.29%. Likewise, while the TOC and MeOH removal efficiencies were 20.21% and 3.30% at pH 1, 43.59% and 48.90% at pH 13.9. Since at high pH levels production of hydroxyl radicals enhanced to the treatment capacity of ECBW, pH 13.9 was chosen due to the highest removal obtained.

3.2. Effect of ozone dose

Ozonation is the one of the most important advanced oxidation process have recently using for several organic pollutants in water and wastewater [31,43,47,48]. Different O_3 doses were studied to investigate the effects of O_3 dose on removal efficiencies of COD, TOC, and MeOH for ECBW. Ozone solubility is known in water is small and slow. Dissolved ozone concentration affected by the oxidation/ mineralization rate of waste water contaminants [38]. Ozone

solubility levels was measured in water and the concentration depending on the flow rate is given in the Table 3.

Fig. 3 shows the effects of O_3 dose on wastewater treatment efficiency. Studies were carried out between 0.075 and 2 g/L h. As seen in the figure, while the O_3 dose increased, COD, TOC, and MeOH removal efficiencies also increased and fixed over 1.5 g/L h. The highest efficiencies was achieved at 1.5 g/L h O_3 dose, pH 13.9, 25°C and 2 h. While O_3 dose at 0.075 g/L h the removal efficiencies for COD, TOC, and MeOH were respectively 12.28% (11430 mg/L), 34.92% (2296 mg/L) and 28.30% (4571 mg/L). On the other hand at 1.5 g/L h O_3 dose COD, TOC, and MeOH removal efficiencies were 62.89% (4835 mg/L), 70.38% (1045 mgL/L) and 87.64% (778 mg/L) respectively. The highest removal efficiencies were achieved with the 1.5 g/L h dose of ozone. Some studies showed that decomposition of different pollutants in wastewater were increasing with ozone dose increment [31,32,49,50]. Thus our experimental ozone dose studies have proved that situation as well.

3.3. Effect of reaction time

The time for a complete oxidation reaction depends, before several variables, on the strength of organic substances [50,51]. In the reaction time experiments, the effects of reaction time were investigated at pH 13.9, 1.5 g/L h O_3 dose and 25°C temperature. Fig. 4 shows the effects of reaction time on wastewater treatment efficiency. As seen in the figure, COD, TOC, and MeOH removal efficiencies increased as the reaction time increased. The COD removal efficiency was 34.69% in a reaction time of 0.5 h, and 93.25% in a reaction time of 9 h. The highest removal results for pH 13.9 and 1.5 g/L h O_3 dose were obtained at a reaction time of 9 h. The COD value

Table 3
The ozone concentration in water depending on the flow rate

Flow rate (g/L h)	0.075	0.15	0.3	0.5	0.75	1.5	2
Ozone concentration (mg/L)	1.08	1.8	2.6	3.3	4.5	8	8.5

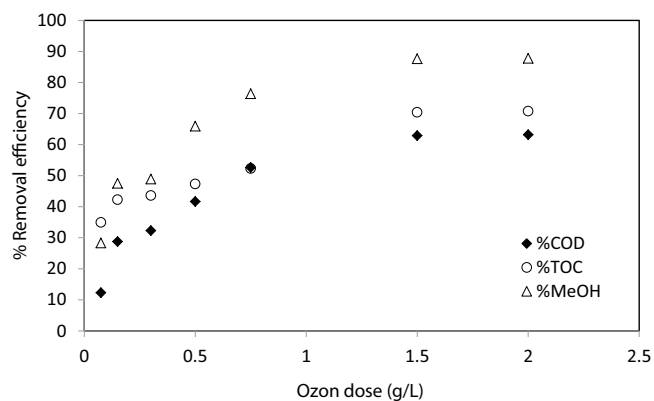Fig. 3. The effect of ozone dose on COD, TOC and MeOH removal efficiency ($C_{0'COD}$ = 13,030 mg/L; $C_{0'TOC}$ = 3,528 mg/L; $C_{0'MeOH}$ = 6,375mg/L; pH = 13.9; t = 2 h; T = 25°C; agitation speed = 120 rpm).
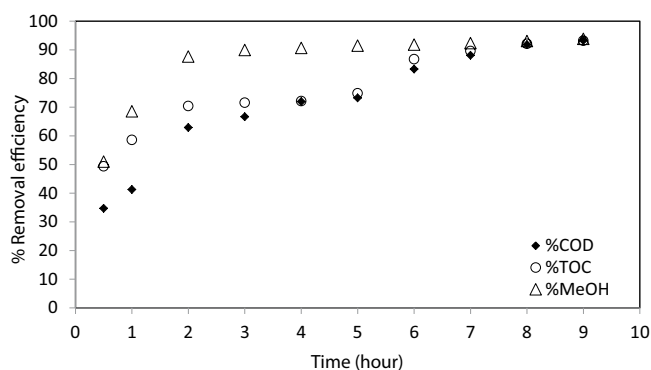

Fig. 4. The effect of reaction time on COD, TOC and MeOH removal efficiency ($C_{0'COD}$ = 13,030 mg/L; $C_{0'TOC}$ = 3,528 mg/L; $C_{0'MeOH}$ = 6,375mg/L; pH = 13.9; ozone dose = 1.5 g/L h; T = 25°C; agitation speed = 120 rpm).

at 0.5 h was 8510 mg/L, while it could be reduced down to 879 mg/L in 9 h. The TOC removal efficiency was 49.38% at 0.5 h and 93.17% at 9 h. The TOC value of 1786 mg/L at 0.5 h could be reduced down to 241 mg/L at 9 h. The MeOH removal efficiency at 0.5 h was 51%, while it was 93.82% at 9 h. The MeOH value of 3123 mg/L at 0.5 h could be reduced down to 394 mg/L at 9 h. The best COD, TOC, and MeOH removal results for pH 13.9 and 1.5 g/L h O_3 dose were obtained in a reaction time of 9 h.

3.4. Effect of temperature

While the decomposition rate of ozone accelerate with rising temperature, the solubility of ozone declines [52,53]. Reaction rates affected by different temperatures. Both the solubility and decomposition rate of ozone effects the removal of wastewater contaminants.

COD, TOC, and MeOH removal efficiencies increased along with increases in temperature as seen in Figs. 5a, 5b and 5c. All experiments conducted for temperature effects were in pH 13.9, 1.5 g/L h O_3 dose and 7 h at different temperatures (25°C, 35°C, and 45°C). The most effective treatment temperature was observed as 45°C. While the concentration of COD was 1,550 mg/L at 25°C, it measured as 257 mg/L at 45°C. In addition for the same temperatures TOC values are evaluated as 368 and 153 mg/L respectively. Also, MeOH concentrations were determined as 487 mg/L at 25°C and 74 mg/L at 45°C. All results proved that for this experimental set up the upward temperature increased the removal efficiency for ECBW.

3.5. Thermodynamics and kinetic evaluation

The kinetic model of TOC and MeOH removal confirms to the linear pseudo-second-order model in the ozone oxidation of ECBW. Linear pseudo-second-order rate constants are calculated according to Eq. (14). The linear pseudo-second-order rate constants are given in Table 4 that shows constants are increasing as the temperature increases. As the reaction results were examined, for TOC and MEOH parameters ozone oxidation reactions rate constants (k) increment has observed with the temperature rise [54,55].
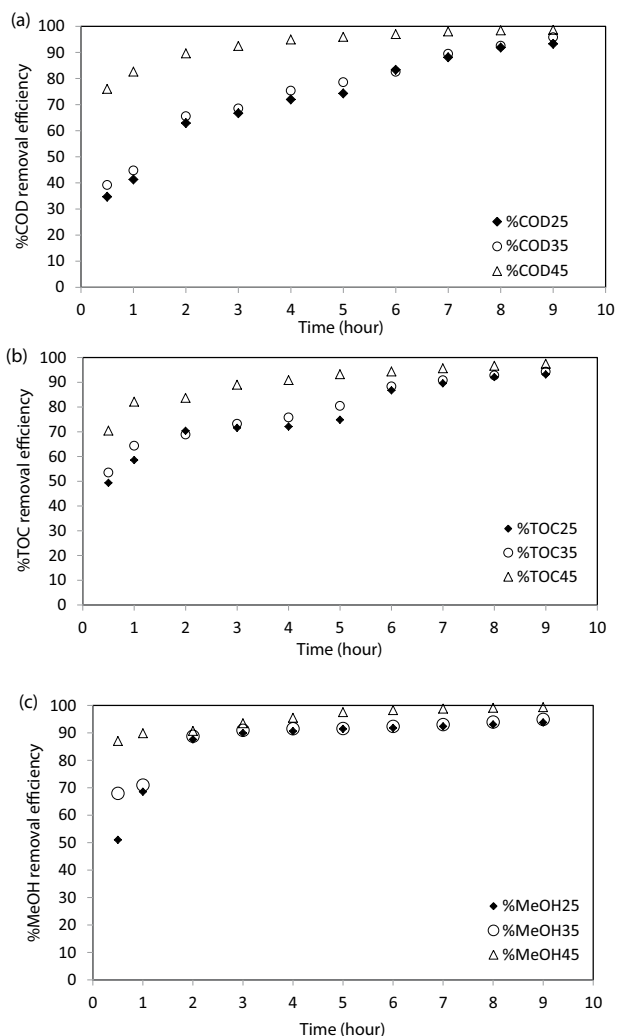
Fig. 5. The effect of temperature on COD (a), TOC (b) and MeOH (c) removal efficiency ($C_{0,COD}$ = 13,030 mg/L; $C_{0,TOC}$ = 3,528 mg/L; $C_{0,MeOH}$ = 6,375mg/L; pH = 13.9; ozone dose = 1.5 g/L h; agitation speed = 120 rpm).

Table 4
Linear pseudo-second-order reaction rate constants

	k_{25}	k_{35}	k_{45}
TOC	4.035	4.274	9.109
MeOH	14.9	20.204	29.594

Linear pseudo-second-order kinetic speeds increase 1.06–2.13 times with each 10°C increase in temperature [56].

Using the reaction rate constants (*k*) activation energy (E_a), Arrhenius constant (*A*) and Gibbs free energy ($\Delta G°$) levels were calculated by the Arrhenius equation (Eq. (15)) and Gibbs free energy equation [Eq. (16)]. Table 5 shows that the thermodynamic parameters for TOC and MeOH removal in ECBW. According to the Gibbs free energy exchange basic principal, $\Delta G°$ must be negative to occur the spontaneous reactions. Negative $\Delta G°$ values occur due to the order of the reaction and temperature increase [44]. The experimental results show that $\Delta G°$ values were changed for the removal of MeOH ($\Delta G°$ = –6,692.8 at 25°C and as $\Delta G°$ = –8,985.3 at 45°C) and TOC (25°C $\Delta G°$ = –3,456.2 at 45°C $\Delta G°$ = –5,841) by temperature. These indicate that probability of reaction appearance as temperature increase.

As a result of study the activation energies of TOC and MeOH removal were found as 31,759.5 and 26,978.6 J/mol, respectively. These results indicate that ozone is advancing with a low energy barrier for the oxidation of ECBW [57].

4. Conclusions

Biodiesel wastewaters involve organic pollutants including fatty acid methyl esters, glycerin and methanol. EC process is treated mostly fatty acid methyl esters however, high rates of MeOH and organic substances remain in the biodiesel wastewater after EC. Receiving environment discharge standard was reached by ozonation process to the ECBW.

As a result of experimental studies the optimum conditions for the treatment of ECBW with ozonation were determined as pH 13.9, 1.5 g/L h O$_3$ dose and 45°C at 7 h reaction time. Under these conditions COD, TOC, and MeOH were removed by 98.03%, 95.66%, and 98.84% respectively. According to the results, biodiesel wastewater can be discharged to the receiving environment only by neutralization.

Because of the high pollution content of biodiesel wastewaters, single-step treatment processes cannot achieve enough removals for organic substances especially MeOH. Thus there is a need for a second step treatment process to reach discharge standards. Since the pre-treated biodiesel wastewater contains high pollutant load, only aerobic biological treatment cannot achieve the standards. In literature studies should also study new applicable final treatment methods by different advanced oxidation methods following EC processes.

Table 5
Activation energy, Arrhenius constant vs Gibbs free energy

T (K)	$\Delta G°$		E_a (J/mol)		A (1/M.sa)	
	TOC	MeOH	TOC	MeOH	TOC	MeOH
298	–3,456.2	–6,692.8				
308	–3,719.6	–7,697.2	31,759.5	26,978.9	1,329,083	782,305
318	–5,841	–8,985.3				

Acknowledgments

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