A design of experiment approach of cattle slaughterhouse wastewater treatment by electrocoagulation method

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ABSTRACT

The aim of this work was to formulate an empirical model using the data of the electrochemical treatment of cattle slaughterhouse wastewater. The empirical model was developed using response surface methodology with optimal design considering an irregular process space. As operational factors, current density, influent pH, flow rate, supporting electrolyte (NaCl or Na_2SO_4) concentrations, and H_2O_2 concentrations were examined. Under these circumstances, the aim was to represent the optimal region shown generally as a surface by obtaining the lowest possible value of chemical oxygen demand (COD). Therefore, as an outcome of experimentation, for current density, flow rate, initial pH of wastewater, and concentrations of H_2O_2 and Na_2SO_4, a linear effect was obtained on the removal of COD. The factors that have a quadratic effect on the removal efficiency of COD are pH and H_2O_2. There are interactive effects between current density and flow rate, between current density and H_2O_2 concentration, and between pH and flow rate on removal efficiency of COD. The best-fitting model was defined with a coefficient of multiple determination value (R^2) of 93.90%. In optimal conditions, according to the model, the removal efficiency of COD is maximized as 91.34% when the following conditions are utilized: current density of 32.36 mA/cm², pH of 4.07, the flow rate of 1,185.12 mL/min, the concentration of H_2O_2 of 0.005 M, and concentration of Na_2SO_4 of 0.008 M. The results showed that the model is appropriate for determining the factors for the electrochemical treatment of cattle slaughterhouse wastewater.

Keywords: Design of experiment; Electrocoagulation; Response surface methodology; Slaughterhouse wastewater; Wastewater treatment

1. Introduction

Processes such as slaughtering, processing, and washing of the equipment cause large amounts of wastewater in slaughterhouses [1]. Because slaughterhouse wastewater contains high concentrations of organic matter, it needs to be treated [2]. Moreover, some potential pathogen strains such as *Escherichia coli* and *Salmonella* could be present in these wastewaters [3]. Mainly aerobic [4,5] and anaerobic [1,6–9] treatments of slaughterhouse wastewater were studied by researchers. The high energy required for aeration and the huge amounts of sludge produced is the disadvantages of aerobic treatment [10]. On the other hand, the accumulation and floating of fats in the reactor in anaerobic treatment may cause a reduction in methanogenic activity and biomass wash-out, which slow down the treatment [10]. An alternative wastewater treatment technology is electrochemical treatment. The advantages of

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electrochemical treatment are using ordinary equipment, applying the method easily, producing low amounts of sludge, and operating at ambient temperature [11,12]. One of the electrochemical treatment methods is electrocoagulation. In electrocoagulation, electrolytic oxidation of the electrode forms the coagulants [13]. The contaminants and particulate suspension become unstable and unstable particles aggregate to form flocs for phase separation [13].

Electrocoagulation, which involves iron electrodes [11] and aluminum electrodes [2], can be summarized according to the reactions shown below.
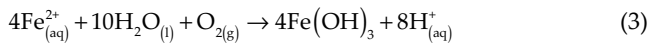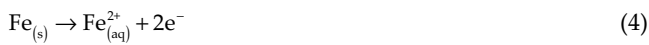
For iron electrodes:
Process I:
Anodic reaction:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \tag{1}$$

Cathodic reaction:

$$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \tag{2}$$

Reaction in solution:

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_3 + 8H^+_{(aq)} \tag{3}$$

Process II:
Anodic reaction:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{4}$$

Cathodic reaction:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{5}$$
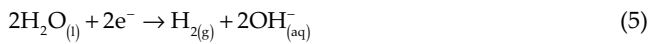
Reaction in solution:

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{6}$$

For aluminum electrodes:
Anodic reaction:

$$Al \rightarrow Al^{3+}_{(aq)} + 3e^- \tag{7}$$

Reaction in solution:

$$Al^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_3 + 3H^+_{(aq)} \tag{8}$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \tag{9}$$
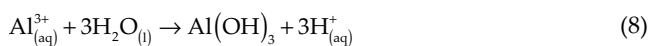
The treatment of slaughterhouse wastewater using electrocoagulation has been investigated in different ways by researchers. Bazrafshan et al. [14] used a bipolar configuration system with four parallel aluminum electrodes for the electrocoagulation of cattle slaughterhouse wastewater (CSW). The chemical oxygen demand (COD) was decreased from 5,817 to 13 mg/L. Bayar et al. [15] investigated the electrocoagulation of poultry slaughterhouse wastewater using five aluminum cathodes and five aluminum anodes in a Plexiglas reactor and the COD of the wastewater was reduced from 2,170 to below 300 mg/L after 30 min of electrocoagulation. Siringi et al. [16] examined the electrocoagulation of meat and poultry processing wastewater using five iron electrodes in Plexiglas and KASELCO reactors separately and 95% COD removal efficiency was the highest removal efficiency achieved.

Despite a huge amount of scientific research has been on the treatment of slaughterhouse wastewater by electrocoagulation, little has been done to formulate empirical models [17,18]. In addition, a number of investigations have used response surface methodology (RSM) for optimization of the parameters of wastewater treatment [19–23]. Thus, an empirical model for several design factors like current density, pH, flow rate, supporting electrolyte, and hydrogen peroxide (H_2O_2) was developed through RSM to optimize the operational conditions for treatment of CSW using electrocoagulation. The present study uses an innovative approach that emphasizes an optimal design considering an irregular process space by using six operational factors. For current density, influent pH, flow rate, and concentrations of supporting electrolyte Na_2SO_4 and H_2O_2, the experiments were designed considering four different levels and with the supporting electrolyte, NaCl considering three different levels. The custom design option represents flexibility for the number of levels for each factor; some of the levels of factors are allowed to be symmetrical and some are not (Table 1). This helps researchers to avoid examining unnecessary, predefined, heuristically known experiment combinations.

2. Materials and methods

2.1. Wastewater and experimental details

The CSW used in this work was obtained from a local cattle slaughterhouse in Eskişehir, Turkey. The wastewater, which included washing water as well, was obtained prior to its entering the conventional treatment plant of the slaughterhouse. The initially measured values of the CSW were as follows: COD of 840 mg/L, the biochemical oxygen demand of 520 mg/L, the conductivity of 18.00 mS/cm, and pH of 7.0.

Table 1
Factors and levels of experiment

Name	Unit	L1	L2	L3	L4
A – current density	mA/cm²	10	20	30	40
Coded		−1	−0.3333	0.3333	1
B – pH		3	5	7	9
Coded		−1	−0.3333	0.3333	1
C – flow rate	mL/min	240	600	1,000	1,400
Coded		−1	−0.379	0.310	1
D – H_2O_2	M	0	0.02	0.04	0.08
Coded		−1	−0.5	0	1
E – Na_2SO_4	M	0	0.05	0.1	0.2
Coded		−1	−0.5	0	1
F – NaCl	M	0	0.05	0.1	
Coded		−1	0	1	

The electrocoagulation experimental setup is shown in Fig. 1. A laboratory-scale iron reactor, which was operated in recycling batch mode, was used for all the experiments. The iron reactor (750 mm in height, 35 mm in diameter, and 675 mL in effective volume) was used as the cathode. Three iron rods (11 mm in outer diameter and 720 mm in height) were located inside the reactor and employed as anodes (Fig. 1). All the electrodes were arranged vertically. The anodes were connected to the positive terminal and the cathode was connected to the negative terminal of a direct current (DC) power supply. A peristaltic pump was used to introduce 800 mL of CSW into the upflow reactor in each experiment.

pH was adjusted using H_2SO_4 or NaOH (1 N, Merck) to a desirable value for examining the effect of pH before each experiment. The supporting electrolytes Na_2SO_4 (Merck) and NaCl (Merck) were used in the experiments to investigate their effects. All chemicals used were analytical grade [24].

The initial concentration of COD in the CSW was measured. After that, a power supply (Statron T 25) provided the current. Each run was conducted for 90 min with a constant current applied. A pH meter (Hanna Instrument 301) and a conductivity meter (Radiometer Pioneer 30) were employed to measure the pH and the conductivity throughout the experiments, respectively. At the end of the experiments, the samples were collected from the effluent at periodic time intervals and centrifuged [23]. The closed reflux method [25] was performed to measure the COD of the effluent. Each sample was analyzed in duplicate. The iron shell and iron rods were washed thoroughly with dilute H_2SO_4 to polish them and washed with purified water at the beginning of each experiment [24].

2.2. Effects of current density, flow rate, pH, supporting electrode, and H_2O_2 on COD concentration

The electrocoagulation process is affected by numerous parameters.

Depending on Faraday's law, current density determines the amount of Fe^{2+} ions released in the electrocoagulation system and this phenomenon results in the appearance of coagulant as well [26].

$$m = \frac{itM}{nF} \tag{10}$$

where m, mass of iron dissolved (g Fe/cm^2); i, current density (A/cm^2); t, time (s); M, molecular weight of Fe (M = 55.85 g/mol); n, number of electrons involved in the oxidation reaction (n = 2); and F, Faraday's constant, 96,486 C/mol [26].

Flow rate, which can also be related to retention time, is another crucial parameter in the electrocoagulation system [19]. The reactants are carried to the surface of the electrode before the electrochemical conversion occurs. As a consequence of electrochemical conversion, the product formed, which is transferred from the electrode, is a coagulant [19]. Correspondingly, the removal efficiency of COD increases because a rising flow rate leads to a boost in mass transfer.

Electrocoagulation is affected by the initial pH because pH determines the type of iron hydroxide species

that appear during the electrocoagulation process [24]. Depending on the Pourbaix diagram of iron, the formation of soluble iron hydroxide species occurs at low and high pHs. The appearance of a hydroxide complex, which is $Fe(OH)^{4-}$, becomes dominant at a high pH and inhibits the development of flocs [19]. At an extremely acidic pH, the collapse of hydroxide ions leads to the appearance of a deficient amount of iron hydroxide [19]. Therefore, a value approximate to neutral pH can be considered to achieve higher COD removal efficiency.

The electrolytic conductivity of the water affects wastewater treatment using electrochemical processes. Current efficiency is enhanced by minimizing the resistance between the electrodes using a supporting electrolyte. Thus, the maximum removal efficiency in an electrocoagulation reactor can be achieved.

The presence of H_2O_2 is also influential in electrocoagulation. Certain hydroxyl radicals occur because of Fenton reactions and these hydroxyl radicals can be described as vigorous non-selective oxidants [24]. Because of oxidation, the removal efficiency of COD increases in electrocoagulation.
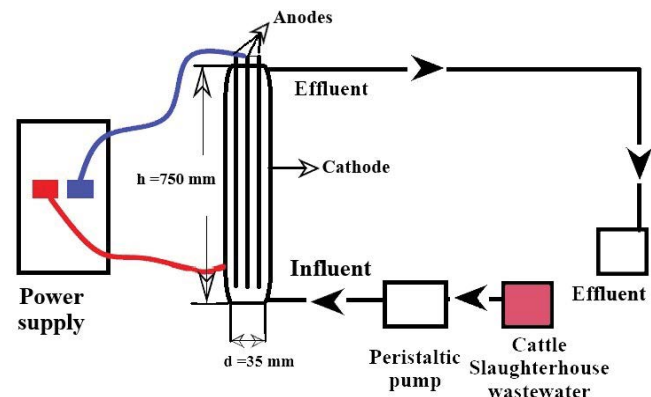

Fig. 1. Electrocoagulation experimental set-up.

2.3. Design of experiment

Obtaining valid and objective conclusions is the aim of planning and conducting experiments and so the design of experiment (DoE) is a method for conducting correctly outlined experiments considering progress. With a predetermined chart for a group of experiments and evaluating the data in line with specific methods, it is possible to obtain a large amount of information from small experiments. More than one variable can be examined at a time, so the experiment is less costly. Additionally, interactions between variables can be defined. Usually, experimental design involves a series of experiments that start by looking broadly at a large number of variables and then focus on a few critical ones [27].

2.4. Response surface methodology

First proposed by Box and Wilson [28], RSM is a tool using mathematical and statistical methods help to create models. The relationship is examined between some

input variables and one or more output variables, which is a response, and the objective is optimizing that so-called response [29]. This methodology basically provides optimization with the help of polynomials fitted to the data obtained through predetermined experiments. In the response surface method, although quadratic polynomials are generally used to model complex systems, it is possible to use higher-order polynomials. In this method, x_i represents the variables that should be more than one and y expresses the response as a value that needs to be optimized. The relation between x_i and y is shown as a function of x_i expressed in several levels:

$$y = f(x_1, x_2, x_3, \ldots, x_i, \ldots, x_k) + \varepsilon \tag{11}$$

where ε shows the error or the noise inspected in the response y, x_i is the independent variable i at x_i, and k at x_k shows the number of variables. The expected response is called the response surface and is denoted as follows:

$$E(y) = f(x_1, x_2, x_3, \ldots, x_i, \ldots, x_k) \tag{12}$$

Generally, in this type of problem, the structure of the interconnection between the independent variables and the response is not known. Therefore, the first action of the RSM is to check conditions to build a convenient estimation to reflect the accurate functional interconnection between y and all variables. If there is only a linear relation between input variables, the approximation function will be a first-order model.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_i x_i + \ldots + \beta_k x_k + \varepsilon \tag{13}$$

If there is an incurvation in the system, the response is modeled by a higher degree polynomial function acting as a second or higher-order model. The approximation function of the second-order mathematical model will include linear, nonlinear, and/or two-factor interaction terms of x_i variables.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \tag{14}$$

Analysis of variance (ANOVA) is developed based on subdividing the total variability into segments. The ANOVA table represents a statistical check of the adequacy of the approximation functions or mathematical models. The ANOVA table includes the sum of squares, which is used as a measure of the overall variability in data. Secondly, the ANOVA table includes degrees of freedom. It gives the number of values used in the exact determination of statistics to be free to change. Estimates of statistical parameters can be based on different amounts of data or information. Thirdly, the ANOVA table includes the mean square, which determines whether factors (treatments) are significant. The treatment means square is obtained by dividing the treatment sum of squares by the degrees of freedom. The treatment means square represents the variation between the sample means, the F-ratio, which can

be regarded as the basis of ANOVA. It enables simultaneous comparison of all sample means to determine whether two or more sample means represent different means and the calculated F-value is decided on by comparing it with the critical value determined according to a certain alpha level and degree of freedom. Finally, the p-value is a critical element of the ANOVA table. It indicates the amount of possible error when a "statistically significant difference" decision is made for comparison. The maximum acceptable level of this error is suggested and accepted as 0.05. If the p-value found in a test result is below 0.05, it means that there is a significant difference as a result of the comparison.

There is another indicator, called desirability. A function was described by Myers and Montgomery [29] that makes use of an objective function, called the desirability function. It reflects the desirable ranges for each response (d_i). The desirable ranges are from zero (least desirable) to one (most desirable). The objective function is a geometric mean of all response values. It also represents the optimum conditions for numerical optimization.

$$D = \left(d_1 \times d_2 \times \ldots\ldots \times d_n\right)^{\frac{1}{n}} = \left(\prod_{i=1}^{n} d_i\right)^{\frac{1}{n}} \tag{15}$$

3. Results and discussion

3.1. Proposed models as functions

In the present study, in a random order, 25 experimental trials were completed in keeping with the optimal (custom) design, which allows a flexible design structure to accommodate custom models, categorical factors, and irregular (constrained) regions. The software Design-Expert 11.0.5.0 (Stat-Ease Inc., Minneapolis, MN, USA) was used to obtain the results. The operating factors, which are independent variables, used in the present study are current density (A), pH (B), flow rate (C), H_2O_2 (D), Na_2SO_4 (E), and NaCl (F). The response is COD value (Y), considered the dependent factor. The performance of the design was evaluated by analyzing the minimization of the COD value. The results of the experiment are given in Table 2.

The calculations were performed by using the coded scale for coefficients of regression model computations. The lowest value setting for each factor is –1 and the highest value is +1 and how other levels are calculated is expressed by the formula below. Both the coded and actual scale models for factors were provided and are shown in Table 1 [30].

$$\text{Coded} = \frac{2 \cdot \left(\text{Actual setting} - \text{Average actual setting}\right)}{\left(\text{Range between low and high actual settings}\right)} \tag{16}$$

The ANOVA results for the current investigation at a 95% confidence interval are summarized in Table 3. The model's significance is proved by an F-value of 18.18. If the p-value is less than 0.05, this indicates that the model terms are significant. In the present study, A, E, AC, BC, BD, B^2, and B^2E are significant model terms. If the p-value is greater

than 0.10, this indicates that the model terms are not significant. It is clear that because of the lack of fit F-value is 0.52, this value is not significantly related to the pure error. Because fit to the model is wanted, a non-significant lack of fit is required.

The actual mathematical model is as follows:

$$\begin{aligned} y = {}& 1{,}083.51408 + 1.78247 \times \text{Current density} - 174.11766 \\ & \times \text{pH} - 0.539299 \times \text{Flow rate} - 6{,}556.82303 \times H_2O_2 \\ & + 7{,}424.00125 \times Na_2SO_4 - 0.009768 \times (\text{Current density} \\ & \times \text{Flow rate}) + 0.122433 \times (\text{pH} \times \text{Flow rate}) + 1{,}304.68254 \\ & \times (\text{pH} \times H_2O_2) - 2{,}096.37694 \times (\text{pH} \times Na_2SO_4) + 5.73977 \\ & \times \text{pH}^2 + 170.72895 \times (\text{pH}^2 \times Na_2SO_4) \end{aligned} \quad (17)$$

The coded mathematical model is as follows:

$$\begin{aligned} y = {}& 399.95 - 93.41A_1 + 127.74B_1 - 28.36C_1 + 50.85D_1 \\ & + 99.20E_1 - 84.98A_1C_1 + 213.03B_1C_1 + 156.56B_1D_1 \\ & - 14.29B_1E_1 + 205.31B_1^2 + 153.66B_1^2E \end{aligned} \quad (18)$$

In this formula, y is coded COD concentrations, A_1 is coded current density, B_1 is coded pH, C_1 is coded flow rate, D_1 is coded H_2O_2, and E_1 is coded Na_2SO_4. To make predictions considering the response for defined levels of any factor, the formula created for coded factors can be used. By checking the factor coefficients, the formula created for coded factors is effective for calculating the relative impact of each factor.

Table 4 also gives the R^2 and R^2_{adj} values for the formula created. These values clearly show that the model has sufficient capacity for the proposed mathematical models of the COD removal efficiency problem. Because the difference is less than 0.2, it is obvious that the predicted R^2 of 0.7380 is in line with the adjusted R^2 of 0.8873. The signal-to-noise ratio is measured by adequate precision. It analyzes the range of the predicted values by a formula to the average forecasting error. The ratio should be greater than 4. In this table, the ratio is 18.818 and it represents an adequate signal. Thus, it is inferred that the proposed model is appropriate to represent changes in the design space.

3.2. Diagnosing the model

The diagnostic details can best be grasped by viewing the most important diagnostic plots available such as

Table 2
Results of experiment with actual values

Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response	Removal efficiency (%)
	A – current density (mA/cm²)	B – pH	C – flow rate (mL/min)	D – H_2O_2 (M)	E – Na_2SO_4 (M)	F – NaCl (M)	COD (mg/L)	
1	30	9	600	0	0	0	198	76.43
2	40	7	600	0	0.05	0	288	65.71
3	40	7	600	0	0.2	0	386	54.05
4	40	7	240	0	0.1	0	235.2	72.00
5	40	3	600	0.02	0	0	268.8	68.00
6	10	9	240	0.04	0	0.05	312.5	62.80
7	10	5	1,000	0.02	0.05	0.1	399.2	52.48
8	10	7	1,000	0	0	0	390	53.57
9	10	7	240	0.02	0.1	0.05	400	52.38
10	40	3	600	0.04	0	0	252	70.00
11	40	5	600	0.08	0	0	235.2	72.00
12	20	5	240	0	0	0	354	57.86
13	20	3	1,000	0	0	0	299	64.40
14	40	7	1,000	0	0.1	0	252	70.00
15	40	7	600	0	0.05	0	202	75.95
16	40	7	1,400	0	0.1	0	235.2	72.00
17	20	7	600	0	0	0	235	72.02
18	30	7	600	0	0	0	202	75.95
19	40	7	600	0	0	0	159.6	81.00
20	40	7	600	0	0.05	0	288	65.71
21	40	3	600	0	0.1	0	604.8	28.00
22	40	7	600	0	0	0.05	201.6	76.00
23	40	5	240	0	0.1	0	504	40.00
24	40	9	600	0	0.1	0	403.2	52.00
25	40	7	1,400	0	0	0	84	90

Table 3
ANOVA for reduced cubic model by using Type III – partial sum of squares

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	2.924×10^5	11	26,584.72	18.18	<0.0001	Significant
A – current density (mA/cm^2)	66,637.03	1	66,637.03	45.57	<0.0001	
B – pH	3,351.22	1	3,351.22	2.29	0.1540	
C – flow rate (mL/min)	3,747.49	1	3,747.49	2.56	0.1334	
D – H$_2$O$_2$ (M)	6,759.95	1	6,759.95	4.62	0.0510	
E – Na$_2$SO$_4$ (M)	27,861.53	1	27,861.53	19.05	0.0008	
AC	18,782.08	1	18,782.08	12.84	0.0033	
BC	18,908.19	1	18,908.19	12.93	0.0033	
BD	9,761.84	1	9,761.84	6.68	0.0227	
BE	196.72	1	196.72	0.1345	0.7197	
B^2	50,960.11	1	50,960.11	34.85	<0.0001	
B^2E	17,404.02	1	17,404.02	11.90	0.0043	
Residual	19,011.33	13	1,462.41			
Lack of fit	14,080.66	11	1,280.06	0.5192	0.8082	Not significant
Pure error	4,930.67	2	2,465.33			
Cor. total	3.114×10^5	24				

Table 4
Fit statistics for proposed model

Std. Dev.	38.24	R^2	0.9390
Mean	295.57	Adjusted R^2	0.8873
C.V. (%)	12.94	Predicted R^2	0.7380
		Adequate precision	18.8179

normal probability plots of the residuals and residuals vs. predicted and run plots. In Fig. 2, the data points are approximately linear. There is a linear pattern and there is no pattern like an S-shaped curve. If there is an S curve in the pattern, it could show non-normality for the error term, meaning the need for transformation. Based on these results, there is no sign of a problem.

In Fig. 3, it is seen the plot represents predicted values vs. actual values. This plot demonstrates the effect of the model and makes a comparison with the null model. If there is no point far from the fitted line or out of the confidence lines and all of the points are close enough, there is a good fit; so here the data points are close enough to the fitted line.

In Fig. 4, the plot represents the residuals vs. predicted values (a) and run (b). These plots do not show any pattern. Therefore, they are not related and distributed randomly; hence there is really no evidence of a significant problem because all points are within the red control limits. This is important to be able to assume the model is correct.

There is a quadratic relationship between COD and pH, current density, flow rate, H$_2$O$_2$, and Na$_2$SO$_4$. A three-dimensional response surface plot of COD vs. current density and pH can be seen in Fig. 5a–d. Moreover, there is no linear relationship between COD and other factors.

In Fig. 6, according to the model, the optimal conditions have been determined. Compared to the best result obtained

Design-Expert® Software
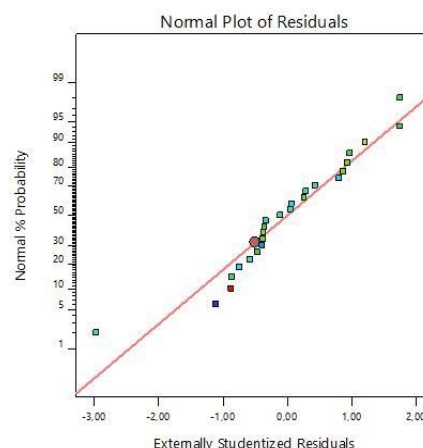
COD

Color points by value of
COD:
84 |||||||||| 604,8

Fig. 2. Normal probability plot.

by the experiment, 84, by the proposed mathematical model a lower result is yielded, 72.77 mg/L. It is obvious that RSM can calculate the best levels by using the appropriate equation.

The effects of current density, pH, flow rate, H_2O_2, and Na_2SO_4 on COD removal are depicted in Fig. 7. It demonstrates that the COD value decreased when pH changed from 9.0 to 4.07 and the current density increased to 36.32 mA/cm^2. Moreover, the COD value decreased when Na_2SO_4 decreased to 0.008 M and the flow rate increased to 1,185.12 mL/min. Based on the results, the minimum COD value is obtained as 72.77 mg/L under these circumstances.

It should be noted that all operating factors except pH affect the COD removal value in a linear way. In addition, there is no effect of NaCl on the slope of the increase or decrease in COD value. It is also worth noting that H_2O_2 does not affect the COD value as much as pH, flow rate, Na_2SO_4, or current density. The results in Fig. 7 are consistent with those in Fig. 8 showing that pH has a dominant effect on COD removal in addition to current density, flow rate, and Na_2SO_4 as variable factors.

The perturbation plot is depicted to compare the effects of all the factors on the response at a particular point. While all the other factors are held constant, the response

Fig. 3. Predicted vs. actual values plot.

Fig. 4. (a) Residuals vs. run and (b) residuals vs. predicted plots.
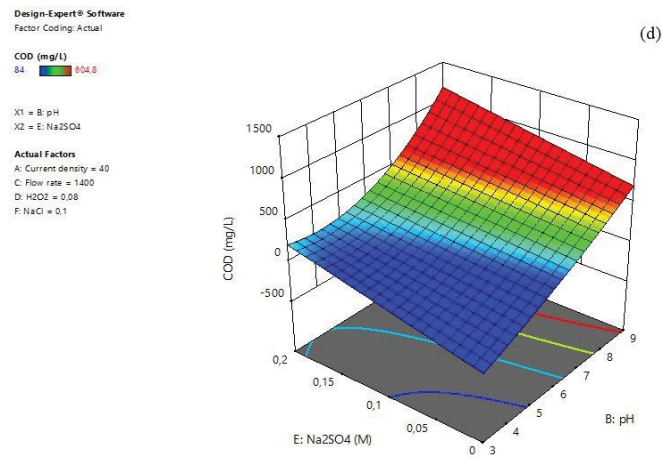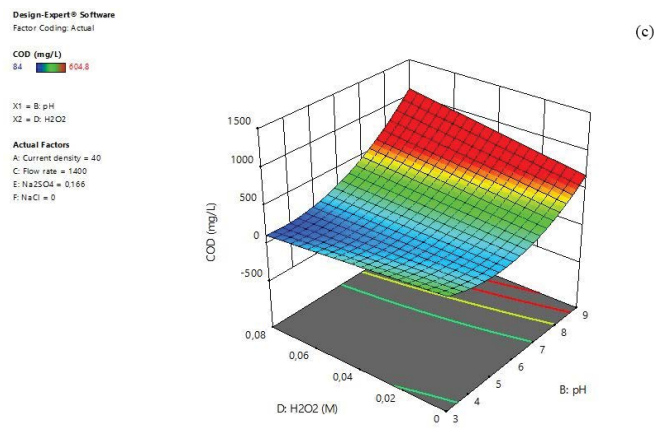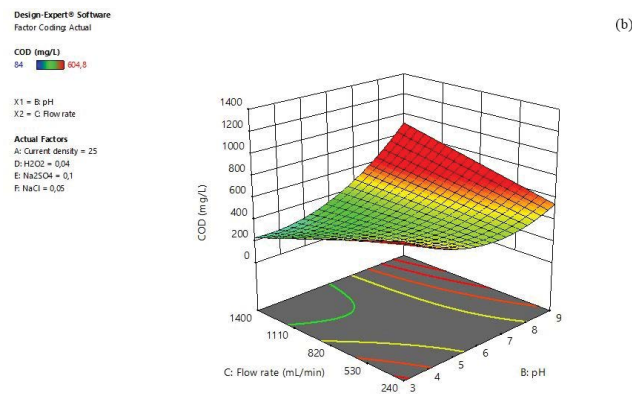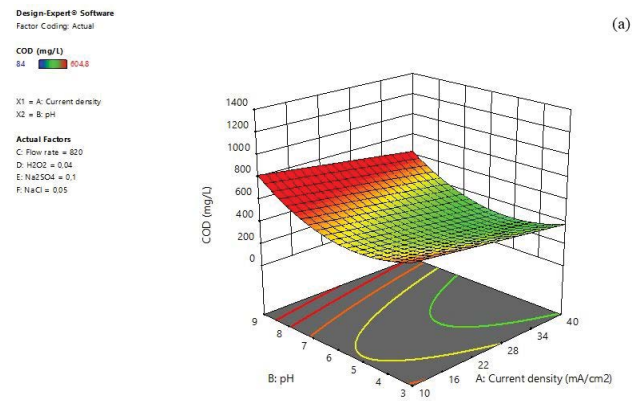
Fig. 5. Surface plot of (a) current density and pH, (b) pH and flow rate, (c) pH and H_2O_2, and (d) pH and Na_2SO_4.
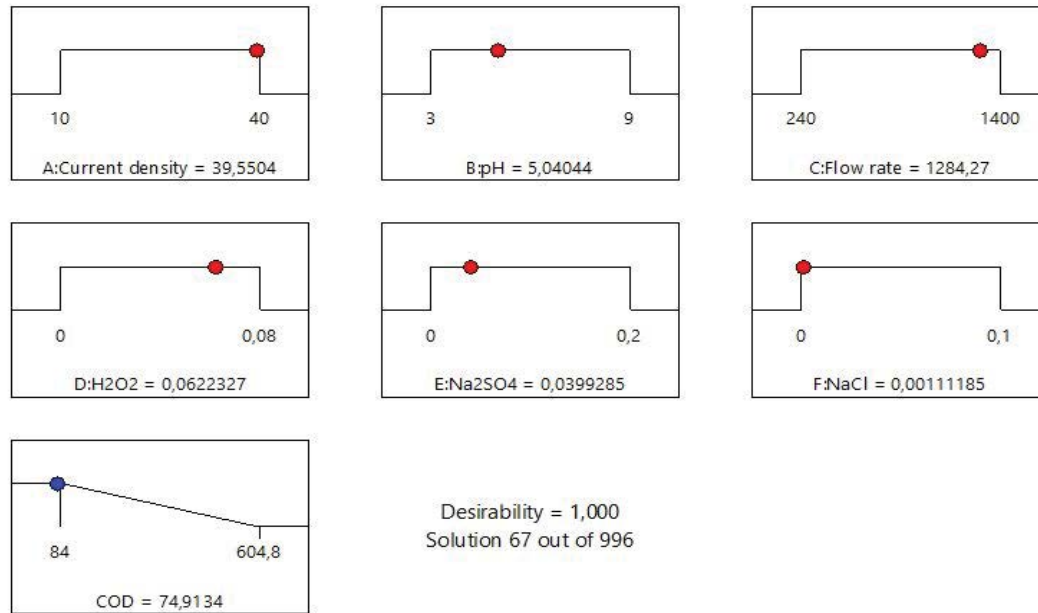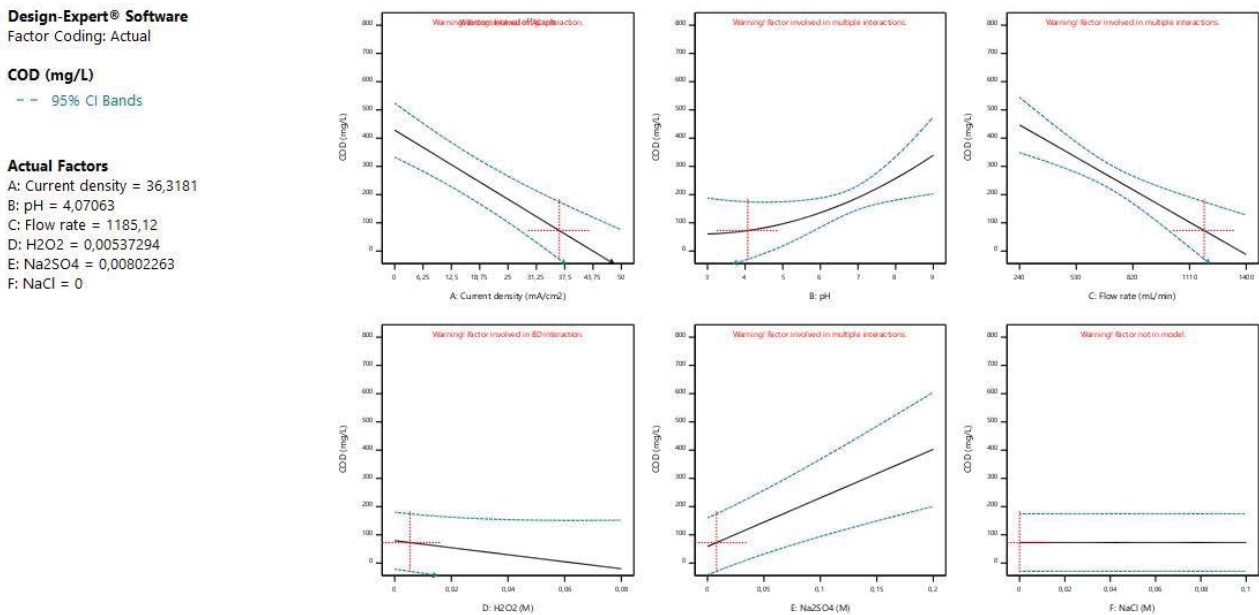
Fig. 6. Optimal conditions.

Fig. 7. All operating (independent variables) factors and their effects on COD value.

is plotted by changing only one factor in its range. In the beginning, it is set as a reference point at the midpoint represented as a coded 0 value for all the factors.

If a factor has an incline or incurvation, it shows that the response is easily affected by that factor. A comparably flat line shows that the factor does not affect response as inclined ones. In the present study, there are six factors, so the perturbation plot could be used to find which response is sensitive to which factors. As seen in Fig. 8, the response is highly sensitive to pH, flow rate, Na_2SO_4, and current density but less sensitive to H_2O_2.

As explained above, the obtained findings expressed by mathematical functions indicate that the removal efficiency of COD is highly correlated with selected factors but not with the supporting electrolyte NaCl.

3.3. Optimization and validation experiment

An adequacy check of the developed regression model is necessary by comparing the data created by the model developed with the experimental data. In the literature, for rechecking the regression model and its prediction

accuracy, Zularisam et al. [31] and Davarnejad and Sahraei [32] describe the validation process. The present study uses the same method for verification. Table 5 indicates the error value between actual experiment values and predicted values by the mathematical model created.

According to the software, this error is acceptable because, as shown in Table 4, the predicted R^2 of 0.7380 is in reasonable agreement with the adjusted R^2 of 0.8873. Thus, the difference is less than 0.2, which is the desired condition. Furthermore, adequate precision should be greater

Design-Expert® Software
Factor Coding: Actual

COD (mg/L)

Actual Factors
A: Current density = 36,3181
B: pH = 4,07063
C: Flow rate = 1185,12
D: H2O2 = 0,00537294
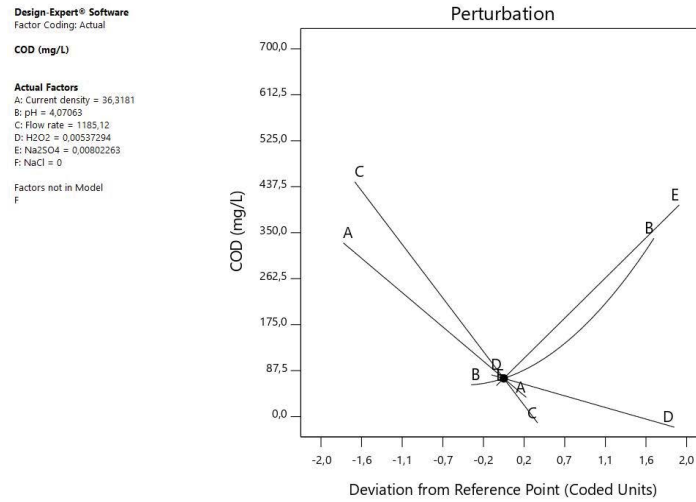E: Na2SO4 = 0,00802263
F: NaCl = 0

Factors not in Model
F

Fig. 8. Perturbation plot of independent variables.

Table 5
Results of operating conditions with experimental design and predicted values by using model

Run	% Error	Residual	Actual COD value	Predicted COD value
1	0.71	1.41	198.00	196.59
2	20.42	58.80	288.00	229.20
3	2.71	−10.46	386.00	396.46
4	32.33	−76.03	235.20	311.23
5	9.24	−24.83	268.80	293.63
6	1.82	−5.69	312.50	318.19
7	2.52	−10.08	399.20	409.28
8	1.59	6.18	390.00	383.82
9	5.10	20.40	400.00	379.60
10	4.45	11.23	252.00	240.77
11	0.37	0.87	235.20	234.33
12	2.45	−8.67	354.00	362.67
13	5.98	17.89	299.00	281.11
14	1.49	−3.76	252.00	255.76
15	13.46	−27.20	202.00	229.20
16	3.67	8.64	235.20	226.56
17	8.52	−20.01	235.00	255.01
18	6.05	−12.23	202.00	214.23
19	8.67	−13.85	159.60	173.45
20	20.42	58.80	288.00	229.20
21	1.46	−8.83	604.80	613.63
22	13.97	28.15	201.60	173.45
23	6.26	31.53	504.00	472.47
24	2.19	8.83	403.20	394.37
25	36.97	−31.05	84.00	115.05
Average % Error	8.51			

than 4 and it is 18.818 for the model produced. This result indicates an adequate signal and that the model can be used.

In numerical optimization, the optimum process parameters to obtain the minimum COD value were analyzed. In this step, the goals of all independent variables were to be in range. The goal for the COD value is minimization. The numerical optimization finds a point or points that maximize the desirability function. In the present study, there are a hundred solutions having a desirability function value of 1.00 and a value of desirability of 1.00 means that the model achieved all goals easily and independent variables are in their assigned target value range. The main aim is not to maximize the desirability value. However, desirability could be simply a mathematical method to find the optimum conditions.

In the present study, considering the variables in the model and to possibly achieve the minimum COD value, one of the conditions that have a desirability function value as 1.00 was selected as the optimal condition. In this condition, the COD value is minimized as 72.77 mg/L when the following conditions are utilized: current density of 32.36 mA/cm^2, pH of 4.07, the flow rate of 1,185.12 mL/min, the concentration of H_2O_2 of 0.005 M, and concentration of Na_2SO_4 of 0.008 M.

4. Conclusion

The aim of the present study was to develop an applicable model by using one of the main methods of DoE, namely RSM, for operational factors for the treatment of CSW using a recycling batch mode electrocoagulation reactor. There were six operational factors affecting the treatment of cattle slaughterhouse wastewater. In the experiments, each factor was identified with different levels. A prediction model for the best fit was defined. By using the designated model, the minimum COD value (72.77 mg/L) was obtained for the optimum condition with a current density of 32.36 mA/cm^2, pH of 4.07, the flow rate of 1,185.12 mL/min, the concentration of H_2O_2 of 0.005 M, and concentration of Na_2SO_4 of 0.008 M. The coefficient of determination value $\bar{R}^2$ is defined as 93.90% and 91.34% removal efficiency of COD was observed by the model prediction, which is pursuant to the experimental data that showed 90.00% removal efficiency of COD. Considering the results, a significant mathematical model could be achieved including each factor that had different levels. The designated mathematical model would provide flexibility in the design of experiment for researchers. Therefore, based on the experiments with different factors and levels, it can be concluded that a determined prediction model created by using RSM is effective for analyzing the optimum points and values of predefined factors with flexibility.

References

[1] V. Del Nery, M.H.Z. Damianovic, F.G. Barros, The use of upflow anaerobic sludge blanket reactors in the treatment of poultry slaughterhouse wastewater, Water Sci. Technol., 44 (2001) 83–88.

[2] U. Tezcan Un, A.S. Koparal, U. Bakir Oğütveren, Hybrid processes for the treatment of cattle- slaughterhouse wastewater using aluminum and iron electrodes, J. Hazard. Mater., 164 (2009) 580–586.

[3] L.S.S. Barros, L.A. Amaral, C.S. Lorenzon, J.L. Junior, J.G. Machado Neto, Potential microbiological contamination of effluents in poultry and swine abattoirs, Epidemiol. Infect., 135 (2007) 505–518.

[4] E.M. Baddour, N. Farhoud, M. Sharholy, I.M. Abdel-Magid, Biological treatment of poultry slaughterhouses wastewater by using aerobic moving bed biofilm reactor, Int. J. Environ. Res. Public Health, 3 (2016) 96–106.

[5] G. Najafpour, P.N. Naidu, A.H. Kamaruddin, Rotating biological contactor for biological treatment of poultry processing plant wastewater using *Saccharomyces cerevisiae*, ASEAN J. Chem. Eng., 2 (2002) 1–6, doi: 10.22146/ajche.50796.

[6] R. Rajakumar, T. Meenambal, P.M. Saravanan, P. Ananthanarayanan, Treatment of poultry slaughterhouse wastewater in hybrid upflow anaerobic sludge blanket reactor packed with pleated poly vinyl chloride rings, Bioresour. Technol., 103 (2012) 116–122.

[7] A.B.G. Valladão, M.C. Cammarota, D.M.G. Freire, Performance of an anaerobic reactor treating poultry abattoir wastewater with high fat content after enzymatic hydrolysis, Environ. Eng. Sci., 28 (2011) 299–307.

[8] P.C. Chávez, L.R. Castillo, L. Dendooven, E.M. Escamilla-Silva, Poultry slaughter wastewater treatment with an up-flow anaerobic sludge blanket (UASB) reactor, Bioresour. Technol., 96 (2005) 1730–1736.

[9] V. Del Nery, I.R. de Nardi, M.H.R.Z. Damianovic, E. Pozzi, A.K.B. Amorim, M. Zaiat, Long-term operating performance of a poultry slaughterhouse wastewater treatment plant, Resour. Conserv. Recycl., 50 (2007) 102–114.

[10] M. Kobya, E. Senturk, M. Bayramoglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard. Mater., 133 (2006) 172–176.

[11] U. Tezcan Un, E. Aytac, Electrocoagulation in a packed bed reactor-complete treatment of color and COD from real textile wastewater, J. Environ. Manage., 123 (2013) 113–119.

[12] J. Radjenovic, D.L. Sedlak, Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water, Environ. Sci. Technol., 49 (2015) 11292–11302.

[13] K. Eryuruk, U. Tezcan Un, U. Bakır Ogutveren, Electrochemical treatment of wastewaters from poultry slaughtering and processing by using iron electrodes, J. Cleaner Prod., 172 (2018) 1089–1095.

[14] E. Bazrafshan, F. Kord Mostafapour, M. Farzadkia, K.A. Ownagh, A.H. Mahvi, Slaughterhouse wastewater treatment by combined chemical coagulation and electrocoagulation process, PLoS One, 7 (2012) e40108, doi: 10.1371/journal.pone.0040108.

[15] S. Bayar, Y.Ş. Yıldız, A.E. Yılmaz, Ş. İrdemez, The effect of stirring speed and current density on removal efficiency of poultry slaughterhouse wastewater by electrocoagulation method, Desalination, 280 (2011) 103–107.

[16] D.O. Siringi, L. Mulimi, P. Home, J. Chacha, Pollutants removal using electro coagulation in meat and poultry processing wastewater, Int. J. Eng. Innovative Technol., 7 (2017) 16–24.

[17] J. Morales-Rivera, B. Sulbarán-Rangel, K.J. Gurubel-Tun, J. del Real-Olvera, V. Zúñiga-Grajeda, Modeling and optimization of COD removal from cold meat industry wastewater by electrocoagulation using computational techniques, Processes, 8 (2020) 1139–1151.

[18] M.H. Bui, Applying response surface methodology to optimize the treatment of swine slaughterhouse wastewater by electrocoagulation, Pol. J. Environ. Stud., 27 (2018) 1975–1981.

[19] U. Tezcan Un, A. Kandemir, N. Erginel, S. Eren Ocal, Continuous electrocoagulation of cheese whey wastewater: an application of response surface methodology, J. Environ. Manage., 146 (2014) 245–250.

[20] N. Rahman, M. Nasir, P. Varshney, A.M. Al-Enizi, M. Ubaidullah, S.F. Shaikh, M.A. Al-Adrabalnabi, Efficient removal of Pb(II) from water using silica gel functionalized with thiosalicylic acid: response surface methodology for optimization, J. King Saud Univ. Sci., 33 (2021) 101232–101239.

[21] M. Elazzouzi, K. Haboubi, M.S. Elyoubi, A. El Kasmi, Development of a novel electrocoagulation anode for real

urban wastewater treatment: experimental and modeling study to optimize operative conditions, Arabian J. Chem., 14 (2021) 102912, doi: 10.1016/j.arabjc.2020.11.018

[22] M.A. Mamelkina, F. Vasilyev, R. Tuunila, M. Sillanpää, A. Häkkinen, Investigation of the parameters affecting the treatment of mining waters by electrocoagulation, J. Water Process Eng., 32 (2019) 100929, doi: 10.1016/j.jwpe.2019.100929.

[23] M.O. Saeed, K. Azizli, M.H. Isa, M.J.K. Bashir, Application of CCD in RSM to obtain optimize treatment of POME using Fenton oxidation process, J. Water Process Eng., 8 (2015) e7–e16.

[24] K. Eryuruk, U. Tezcan Un, U. Bakır Ogutveren, Electrocoagulation in a plugflow reactor: the treatment of cattle abattoir wastewater by iron rod anodes, Int. J. Environ. Res., 8 (2014) 461–468.

[25] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation, 2012.

[26] M. Kumar, F.I.A. Ponselvan, J.R. Malviya, V.C. Srivastava, I.D. Mall, Treatment of bio-digester effluent by electrocoagulation using iron electrodes, J. Hazard. Mater., 165 (2009) 345–352.

[27] N.R. Tague, The Quality Toolbox, 2nd ed., ASQ Quality Press, Wisconsin, 2005.

[28] G.E.P. Box, K.B. Wilson, On the experimental attainment of optimum conditions, J. R. Stat. Soc. Ser. B (Methodological), 13 (1951) 1–45.

[29] R.H. Myers, D.C. Montgomery, C.M. Anderson-Cook, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, 4th ed., John Wiley & Sons Inc., New Jersey, 2016.

[30] Statease, 2021. Available at: https://www.statease.com/docs/v11/contents/advanced-topics/convert-coded-response-surface-model-to-actual/ (accessed 15 January 2021).

[31] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah Abdul Munaim, T. Matsuura, Application of coagulation–ultrafiltration hybrid process for drinking water treatment: optimization of operating conditions using experimental design, Sep. Purif. Technol., 65 (2009) 193–210.

[32] R. Davarnejad, A. Sahraei, Industrial wastewater treatment using an electrochemical technique: an optimized process, Desal. Water Treat., 57 (2016) 9622–9634.

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