Sigma J Eng & Nat Sci 38 (4), 2020, 1767-1780

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

BOX-BEHNKEN DESIGN OPTIMIZATION OF ELECTRO-FENTON/-PERSULFATE PROCESSES FOLLOWING THE ACIDIFICATION FOR TSS REMOVAL FROM BIODIESEL WASTEWATER

Senem YAZICI GUVENC*[1], Gamze VARANK[2]

[1]*Dept. of Environmental Eng., Yıldız Technical University, ISTANBUL;* ORCID: 0000-0002-2877-0977
[2]*Dept. of Environmental Eng., Yıldız Technical University, ISTANBUL;* ORCID: 0000-0003-3437-4505

Received: 09.05.2020 Revised: 23.09.2020 Accepted: 26.09.2020

ABSTRACT

In this study, biodiesel wastewater was first subjected to acidification process, and then in the second step, Electro-Fenton (EF) and Electro-Persulfate (EP) processes were applied as treatment method. Box-Behnken Design (BBD) method was used for the optimization of process parameters in total suspended solids (TSS) removal from biodiesel wastewater, and for formation of mathematical model. Current (1-4 A), H_2O_2/ Chemical Oxygen Demand (COD) (0.4-2.0) and time (15-45 min) for EF process and current (1-4 A), persulfate/COD (1-5) and time (15-45 min) for EP process were selected as the independent variables whereas TSS removal was selected as response. Optimum conditions were determined by means of variance analysis (ANOVA), and response surface graphics, and second degree regression models were developed by the use of Design Expert 11.0.1.0 software program for the estimation of TSS removal. According to the results obtained by the application of response surface method, correlation coefficients of second degree polynomial equation were determined as very high for the TSS removal of both processes, and the model's compliance was observed. Model's correlation coefficient (R^2) for EF and EP processes were determined as 92.67% and 93.03% respectively. High R^2 values indicate that the experimental data are in conformity with the model's results. As the result of experimental study actualized under optimum conditions determined by the model for obtaining maximum contaminant removal, TSS removal efficiencies were determined as 98.9% and 90.6% respectively for the EF and EP processes. EF and EP processes, following the acidification process, are suitable treatment alternatives for the removal of TSS from biodiesel wastewater, and BBD method is suitable for the optimization of process.
Keywords: Biodiesel wastewater, electro-fenton, electro- persulfate, Box-Behnken Design.

1. INTRODUCTION

Increasing energy requirement, increase in the prices of crude oil, global warming arising from greenhouse gas emissions, environmental pollution, and rapid decrease in the amount of fossil fuels have directed to seeking alternative energy resources. Due to advantages of biodiesel as being a renewable energy resource as an alternative energy resource, as being a non-toxic fuel, as having less harmful emission, and as being renewable and biodegradable, it forms an alternative to petroleum based fuels [1, 2]. Biodiesel waste is able to be generated from animal fat

* Corresponding Author: e-mail: syazici@yildiz.edu.tr, tel: (212) 383 53 83

and domestic sludge, but its main raw material is vegetable oils [3]. Biodiesel (fatty acid with methyl esters, or with eth yl esters) is being generated as the result of transesterification in the presence of triglycerides (vegetable oil and animal fat), alcohols such as methanol and ethanol, and basic or acidic catalyst [4-6]. But the generated biodiesel includes various contaminants such as free glycerol, soap, methanol or ethanol, free fatty acids, catalyst and glyceride, and in case these contaminants are not removed, they show negative effect on the performance and resistance of diesel engines [5]. For this reason, it is required to apply purification process for purifying biodiesel from contaminants. During the classic purification method, high amount of wastewater, required to be treated prior discharge, forms [7].

Biodiesel wastewaters have a complex structure. Despite the wastewater has high pH value, and high rate of oil and solid matter content depending on residual alkali catalyst, and thus high concentrations of COD and TOC content, it includes low concentrations of nitrogen and phosphorus constituents [4]. It is not possible for biodiesel wastewater, having high COD and low nitrogen concentration, to be directly directed to biological treatment. The characteristic structure of wastewater requires the use of physico-chemical processes, advanced oxidation processes or integrated systems [8-10].

Advanced oxidation processes (AOPs) are ones that ensure disintegration of contaminants in the presence of a strong oxidant and catalyst. Hydroxyl and sulfate radicals generated in AOPs have high oxidation levels. At the beginning of AOPs comes the EF process in which hydroxyl radicals are being used as strong oxidant, and which ensure ease of implementation, low reaction time, simple installation, high rate of contaminant removal and formation of low amounts of sludge. EF process is an effective advanced oxidation process in which the iron ions –used as catalyst as different from the classic Fenton process- form on the anodic surface by the dissolution of electrolyte, and which ensure the formation of hydroxyl radicals and the disintegration of organic contaminants by the addition of H_2O_2 under acidic conditions and by the generation of H_2O_2 in the presence of oxygen in cathodic area (Eq. 1-3) [11].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Persulfate is a new alternative chemical oxidant being extensively used in the treatment of wastewater. It is a stable and strong oxidant having oxidation potential with E_0 =2.01 V. Various activation methods are being used for the formation of sulfate radicals –from persulfate- which are stronger oxidants having oxidation potential at the range of E_0 =2.5-3.1 V [12, 13]. For the activation of persulfate, transition metals [14, 15], UV [16], and heat [17] are extensively used activation methods. Iron ion is a homogenous and conventional catalyst for the formation of radical from oxidants such as hydrogen peroxide and persulfate [18].

$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{-} + Fe^{3+} + SO_4^{2-} \quad (4)$$

Fe^{2+} ion mix in the solution electrochemically by anodic dissolution in the electrochemical reactor in which iron is being used as anode [19]. On the other hand, formation of Fe^{2+} is observed on the cathode by the reduction of Fe^{3+} arising as the result of reaction in the equation. Thus, the activation of persulfate, and amount of sulfate radical forming accordingly also shows increase [18].

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{+2} + 2e^- \quad (5)$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \quad (6)$$

Fe^{+2} ion reacts with the hydroxide forming on the cathode, and the arising coagulant agent ensure the settlement of organic and inorganic compounds over the adsorption mechanism. In this process that is defined as electropersulfate, coagulation and oxidation mechanisms actualize synchronously, and Fe^{3+} ion plays a significant role in both processes [20].

Today, response surface meth od is being used being effective in the design of tests of various water and wastewater treatment processes, in modeling of data, in the assessment of parameters affecting the process, and in the determination of optimum conditions for the responses [21]. Among all the response surface methods BBD is able to actualize optimization of process by the implementation of less test sets [22, 23]. Moreover, BBD allows the determination of interactive effects and measurement of effect level of parameters [24].

Previously in the literature, although the acidification process was applied to biodiesel wastewaters with high organic load, followed by different advanced oxidation processes, there is no study in the literature evaluating the performances of EF and EP process after the acidification process. The novelty of this study is that it both compares these two advanced oxidation processes and models and optimizes TSS removal using BBD.

In this study, biodiesel wastewater was first subjected to acidification process, and then in the second step, EF and EP processes were applied as treatment method. By the EF and EP processes, TSS removal from wastewater, optimization of variables affecting the performance of process, and determination of interaction among the variables were intended. Combined effects of independent variables (current, H_2O_2 or Persulfate/COD ratio, and time) on the efficiencies of removal were determined by the use of BBD method by which the mathematical models are being developed, and by which 3 dimensional surface graphs are being obtained.

2. MATERIALS AND METHODS

2.1. Biodiesel Wastewater

Biodiesel production wastewater used in experimental studies was obtained from biodiesel production plant operating in Tuzla, Istanbul. In the plant frying and cooking oil waste is used for biodiesel. About 30 L wastewater samples were taken from this stage and stored at 4 ºC to prevent biological activity. Prior to processes, the biodiesel wastewater had 128000 mg/L COD concentration, 2370 mg/L TSS concentration, 4300 mg/L oil and grease concentration, and 7.32 pH value, and following the acidification, COD concentration had decreased to 9500 mg/L, TSS concentration to 1300 mg/L, oil and grease concentration to 1360 mg/L, and its pH value had been 2.

2.2. Analytical Methods

The Standard Methods (SM) was performed to determine the COD, TSS and oil and grease values of biodiesel wastewater and treated wastewater samples (APHA 2005). The pH and conductivity values were measured using the WTW Multi 9620 IDS device. The analysis of each parameter in before and after treatment methods was performed in three replicates. Also, the pollutant removal efficiency was calculated using following Eq.(7);

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (7)$$

where, R represents the pollutant removal efficiency, C_0 is initial pollutant concentration (mg/L), C_t is the pollutant concentration of treated wastewater.

2.3. Pretreatment by Acidification

Raw biodiesel wastewater was acidified by the addition of 6 N H_2SO_4 to remove free fatty acids. According to the method used by Ngamlerdpokin et al. [5], pH of raw wastewater was adjusted to 2. 1000 mL wastewater was shaken for 2 h then left for 2 h to allow the complete phase separation between the upper oil-rich phase and the lower acidic aqueous phase. The remaining aqueous phase was collected for treatment by EF and EP processes.

2.4. Electro-Fenton/-Persulfate Processes

The schematic view of the electrochemical reactor in which experimental studies are carried out is shown in Figure 1. Plexiglass electrochemical reactor having 9 cm diameter and 13 cm height was used for experimental study. 500 mL pre-treated wastewater was fed to the reactor with two-mono polar iron electrodes having 6.4 cm x 12 cm dimensions for each experimental set. The distance between the iron electrodes was kept constant at 3 cm. Before each experimental set, the iron electrodes were washed by 1 N HCl solution and dried at 105 ºC. All experimental sets were carried out at room temperature. Before each experimental set, the pH value of pre-treated wastewater was measured and kept constant at 2 by using H_2SO_4. The experimental sets determined by BBD and the ranges of independent variables were given in Table 1.

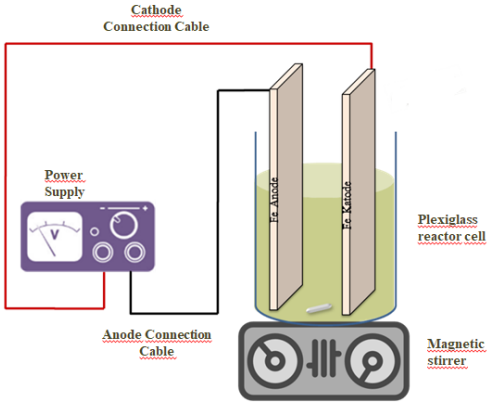

Figure 1. Schematic view of electrochemical reactor

2.5. Box-Behnken Design (BBD)

In this study, by the use of RSM, the optimization of operating parameters –being effective on the process- as well as the optimization of EF and EP processes was intended. RSM, by decreasing the experimental work – time load and cost of process, has the ability of analyzing the effects of complex operating parameters on the process as well as the ability of determination of optimum conditions [22, 25]. BBD that arises as an alternative to full factorial design, is a three-level defective factorial design and second degree multiple variable design method, and it is one of the sub-design models of RSM [26]. The number of test sets, required to be implemented for BBD Design, was determined by the use of Eq. (8).

$$\text{Experiment number} = 2k(k-1) + C_0 \quad (8)$$

In here, k expresses the number of factors, and C_0 expresses the number of center points. In BBD experimental design matrix, 3 center points were used, and thus the number of test sets was calculated as 15.

Design Expert 11.0.1.0 software program was used for actalizing the BBD experimental design. As seen in Table 1, A: current (A), B: H_2O_2 or Persulfate /COD ratio and C: reaction time were selected as independent variables, and coded levels for three level (-1, 0, 1) design were determined.

Table 1. Independent variables and their coded levels

Process	Symbol	Factor	Coded levels		
			-1	0	+1
EF	A	Current, A	1	2.5	4
	B	H_2O_2/COD	0.4	1.2	2.0
	C	Time, min	15	30	45
EP	A	Current, A	1	2.5	4
	B	Persulfate/COD	1	3	5
	C	Time, min	15	30	45

Each independent variable was coded as per the following Eq. (9):

$$x_i = \frac{X_i - X_0}{\Delta X} \quad (9)$$

In here, x_i represents the dimensionless value of the variable, Xi represents the real value of the variable, X_0 represents the real value of variable at center point, and ΔX represents the step change.

Statistical analysis of the model was made by assessing the ANOVA by the assistance of Design Expert 11.0.1.0 software program. In order to define the relationship in between the operating parameters and responses of the model, second degree equation in Eq. (10) was used.

$$M = \omega_0 + \sum_{i=1}^{k} \omega_i x_i + \sum_{i=1}^{k} \omega_{ii} x_i^2 + \sum \sum_{i<j} \omega_{ij} x_i x_j + \delta_r \quad (10)$$

M indicates the response estimated by the model, ω_0 indicates the constant of the model, ω_i indicates the linear coefficients, ω_{ii} indicates the quadratic coefficients, ω_{ij} indicates the interaction coefficients, k indicates the number of variables, and δ_r indicates the statistical error [24].

3. RESULTS AND DISCUSSION

Equations of the model developed in Design Expert 11.0.1.0 software program are used to define the relationship among the variables of the process and responses of the model. In this study, BBD with three independent variables – three levels was used, and its effects on the suspended solid selected as response were searched. The equation of BBD model, obtained for TSS removal from biodiesel wastewater by EF and EP processes, is given in Eqs. (11-12).

$$TSS\ removal_{EF} = +95.67 + 0.5875A - 0.05B + 0.7125C - 1.27AB + 0.85AC - 0.7250BC + 1.72A^2 - 0.0083B^2 - 0.4833C^2 \quad (11)$$

$$TSS\ removal_{EP} = +95.07 + 1.42A + 1.55B + 0.3C - 0.875AB - 0.175AC + 0.275BC + 0.6042A^2 + 0.0042B^2 + 0.1042C^2 \quad (12)$$

In here, A represents the current (A), B represents the H_2O_2/COD ratio, and C represent the reaction time (min). Estimated and experimental values obtained for TSS removal by EF and EP processes are listed in Table 2, and the graphical view of the data is given in Figure 2. It is being seen from Table 2 and Figure 2 that the data estimated by the assistance of the model and the experimental data are in conformity. Also, Figure 2 shows the normal plot of residuals on TSS removal for EF and EP processes. As seen in Figure 2, residual values had been randomly distributed at the lower and top part of the normal distribution line, and it can be said that they are placed very close to the line. Adequacy of the model may be assessed by applying diagnostic plots actual values versus predicted values). As seen from Figure 2 the predicted versus actual value plot approximates along a straight line implying that the second-order regression model was satisfactory.

The positive state of the coefficients indicates the synergic effect of the relevant parameter, and the negative state of the coefficients indicates the antagonistic effect of the relevant parameter

[27]. In the TSS removal from biodiesel wastewater by EF process, current and reaction time –from among linear parameters-, current –from among quadratic parameters-, and current and reaction time –from among interactive parameters- have positive effect. And in EP process, all linear parameters, all quadratic parameters, and the interactive parameters of H_2O_2/COD and reaction time have positive effect on the removal efficiency of TSS.

The R^2 values of graphs being above 90% express that the estimation capacity of regression equations is high. Determination coefficients of graphs, in which the data estimated by the model and experimentally obtained for removal of TSS from biodiesel wastewaters by EF and EP processes was compared, were determined as 92.67% and 93.03%, respectively. This means that only 7.33% and 6.97% of the total variation for EF and EP processes cannot be explained by the model. It is being seen from Figure 2 that experimental and estimated values obtained for the system's responses are very close to each other. R^2 value being higher than the value 0.80 is sufficient for the verification of conformity in between the experimental and estimated values [28].

Table 2. BBD of three independent variables and responses

				Factor			**EF** $_{\text{TSS removal, \%}}$			**Factor**			**EP** $_{\text{TSS removal, \%}}$	
Run	A	B	C	Current, A	H_2O_2/COD	Time, min	Act.	Pred.	Current, A	Persulfate/COD	Time, min	Act.	Pred.
1	-1	-1	0	1	0.4	30	95.00	95.56	1	1	30	91.20	91.83
2	+1	-1	0	4	0.4	30	99.10	99.29	4	1	30	96.20	96.43
3	-1	+1	0	1	2	30	98.20	98.01	1	5	30	96.90	96.68
4	+1	+1	0	4	2	30	97.20	96.64	4	5	30	98.40	97.78
5	-1	0	-1	1	1.2	15	96.30	96.45	1	3	15	93.70	93.88
6	+1	0	-1	4	1.2	15	95.40	95.92	4	3	15	96.50	97.08
7	-1	0	-1	1	1.2	45	96.70	96.18	1	3	45	95.40	94.83
8	+1	0	-1	4	1.2	45	99.20	99.05	4	3	45	97.50	97.33
9	0	-1	+1	2.5	0.4	15	94.50	93.79	2.5	1	15	94.40	93.60
10	0	+1	+1	2.5	2	15	95.10	95.14	2.5	5	15	96.10	96.15
11	0	-1	+1	2.5	0.4	45	96.70	96.66	2.5	1	45	93.70	93.65
12	0	+1	+1	2.5	2	45	94.40	95.11	2.5	5	45	96.50	97.30
13	0	0	0	2.5	1.2	30	95.80	95.67	2.5	3	30	94.80	95.07
14	0	0	0	2.5	1.2	30	95.80	95.67	2.5	3	30	95.00	95.07
15	0	0	0	2.5	1.2	30	95.40	95.67	2.5	3	30	95.40	95.07

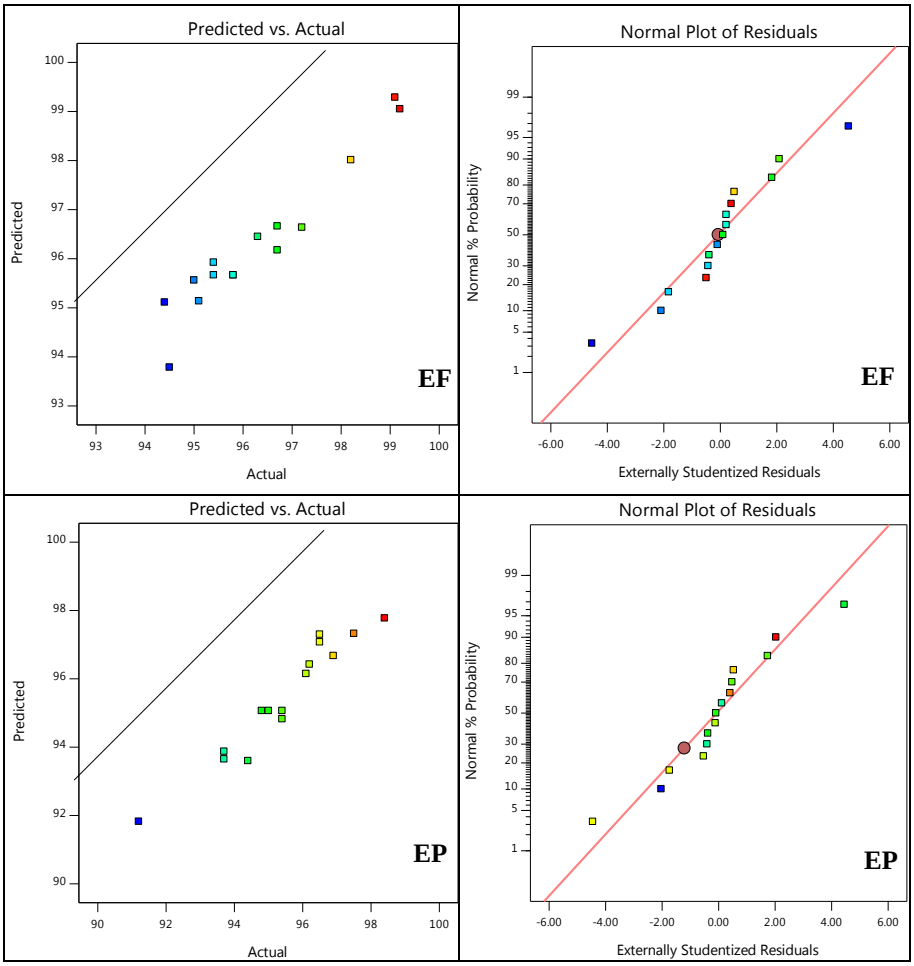

Figure 2. The predicted vs. actual plots and the normal plot of residuals

In Table 3, ANOVA analysis of regression parameters of quadratic model is given. High F value, low p value, and high sum of squares value obtained for the model indicate that the model is significant. According to the results of ANOVA of second degree response surface model applied for TSS removal from biodiesel wastewater by EF and EP processes, F values were obtained as 7.03 and 7.41 respectively, and p values were obtained as lower than the value of 0.05 for both processes. The Prob>F value being smaller than the value 0.05 indicates that the model is significant, and it being smaller than the value 0.0001 indicates that it is very significant [29]. And the values of sum of squares were found as high (Table 3). For EF process, current –from among linear and quadratic parameters-, and current and reaction time, and H_2O_2/COD ratio and reaction time –from among interactive parameters- were found to be significant. And for EP process, current and Persulfate/COD ratio –from among linear parameters- are significant. Lack of fit value was found to be insignificant for both processes. The lack of fit value being insignificant is an indicator that the predictability capacity of the model is high.

Pareto analysis is being applied in the determination of effect value of the factors. In Figure 3, graphical Pareto analysis is given. The contribution level of each parameter (linear, quadratic, or interactive) on TSS removal efficiency, being the system response was calculated by the following equation, and the graph of Pareto analysis by which the linear, quadratic and interactive effects of independent variables on the response were being shown is given in Figure 3. It is being observed from Figure 3 that reaction time and current –from among linear parameters-, current –from among quadratic parameters-, and again current and H_2O_2/COD ratio –from among interactive parameters- are effective in the TSS removal by EF process. The most effective linear parameters in TSS removal by EP process are current, and Persulfate/COD ratio. And Persulfate /COD ratio –from among quadratic parameters-, and current –from among interactive parameters- are effective.

$$P_i = \frac{b_i^2}{\sum b_i^2} x100 \ (i \neq 0) \quad (13)$$

Table 3. ANOVA results of quadratic models

Source	SS	DF	MS	F-value	P-value	Remark
			Electro-Fenton			
Model	**30.66**	**9**	**3.41**	**7.03**	**0.0225**	**S**
A-Current, A	2.76	1	2.76	5.70	0.0627	NS
B-H_2O_2/COD	0.0200	1	0.0200	0.0413	0.8471	NS
C-Time, min	4.06	1	4.06	8.38	0.0340	S
AB	6.50	1	6.50	13.41	0.0146	NS
AC	2.89	1	2.89	5.96	0.0585	S
BC	2.10	1	2.10	4.34	0.0918	S
A^2	10.88	1	10.88	22.44	0.0052	S
B^2	0.0003	1	0.0003	0.0005	0.9825	NS
C^2	0.8626	1	0.8626	1.78	0.2398	NS
Residual	2.42	5	0.4848			
Lack of Fit	2.32	3	0.7725	14.48	0.0653	NS
Pure Error	0.1067	2	0.0533			
Corr. Total	33.08	14				
			Electro-persulfate			
Model	**41.04**	**9**	**4.56**	**7.41**	**0.0200**	**S**
A-Current, A	16.24	1	16.24	26.40	0.0037	S
B-Persulfate/COD	19.22	1	19.22	31.24	0.0025	S
C-Time, min	0.7200	1	0.7200	1.17	0.3288	NS
AB	3.06	1	3.06	4.98	0.0761	NS
AC	0.1225	1	0.1225	0.1991	0.6741	NS
BC	0.3025	1	0.3025	0.4916	0.5145	NS
A^2	1.35	1	1.35	2.19	0.1990	NS
B^2	0.0001	1	0.0001	0.0001	0.9923	NS
C^2	0.0401	1	0.0401	0.0651	0.8088	NS
Residual	3.08	5	0.6153			
Lack of Fit	2.89	3	0.9633	10.32	0.0896	NS
Pure Error	0.1867	2	0.0933			
Corr. Total	44.12	14				

*SS:Sum of square, MS: Mean square, S: Significant, NS: Not significant

Numeric optimization was applied based on response surface model for the determination of optimum process parameters for maximum TSS removal by EF and EP processes. Table 4 shows

the optimum conditions and maximum TSS removal effciencies for both processes. Optimized conditions are current of 3.85 A, H_2O_2/COD ratio of 0.67, and reaction time of 41.2 min for EF process; and current of 1 A, Persulfate/COD ratio of 1, and reaction time of 15.6 min for EP process. According to the experimental results obtained under the optimum conditions obtained by the assistance of the model, TSS removal efficiencies were determined as 98.9% and 90.6% for EF and EP processes, respectively. Additionally, TSS removal efficiencies were found to be 97.3% and 86.8% for EF and EP processes through validation experiments, respectively.

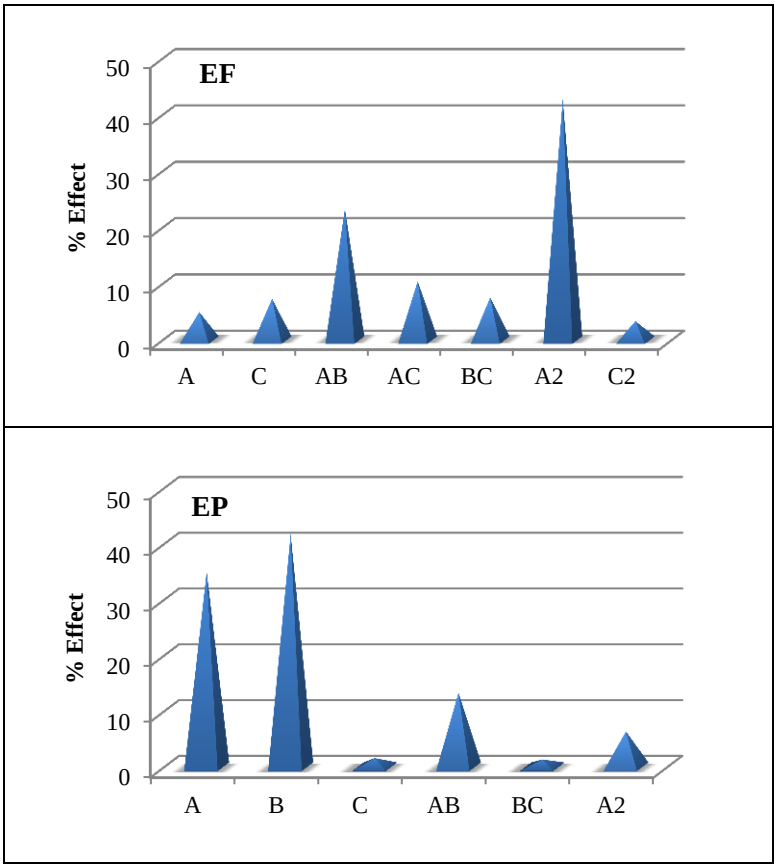

Figure 3. Pareto curve for TSS removal

Table 4. Optimum conditions for EF and EP processes and maximum TSS removal efficiencies

Parameter	Lower Limit	Upper Limit	**EF**	**EP**
A:Current	1	4	3.85	1
B_{EF}:H_2O_2/COD	0.4	2	0.67	-
B_{EP}: Persulfate/COD	1	5	-	1
C:Time	15	45	41.2	15.6
Pred. TSS removal, %	-	-	98.9	90.6
Act. TSS removal, %	-	-	97.3	86.8

Graphs of response surface model are given in Figure 4. As observed from Figure 4, while one variable is being kept fixed at the center, the other two variables are getting values within the determined limits. Response surface and contour graph are a function of a variable being kept fixed, and of two variables getting values within the limits.

As can be seen in Figure 4a, 4b, 4d and 4e, TSS removal increases as the electrical current increases at both processes. The electric current is the primary parameter that controls the reaction rate in electrochemical processes [30].

According to Faraday's Law, the increase electric current increases the formation of metal ions on the sacrificial anode surface. In electrochemical processes using iron electrodes, the increase in electric current increases the rate of iron ions formation.

Depending on the increase of electrical current, the formation of iron ions and the rate of persulfate degradation increases, which ensures the production of sulfate radical, thereby increasing the removal of organic matter. The generation of sulfate radicals was enhanced by the combination of electron transfer reactions and quenching of radicals [31]. At low current values H_2O_2 formation is not enough, and at high current values, O_2 and H_2 accumulate and settle due to the reactions occurring at the anode and the cathode [32]. Therefore, increasing current and H_2O_2/COD ratio increases TSS removal by increasing hydroxyl radical formation. This increase in the removal efficiency is shown in Figure 4a and 4c. Increasing the persulfate dose increases the possibility of more sulfate radical formation, however, as the amount of sulfate radicals reaches high values, excess sulfate radicals in the solution react with each other instead of reacting with organic matter and as a result persulfate formation occurs again [33]. As can be seen from Figure 4d and 4f, TSS removal efficiency increases as the Persulfate/COD ratio increases. It can be observed from Figure 4b and 4c that TSS removal efficiency shows increase up to a specific reaction time, and then that the efficiency does not change significantly as the reaction time increases. In EF process, organic matter rapidly degrades in the initial 30 minutes. As for EP process, Figure 4e and 4f show that the reaction time of 15 minutes is sufficient for maximum TSS removal.

Similar to this study, high TSS removal efficiencies were obtained by Chavalparit and Ongwandee [34], Srirangsan et al. [35].

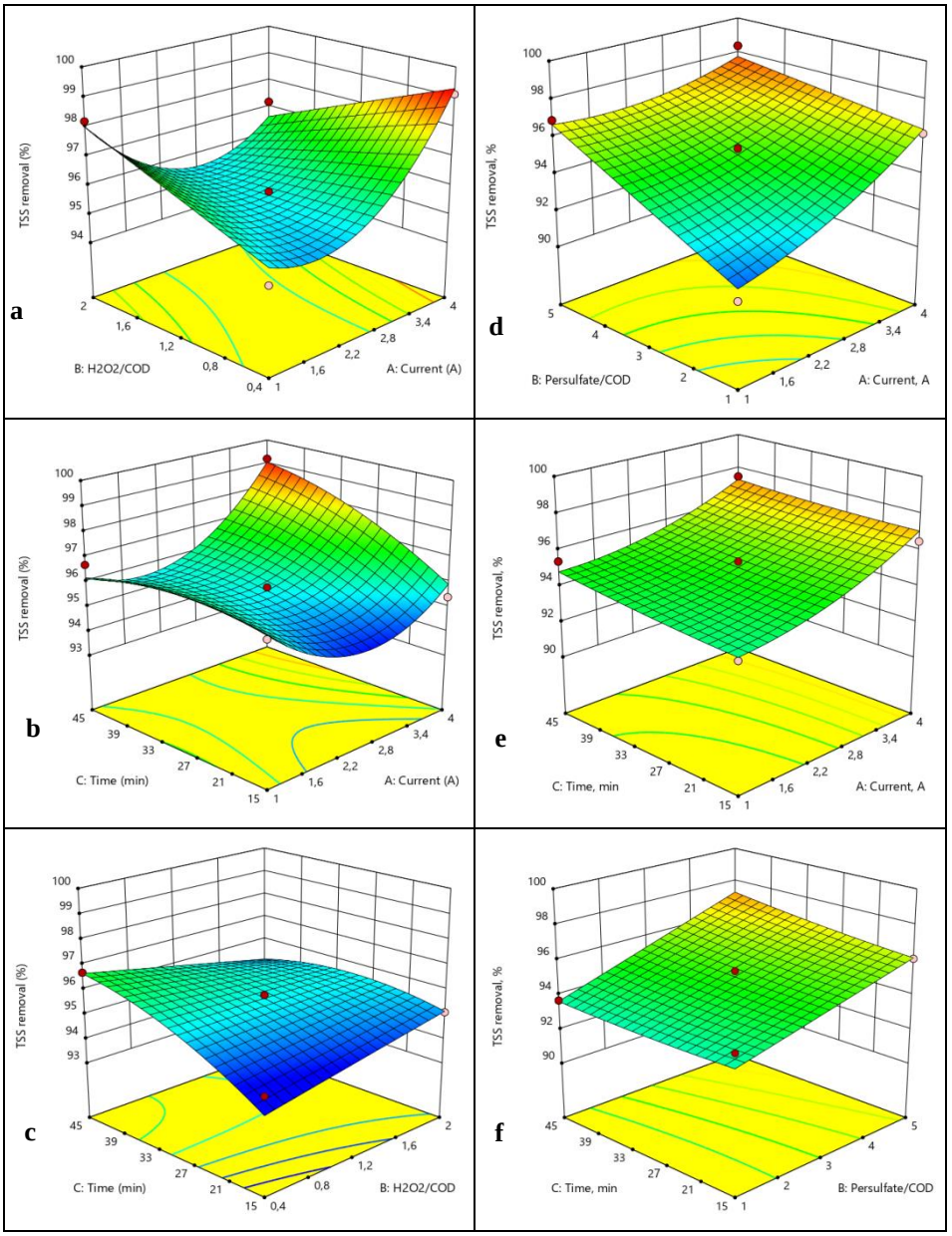

Figure 4. 3-D plots showing effects of independent variables for EF (a-b-c) and EP (d-e-f) processes

4. CONCLUSION

In this study, treatment of biodiesel wastewater by EF and EP processes following acidification process was investigated. The removal of TSS from biodiesel wastewater was modeled using the BBD, which is one of the response surface method designs. According to ANOVA results, 92.67% and 93.03% of the high determination coefficients for EF and EP processes, respectively. TSS removal efficiencies were determined as 98.9% and 90.6% for EF and EP processes, respectively. Optimized conditions are current of 3.85 A, H_2O_2/COD ratio of 0.67, and reaction time of 41.2 min for EF process; and current of 1 A, Persulfate/COD ratio of 1, and reaction time of 15.6 min for EP process. This validation explains good correlation between the values of experimental and predicted responses and the reliability of modeling by RSM. Sequentially applied acidification-both processes are suitable treatment alternatives for TSS removal from biodiesel wastewater.

Acknowledgment

Authors acknowledge the financial support by "Yildiz Technical University-The Scientific Research Projects Coordinatorship" with the research project number of FBA-2020-3906."

REFERENCES

[1] Biermann U., Bornscheuer U., Meier M.A.R., Metzger J.O., Schafer H.J., (2011) Oils and Fats As Renewable Raw Materials in Chemistry, *Angewandte Chemie International Edition*, 50, 3854– 3871.

[2] Bharathiraja B., Yogendran D., Kumar R., Chakravarthy M., Palani S., (2014) Biofuels from Sewage Sludge-A Review, *International Journal of ChemTech Research*, 6, 974–4290.

[3] Brito G.F.S., Oliveira R., Grisolia C.K., Guirra L.S., Webera I.T., Almeida F.V., (2019) Evaluation of Advanced Oxidative Processes in Biodiesel Wastewater Treatment, *Journal of Photochemistry & Photobiology A: Chemistry*, 375, 85–90.

[4] Chavalparit O., Ongwandee M., (2009) Optimizing Electrocoagulation Process for The Treatment of Biodiesel Wastewater Using Response Surface Methodology, *Journal of Environmental Sciences*, 21, 1491–1496.

[5] Ngamlerdpokin K., Kumjadpai S., Chatanon P., Tungmanee U., Chuenchuanchom S., Jaruwat P., Lertsathitphongs P., Hunsom M., (2011) Remediation of Biodiesel Wastewater by Chemical and Electro-Coagulation: A Comparative Study, *Journal of Environmental Management*, 92, 2454-2460.

[6] Low S.C., Gan G.K., Cheong K.T., (2011) Separation of methyl ester from water in a wet neutralization process, *Journal of Sustainable Energy Engineering*, 2, 15–19.

[7] Berrios M., Skelton R.L., (2008) Comparison of Purification Methods of Biodiesel, *Chemical Engineering Journal*, 144, 459-465.

[8] De Boni L.A.B., Goldani E., Milcharek C.D., Santos C.D., Dos F.A., (2007) Physicochemical Treatment of Wastewater from Biodiesel Purification, *Periód Tch Quím*, 4, 41–50.

[9] Phukingngam D., Chavalparit O., Somchai D., Ongwandee M., (2011) Anaerobic Baffled Reactor Treatment Of Biodiesel-Processing Wastewater with High Strength of Methanol and Glycerol: Reactor Performance and Biogas Production, *Chemical Papers*, 65, 644–651.

[10] Patiño K.V., Arroyave S.M., Marín J.M., (2012) Electrochemical oxidation and ozonation applied to the treatment of wastewaters from biodiesel production, *Information's Technological*, 23, 41–52.

[11] Díez A.M., Iglesias O., Rosales E. , Sanromán M.A., Pazos M., (2016) Optimization of two-chamber photo electro Fentonreactor for the treatment of winery wastewater, *Process Safety and Environmental Protection*, 101, 72–79.

[12] Jaafarzadeh N., Omidinasab M., Ghanbari F., (2016) Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater, *Process Safety and Environmental Protection*, 102, 462–472.

[13] Zhang H., Wang Z., Liu C., Guo Y., Shan N., Meng C., L. Sun, (2014) Removal of COD from Landfill Leachate by an Electro/Fe2+/peroxydisulfate Process, *Chemical Engineering Journal*, 250, 76–82.

[14] Oh W.D., Dong Z., Lim T.T., (2016) Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: current development, challenges and prospects, *Applied Catalysis B: Environmental*, 194, 169–201.

[15] Wei X., Gao N.,Li C., Deng Y., Zhou S., Li L., (2016) Zero-valent iron (ZVI) activation of persulfate (PS) for oxidation of bentazon in water, *Chemical Engineering Journal*, 285, 660-670.

[16] Moradi M., Ghanbari F., Manshouri M., Angali K.A., (2016) Photocatalytic degradation of azo dye using nano-ZrO2/UV/Persulfate: Response surface modeling and optimization, *Korean Journal of Chemical Engineering*, 33, 539–546.

[17] Park S., Lee L.S., Medina V. F., Zull A., Waisner S., (2016) Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation, *Chemosphere*, 145, 376-383.

[18] Akbari S., Ghanbari F., Moradi M., (2016) Bisphenol A degradation in aqueous solutions by electrogenerated ferrous ion activated ozone, hydrogen peroxide and persulfate: Applying low current density for oxidation mechanism, *Chemical Engineering Journal*, 294, 298-307.

[19] Moradi M., Ghanbari F., (2014) Application of response surface method for coagulation process in leachate treatment as pretreatment for Fenton process: Biodegradability improvement, *Journal of Water Process Engineering*, 4, 67-73.

[20] Ahmadi M., Ghanbari F., (2016) Optimizing COD removal from greywater by photoelectro-persulfate process using Box-Behnken design: assessment of effluent quality and electrical energy consumption, *Environmental Science and Pollution Research*, 23, 19350–19361.

[21] Sangal V.K., Kumar V., Mishra M.I., (2013) Optimization of a divided wall column for the separation of C4–C6 normal paraffin mixture using Box–Behnken design, *Computers & Chemical Engineering*, 19, 107–119.

[22] Ahmadi M., Rahmani K., Rahmani A., Rahmani H., (2017) Removal of benzotriazole by photo-Fenton like process using nano zero-valent iron: response surface methodology with a Box–Behnken design, *Polish Journal of Chemical Technology*, 19, 104–112.

[23] Mohadesi M., Shokri A., (2019) Treatment of oil refinery wastewater by photo-Fenton process using Box–Behnken design method: kinetic study and energy consumption, *International Journal of Environmental Science and Technology*, 16, 7349–7356.

[24] Kaur P., Sangal V.K., Kushwaha J.P., (2019) Parametric study of electro-Fenton treatment for real textile wastewater, disposal study and its cost analysis, *International Journal of Environmental Science and Technology*, 16, 801–81.

[25] Sahoo C., Gupta A.K., (2012) Optimization of photocatalyticdegradation of methyl blue using silver ion doped titaniumdioxide by combination of experimental design and responsesurface approach, *Journal of Hazardous Materials*, 215, 302–310.

[26] Khodadoust S., Ghaedi M., (2014) Application of response surface methodology for determination of methyl red in water samples by spectrophotometry method, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 133, 87–92.

[27] Bajpai S., Gupta S.K., Dey A., Jha M.K., Bajpai V., Joshi S., Gupta A., (2012) Application of Central Composite Design approach for removal of chromium (VI) from aqueous solution using weakly anionic resin: Modeling, optimization, and study of interactive variables, *Journal of Hazardous Materials*, 227–228, 436-444.

[28] Olmez T., (2009) The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology, *Journal of Hazardous Materials*, 162, 1371-1378.

[29] Sangeetha V., Sivakumar V., Sudha A., Kannan, K. (2015) Electrochemical Degradation of Sago wastewater using Ti/PbO_2 Electrode: optimisation using Response Surface Methodology, *International Journal of Electrochemical Science*, 10, 1506 – 1516.

[30] Parsa J.B., Vahidian H.R., Soleymani A.R., Abbasi M. (2012) Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption, *Desalination*, 44, 29-35.

[31] Chan T.W., Graham N.J.D., Chu W. (2010) Degradation of iopromide by combined UV irradiation and peroxydisulfate, *Journal of Hazardous Materials*, 181, 508–513.

[32] Zhou X., Hou Z., Lv L., Song J., Yin Z. (2020) Electro-Fenton with peroxi-coagulation as a feasible pre-treatment for high-strength refractory coke plant wastewater: Parameters optimization, removal behavior and kinetics analysis, *Chemosphere*, 238, 124649.

[33] Akbari S., Ghanbari F., Moradi M. (2016) Bisphenol A degradation in aqueous solutions by electrogenerated ferrous ion activated ozone, hydrogen peroxide and persulfate: Applying low current density for oxidation mechanism, *Chemical Engineering Journal*, 294, 298-307.

[34] Chavalparit O., Ongwandee M. (2009) Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology, Journal of Environmental Science, 21, 1491–1496.

[35] Srirangsan O., Ongwandee A., Chavalparit M. (2009) Treatment of biodiesel wastewater by electrocoagulation process, Environment Asia, 2, 15–19.