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Response surface modeling of COD removal from metal cutting wastewaters via electrooxidation process: Effect of direct photovoltaic solar panel on energy consumption

Metal kesme atıksularından elektrooksidasyon prosesi ile KOİ gideriminin yanıt yüzey modellemesi: Doğrudan fotovoltaik güneş panelinin enerji tüketimine etkisi

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Abstract

Today, water and wastewaters are effectively treated with many treatment technologies. However, there are deficiencies in the integration of treatment technologies with renewable energy sources. In this study, the integration of solar energy, one of the renewable energy sources, into electrooxidation (EO) process, which is one of the new generation advanced wastewater treatment techniques, is provided. Parameters affecting the EO process such as pH, current density (C.D.) and electrolysis time (E.T.) was optimized by Box Behnken Design (BBD) on elimination of soluble Chemical Oxygen Demand (sCOD) from metal processing wastewater. The study also tried to determine the optimum conditions for the treatment of metal processing wastewater with EO process by developing different scenarios. The scenario in which the energy requirement was 18.33 kWh/m³ and the COD removal efficiency was 75.23%, i.e. the scenario that maximizes the COD removal efficiency and minimizes the energy consumption (E.C.), is considered to be appropriate. In this case, the optimum pH for the EO process was 5, C.D. was 80 A/m², E.T. was 22.15 minutes with a desirability of 1. At the optimum conditions (for the 2nd scenario), the E.C. of the EO process was fulfilled from solar panel in a ratio of 15% and 318% in overcast and sunny weather, respectively. Thus, it has been determined that the solar panel integrated EO process is an approach that reduces E.C. and accordingly operating cost, and also has the potential to obtain enough energy to be stored especially in sunny weather.

Keywords: Electrooxidation, Metal cutting wastewater, Graphite/Titanium electrode, Box-Behnken Design, Photovoltaic Solar Panel, Renewable energy.

Öz

Günümüzde su ve atıksular birçok arıtma teknolojisi ile etkin bir şekilde arıtılmaktadır. Ancak, arıtma teknolojilerinin yenilenebilir enerji kaynakları ile entegrasyonu konusunda eksiklikler bulunmaktadır. Bu çalışmada, yenilenebilir enerji kaynaklarından biri olan güneş enerjisinin yeni nesil ileri arıtma tekniklerinden biri olan elektrooksidasyon (EO) prosesine entegrasyonu sağlanmıştır. EO prosesini etkileyen pH, akım yoğunluğu (A.Y.) ve elektroliz süresi (E.S.) gibi parametreler Box Behnken Tasarımı (BBT) ile metal işleme atıksuyundan Çözünmüş Kimyasal Oksijen İhtiyacının (KOİ) giderimi üzerine optimize edilmiştir. Çalışmada ayrıca farklı senaryolar geliştirilerek metal işleme atıksularının EO prosesi ile arıtımı için optimum koşullar belirlenmeye çalışılmıştır. Enerji ihtiyacının 18.33 kWh/m³ ve KOİ giderim veriminin %75.23 olduğu senaryo, yani KOİ giderim verimini maksimize eden ve enerji tüketimini minimize eden senaryonun uygun olduğu düşünülmektedir. Bu durumda, EO prosesi için optimum pH 5, A.Y. 80 A/m², E.S. 22.15 dakika olmuştur. Optimum koşullarda (2. senaryo için), EO prosesinin enerji tüketimi kapalı ve güneşli havalarda sırasıyla %15 ve %318 oranında güneş panelinden karşılanmıştır. Böylelikle, güneş paneli entegreli EO prosesinin enerji tüketimini ve buna bağlı olarak işletme maliyetini azaltan, ayrıca özellikle güneşli havalarda depolanacak kadar enerji elde edilebilme potansiyeli olan bir yaklaşım olduğu belirlenmiştir.

Anahtar kelimeler: Elektrooksidasyon, Metal kesme atıksuları, Grafit/Titanyum elektrot, Box-Behnken Tasarımı, Fotovoltaik Güneş Paneli, Yenilebilir Enerji.

1 Introduction

Metal processing industry is an important water consuming and a large quantity of wastewater production sector. Metal processing wastewaters contain COD (Chemical Oxygen Demand), SS (suspended solids), heavy metals (mainly chromium, nickel, zinc and copper), solvents, oil and fat. To remove these pollutants, they generally use chemical treatment methods, although they vary according to the type of pollutants. Chemical processes treat wastewater but not enough to reuse of wastewater again to the production. Systems that are based on electrochemical technology to be used effectively to remove pollutants are being developed. The treatment of industrial wastewaters has lately seen an upsurge in the use of electrochemical reactors, particularly electrocoagulation (EC) [1], electrooxidation (EO) [2], and hybrid electrochemical processes [3]-[6]. Due to its numerous benefits, including its high organics degradation efficacy, cost-effectiveness, and ease of operation, the EO process plays a significant role in the

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treatment of wastewater from metal processing. COD removal efficiency of the electrochemical technologies from industrial wastewaters are reported by some researchers [7],[8]. In EO process electrodes made of inert metal or metal alloys (such as TiO_2, PlO_2, Ti/RuO_2, Ti/IrO_2, PbO_2, BBD, graphite, stainless steel) are used.

The degradation mechanism of organic matter by the EO process can be realized by two mechanisms as direct and indirect oxidation. Among these mechanisms, the direct oxidation process takes place in two stages. In the first stage, diffusion of organic pollutants from the bulk solution and adsorption of them on the anode electrode surface. In the second stage, oxidation of pollutants on the anode electrode surface by the direct electron transfer reaction (Eq. 1). [9].

$$M + R \rightarrow M(.R) + ne^- \rightarrow \text{products} \quad (1)$$

where R is an organic compound, M is an active site on the anode surface.

In the indirect oxidation, oxidation of water on the electrode surface and formation of hydroxyl radicals occurs. And thus formed hydroxyl radicals are adsorbed on the anode electrode surface and indirectly oxidize the organic pollutants (Eq 2-3) [10].

$$M + H_2O \rightarrow M(\ ^{\cdot}OH) + H^+ + e^- \quad (2)$$

$$M(\ ^{\cdot}OH) + R \rightarrow M + RO + H^+ + e^- \quad (3)$$

The effectiveness of the current utilized to release oxygen might be decreased. The Eq. 4 represents the oxygen release process [9].

$$M(\ ^{\cdot}OH) + H_2O \rightarrow M + O_2 + 3H^+ + 3e^- \quad (4)$$

The most important parameter that effects the operating cost in electrochemical methods is E.C. Minimization of the E.C. can be significantly decreasing the total operating cost. There are some methods to reduce energy consumption of the electrochemical processes as adding electrolytes, treating a pretreated wastewater but the most preferred method is the usage of renewable energy. The application of renewable energy on electrochemical systems is increased in recent years as an effective method of minimization of E.C. [11]-[14].

In order to enhance various pollutant removal processes by addressing the interactions between the variables, the use of statistical experimental design models has grown recently [15]. One of these statistical experimental design approaches is the response surface methodology (RSM), a regression analysis that forecasts the value of the dependent variable based on the controlled values of the independent [16]. In terms of identifying study results, this methodology has benefits as including identifying the ideal theoretical conditions, minimizing the number of runs, and characterizing the interactions between variables [17], [15]. It has been effectively used in the optimization of electrochemical treatment of different types of wastewater such as textile, petroleum processing, dairy processing, distillery effluent etc. [14], [18]-[20].

The methodology of the study is based on the positive impact of direct photovoltaic solar panel integration on the energy consumption of the EO process for the removal of dissolved COD from metalworking wastewater. The photovoltaic solar panel was connected directly to the EO process, without the use of batteries or any other kind of energy storage. This technique was applied to minimize energy consumption and eliminate or reduce this dependency, which causes limitations in the use of the EO process in rural areas or other locations without access to commercial energy. The study's goal was to assess the efficacy of the EO procedure for COD removal from metal cutting wastewaters, to determine the E.C. of the processes using an experimental design methodology and to minimize the E.C. of the EO process by photovoltaic solar panel. The following are the study's specific goals:

i) To identify the effect of the operating parameters (pH, C.D., E.T.) of EO process,
ii) Model the COD removal efficiency and the E.C. by BBD,
iii) To develop scenarios for optimal conditions,
iv) To integrate a photovoltaic solar panel to the EO process to minimize the E.C. of the process.

2 Material and method

2.1 Characterization of wastewater

The wastewater used in the experimental studies was obtained from a metal cutting industry in Düzce/Türkiye. Characterization of raw wastewater is seen in Table 1.

Table 1. Raw wastewater characterization.

Parameter	Value/ Concentration
pH	7,68
Conductivity(mS/cm)	570±10
SS (mg/L)	122±5
COD (mg/L)	71±2
Colour (RES) (m^{-1})	
436 nm	11,8
525 nm	8,6
620 nm	6,7

2.2 Experimental study

Experimental studies were carried out under batch flow. In the batch experimental studies where COD removal is performed with EO process, current and voltage was controlled by using DC Power Supply (GPS-3303 model, 0-30V, 0-3A). The mixing process was carried out with the IKA RCT basic mixer. Electrodes were placed in the reactor made of plexiglass material with a volume of 500 mL. In each experiment, 480 ml of metal processing wastewater was added to the electrolytic cell. In EO process electrode type is important for the organic pollutant degradation. Also, the electron transfer rate will be quicker and the fouling impact will be lessened with better anode material electrocatalytic activity. In the study, graphite and titanium (Ti) electrodes were used as anode and cathode. Because the oxidation potential of graphite anode is high as 1.7V [9]. In EO process, 4 electrodes with a dimension of 35 cm x 70 cm and a thickness of 0.5 mm were used (Active surface area: 0.18 m^2), (Figure 1).

EO reactor and solar panel integrated into the system is given in Figure 2. The dimensions of the solar panel used in experimental studies were as 1650 mm x 992 mm x 40 mm. The input voltage value was 38.00V. Solar module type was SPE 250.

Figure 1. Schematic view of the experimental system.

Figure 2. Solar panel integrated EO reactor.

2.3 Optimization studies

The effect of pH, C.D. and E.T. parameters on the removal of COD from metal processing industry by EO model reactor was determined under batch test conditions. A three-level Box-Behnken factorial design was used with 17 runs. Design Expert Trial version was used for the statistical analysis. The experimental datas were analyzed by RSM procedure as seen in Eq. 5. In Eq. 5, Y is response (COD removal efficiency (%) and/or energy consumption (kWh/m³)); $\beta_0 \beta_i$ (i = 1,2,3), β_{ij}(i = 1,2,3; j = 1,2,3) are the model coefficients; X_i and X_j the coded independent variables.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{i=1}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad (5)$$

In optimization studies, pH (X_1), current density (X_2), electrolysis time (X_3) parameters were considered as the main factors affecting the efficiency of EO process. Table 2 shows the process factors and levels.

Table 2. Operating parameters and levels.

			Levels		
Coded Variables (X_i)	Factors	Unit	Low (-1)	Center (0)	High (+1)
(X_1)	pH	-	5	7	9
(X_2)	C.D.	A/m²	20	50	80
(X_3)	E.T.	min.	10	25	60

C.D. Current Density, E.T. Electrolysis Time.

2.4 Chemical analysis

All the parameter analysis was performed by the Standard Methods (SM) [21]. The sCOD concentration (after filtering from 0.45µm filter) was measured with the SM of 5220 D by using of UV-VIS spectrophotometer (WTW 6100). SS concentration levels were determined through gravimetric method of 2540-D. The wastewater turbidity was measured with SM of 2130-B, using a UV-VIS spectrophotometer (WTW 6100). pH was measured with SM of 4500-B, using a pH meter (Hanna model), and the conductivity was determined with conductivity meter (Hach 7100e model) (SM 2510-B).

2.5 Equations

2.5.1 Current density

The C.D. which effects the electrochemical processes was calculated by the Eq. 6.

$$J = I/A \qquad (6)$$

In the equation, J: Current density, A / m², I: Current (Ampere), A: Active anode surface area (m²).

2.5.2 Energy consumption

To determine the E.C. of EO process, Eq. 7 was used.

$$E.C. = V.i.t/\forall \qquad (7)$$

In the equation, E.C.: Energy Consumption, Wh, I: Current, t: Electrolysis time (Hour-h.), ∀: Volume (m³).

3 Results and discussion

3.1 Statistical evaluation of ANOVA

Three factors with three levels of the Box Behnken Design were applied to optimize the effective process variables on the COD removal response. For a 3-factor design, the total number of experiments was 17, at the design center with five repetitions.

To determine the significance and/or the adequacy of the model, analysis of the variance has to be evaluated [22] According to the statistical results, it was concluded that the quadratic model obtained with RSM can explain the COD removal efficiency and the E.C. of the process. R^2, adjusted R^2 were checked to determine the adequacy of the models (see Table 3). The quadratic model had a high signal, which is thought to explain the EO process for COD removal and E.C. responses.

The F value is a reliable indicator of the variables' ability to appropriately explain the variance in the mean data [22]. The F-value of the model was 7.03 and 94.65 for COD removal and E.C., respectively, with a very low probability value (0.0088 and <0.0001). This indicates that the model is statistically accurately fitting and shows that it is significant. When a large F value is determined, it shows that the regression equation can explain the variation in the response [16]

The model for COD elimination and E.C. was found to have a "lack fit p-value" of 0.0029 and 0.0018, respectively, indicating that there was no appreciable error in the data.

The signal-to-noise ratio is measured by the adequacy of precision. The ratio of A.P. of at least 4 is preferred. In the study, the A.P. of COD removal and E.C. was determined to be 11.1 and 36.96, respectively. Additionally, A.P. was greater than 4 in two responses.

To determine the fitting quality of the model at each point in the design, the PRESS value was used. PRESS was obtained as 5426 and 536 for COD removal and E.C., respectively.

Table 3. ANOVA of the EO process.

	COD Rem. (%)		Energy Cons. (kWh/m³)	
Source	F Value	P Value	F Value	P Value
Model	7.03	0.0088	94.65	< 0.0001
X_1-pH	2.09	0.1913	3.43	0.1065
X_2-C.D.	41.40	0.0004	390.69	< 0.0001
X_3-E.T.	8.37	0.0232	319.20	< 0.0001
X_1X_2	0.24	0.6366	0.39	0.5508
X_1X_3	4.48	0.0721	1.49	0.2614
X_2X_3	1.61	0.2448	125.69	< 0.0001
X_1^2	1.43	0.2713	7.94	0.0258
X_2^2	0.16	0.7025	1.36	0.2809
X_3^2	3.68	0.0967	2.25	0.1770
Lack of Fit	32.17	0.0029	41.98	0.0018

	COD Rem. (%)	Energy Cons. (kWh/m³)
R^2	0.9004	0.9918
Adj R^2	0.7723	0.9814
Adeq. Prec.	11.059	36.958
Std. Dev.	7.09	2.22
Mean	56.18	19.15
C.V. %	12.62	11.59
PRESS	5425.88	535.85
Equation Type	Quadratic	Quadratic

C.D. Current Density, E.T.: Electrolysis Time.

With the decrease of "p> F", the importance of the parameter used in the model increases. In the obtained model, effective parameters were evaluated according to p<0.05 values. If "Prob > F" is less than 0.05, the model terms are likely to be effective. Model terms are not significant if the value is higher than 0.10. X_2, X_3 are significant model terms for COD removal and E.C. responses.

As a result, statistical values are consistent with the quadratic model, and the predicted response values produced using the statistical model are in good agreement with the experimental data.

The results for the COD removal and E.C. responses with the predicted values are given in Table 4. As per the results, COD removal efficiency was varied from 27% to 82% in EO process, whereas E.C. was in the range of 2.33-66.76 kWh/m³.

Table 4. Experimental Results for EO Process

				COD Rem. (%)		E.C. (kWh/m³)	
	X_1	X_2	X_3	Act.	Pred.	Act.	Pred.
1	7	50	35	59	58	18.6	19.20
2	5	50	10	37	45	4.15	3.69
3	7	50	35	56	45	18.6	19.22
4	9	80	35	69	71	32.8	35.09
5	7	50	35	60	58	19.6	19.20
6	5	50	60	79	74	27.3	29
7	9	50	60	59	52	34.1	34.62
8	5	80	35	82	82.25	29.7	30.8
9	7	20	60	38	45	7.57	8.2
10	5	20	35	49	47	3.42	1.18
11	7	20	10	27	22	2.33	5.03
12	9	20	35	43	42.75	3.77	2.7
13	7	80	60	64	68	66.7	64
14	7	80	10	71	64	11.7	11.17
15	7	50	35	56	58	19.6	19.22
16	9	50	10	47	53	5.51	3.9
17	7	50	35	59	58	19.6	19.22

Act.: Actual, Pred. Predicted.

The coded equations of the COD removal and E.C. response for EO process is given in Eq. 8. The coded equation can be applied to predict the amount of response for the level of each variable. Here, Y_1 is the predicted COD removal efficiency for EO ($0 < Y1 \leq 100\%$), X_1, X_2, and X_3 are the pH ($5 \leq X1 \leq 9$), current density ($20\ A/m^2 \leq X_2 \leq 80\ A/m^2$), and electrolysis time (10 min. $\leq X_3 \leq 60$ min.), respectively. The sign of the coefficients in the equations indicates how the parameters affect the main output. The coefficient of pH has a negative sign. The increase of the pH decreases the COD removal efficiency. C.D and E.T. have positive sign. The increase of these parameters increases the COD removal efficiency. In Y_1 equation, C.D. and E.T. was positively affected the COD removal efficiency, while pH was negatively affected it. In other words, the increase in C.D. and E.T. increases the COD removal efficiency, while it decreases with the increase in pH.

The C.D. and E.T. parameters are quite effective, while pH has a limited effect for all responses. The significance of the main factors on the COD removal efficiency was: CD > ET > pH and CD = ET > pH for E.C.

$$\text{COD removal} - Y_1 = 58 - 3.62 \times A + 16.13 \times B + 7.25 \times C - 1.75 \times AB - 7.5 \times AC - 4.5 \times BC + 4.12 \times A^2 - 1.38 \times B^2 - 6.63 \times C^2 \quad (8)$$

The predicted values of the E.C. responses were obtained from quadratic model in EO process. The response equations for E.C. is given in Eq. 10. Here, Y_2 is the predicted E.C. of EO process.

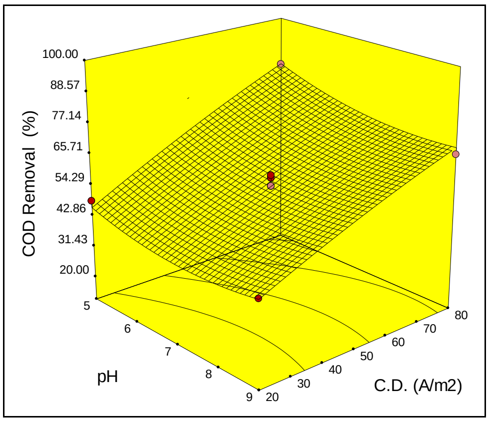
It is seen from the Eq. 9 that all coefficients of the parameters have positive sign that E.C. varies directly proportional to pH, C.D. and E.T. The increase of these parameters increases the COD removal efficiency. And it can be said that the coefficient of C.D. (15.5) and E.T. (14.01) is higher than pH (1.45). This indicates the importance and/or effectiveness of the parameters.

$$\text{Energy consumption } \left(\frac{\text{kWh}}{\text{m3}}\right) - Y_2 = 19.22 + 1.45 \times A + 15.5 \times B + 14.01 \times C + 0.69 \times AB + 1.36 \times AC + 12.44 \times BC - 3.05 \times A^2 + 1.26 \times B^2 + 1.62 \times C^2 \quad (9)$$

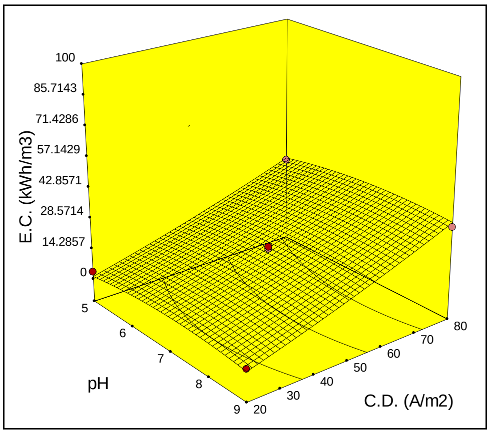
3.2 Evaluation of interactive effects of the EO process

The interactive effect of pH/C.D. on COD removal efficiency is given in Figure 3(a). When the E.T. is constant (35 min.), the COD removal efficiency of the EO process increased with the increase of C.D., while pH did not affect COD removal. C.D. is the main parameter which effects the COD removal efficiency.

The effect of pH/C.D. on energy consumption of EO process is seen in Figure 3(b). According to Figure 3(b), when the E.T. is constant (35 min.), the E.C. increases with the increase of the C.D. 20 to 80 A/m². The greater the C.D., the better the oxidation capacity and it can be offering an effective removal efficiency. However, applying of more than necessary C.D. will increase the E.C. and operating cost [16].



(a): COD removal (E.T. 35 min.)



(b): Energy consumption (E.T. 35 min.)

Figure 3. Effect of pH/C.D.

The effect of pH/E.T. on COD removal is given in Figure 4(a). When the C.D. is constant (50 A/m²), the COD removal efficiency of the EO process increased with the increase of E.T. High COD removal efficiency was determined at a condition of pH 5 and 60 min. of E.T. As it is seen from the Eq. 10 and 11 that to generate oxygen anode potential in acidic and alkaline conditions is 1.229 V and 0.401 V, respectively.

In acidic medium

$$2H_2O \rightarrow 4H^+ + O_2 + 4e \ (1.229\ V) \qquad (10)$$

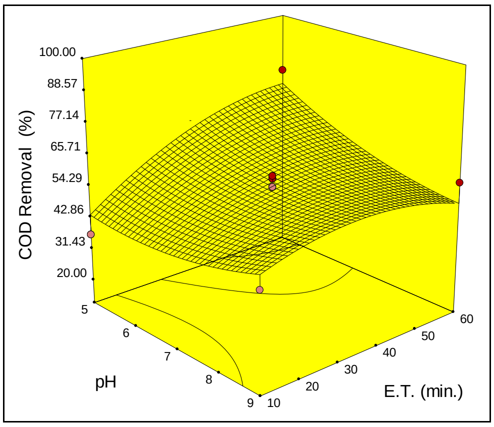
In alkaline medium

$$4OH^- \rightarrow 2H_2O + O_2 + 4e \ (0.401\ V) \qquad (11)$$

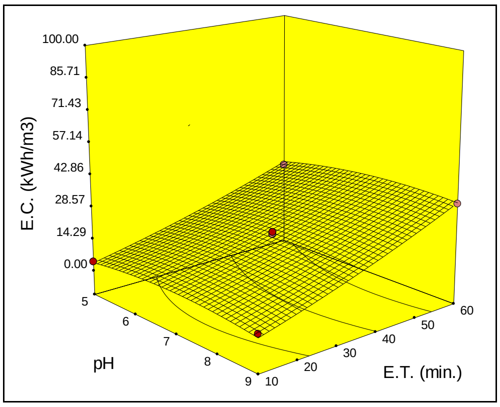
As it is mentioned by Guo et al., (2022) that EO process is significantly affected by pH variations. Therefore, in solution producing of the side reactions that release oxygen can be more than that under acidic conditions [23],[9].

A poor interactivity occurs between hydroxyl radicals and the electrode surface at the acidic media, thus oxygen release of the electrochemical system is low and develops the higher chemical reactions to degrade the organic pollutants [9]. At a pH value of 5-7, hypochlorous acid is dominant in the solution while pH is higher than 8, ClO- chemical is dominant. This means that indirect oxidation mechanism is effective at alkaline medias [24],[9]. In the study, the effective pH was determined in the range of 5-5.72. Therefore, it can be mentioned that hypochlorous acid was dominant and direct oxidation mechanism could be active.

Effect of pH/E.T. on E.C. of EO process is seen in Figure 4(b). When the C.D. is constant (50 A/m²), the E.C. of EO process increases with the increase of the E.T. from 20 to 60 min. The electrolysis time should be in sufficient range to ensure contact of organic pollutants with the anode electrode surface. However, prolonged electrolysis time results in increased energy consumption.



(a): COD removal (C.D. 50 A/m²).

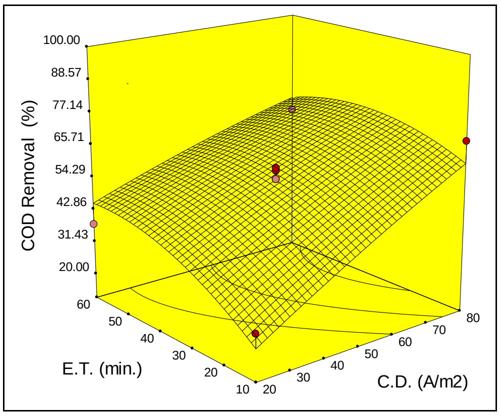


(b): Energy consumption (C.D. 50 A/m²).

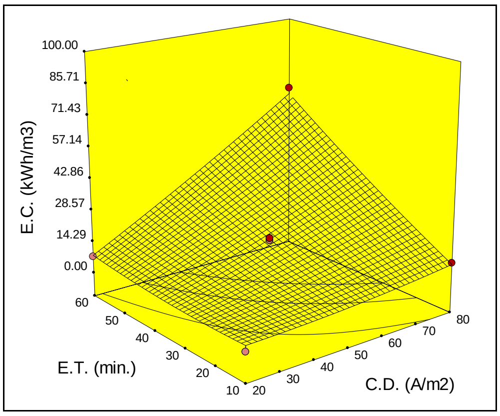
Figure 4. Effect of pH/E.T.

The effect of C.D./E.T. on EO process is given in Figure 5(a). When the pH is constant (pH 7), the COD removal efficiency of the EO process increased with the increase of C.D. and E.T. The degradation mechanism of the EO process changes with the C.D. While at low current densities active species do not occur and direct oxidation is dominant; at high current densities direct and indirect oxidation is dominant and it plays important role to produce active species [25]. When comparing the direct and indirect oxidation process, it was discovered that some anode materials perform best when subjected to direct electro-oxidation, while other materials have demonstrated their effectiveness when used in indirect electrooxidation setups [26]. Even though the indirect oxidation method is said to be excellent in removing pollutants like COD and color, it has the inherent drawback of producing additional byproducts of chlorine synthesis that must be sorted out and handled. After direct electrooxidation, no such by-product separation is necessary [26],[27].

The effect of C.D./E.T. on E.C. of the EO process is seen in Figure 5(b). When the pH is constant (pH 7), the E.C. of the EO was maximum with an E.T. of 60 min. and with a C.D. of 80 A/m². Applying a high voltage to the electrochemical system resulted in a higher E.C. The electrooxidation process cost and processing efficiency depend on the current density and electrolysis time, making them a critical performance indicator [9].



(a): COD removal (pH 7).



(b): Energy consumption (pH 7).

Figure 5. Effect of C.D./E.T.

3.3 Optimization of EO process

The optimization study was evaluated in four scenarios (Table 5). In 1st scenario, the development of results that maximize COD removal efficiency; In 2nd scenario, the development of optimum conditions that maximize COD removal efficiency and minimize E.C.; In 3rd scenario, the development of optimum conditions that maximize E.C.; In 4th scenario, the development of optimum conditions that maximize COD removal efficiency and maximize E.C.

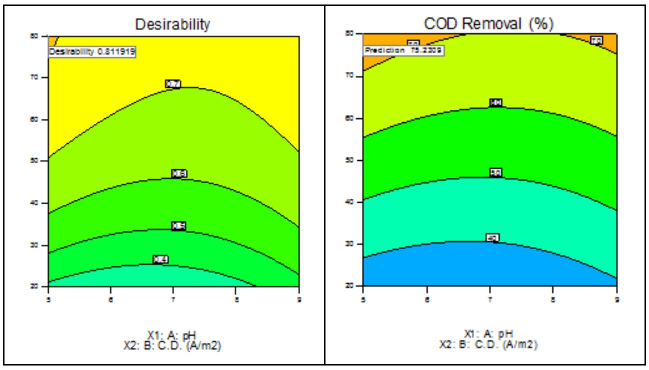
In 1st scenario, the optimum conditions for EO process were determined to be an initial pH of 5.09, a C.D. of 79.71 A/m², a reaction time of 58.1 min. in which COD removal of 85.03% with an E.C. of 49.51 kWh/m³ and with a desirability of 1 was achieved.

In 2nd scenario as seen in Table 5 that the optimum conditions for EO process were determined to be an initial pH of 5, a C.D. of 80 A/m², a reaction time of 22.15 min in which COD removal of 75.23% with an E.C. of 18.33 kWh/m³ and with a desirability of 0.812 was achieved.

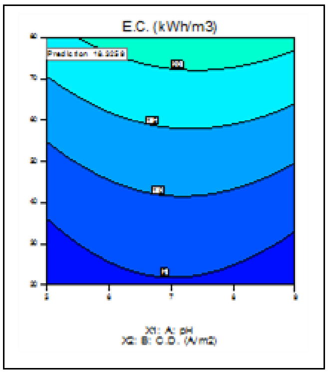
In 3rd scenario, the optimum conditions for EO process were determined to be an initial pH of 5.01, a C.D. of 80 A/m², a E.T. of 60 min in which COD removal of 85.77% with an E.C. of 57.56 kWh/m³ and with a desirability of 0.857 was achieved. In all scenarios high COD removal was determined at acidic conditions.

In 4th scenario, the optimum conditions for EO process were determined to be an initial pH of 5, a C.D. of 80 A/m², a reaction time of 57 min in which COD removal of 86.09% with an E.C. of 56.31 kWh/m³ and with a desirability of 0.904 was achieved. In all scenarios high COD removal was determined at acidic conditions.

The 2nd scenario in which the energy requirement was 18.33 kWh/m³ and the COD removal efficiency was 75.23%, i.e. the scenario that maximizes the COD removal efficiency and minimizes the energy consumption (E.C.), is considered to be more feasible than other scenarios. In this case, the optimum pH for the EO process was 5, C.D. was 80 A/m2, E.T. was 22.15 minutes with a desirability of 1 Figure 6(a)-(c).



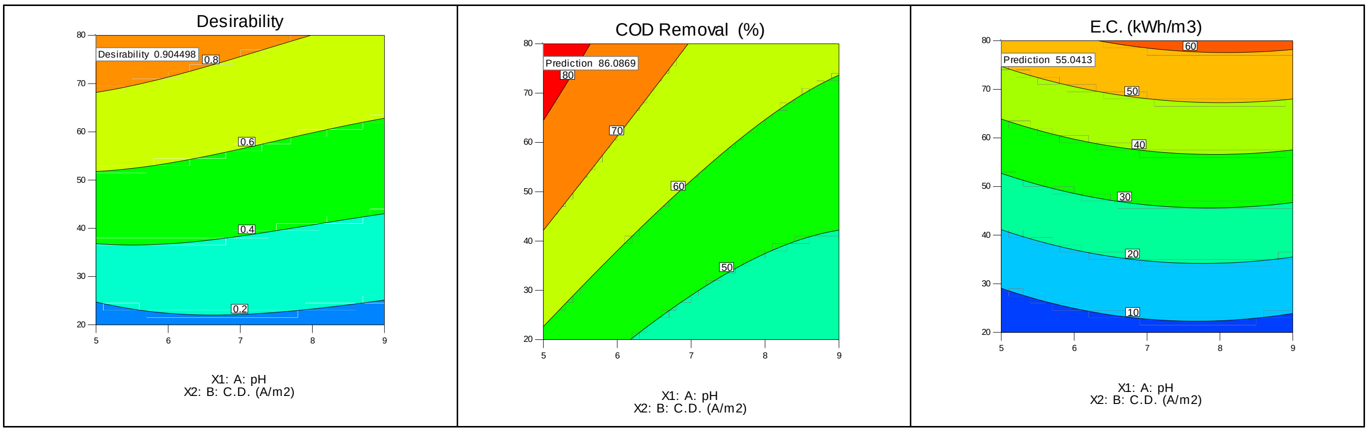
(a) (b)



(c)

Figure 6. Optimum conditions for the 1st scenario.

If the highest COD removal is desired, the 4th scenario, which maximizes energy consumption and COD removal efficiency, can be preferred. In this case, the COD removal efficiency is 86.09% with a desirability of 0.904 Figure 7(a)-(c). It was determined that the COD removal efficiency of the EO process was varied from 75 to 86% in present study, while it was observed from 35 to 99.99% in the literature [28]-[34], (see Table 5).



(a) (b) (c)

Figure 7. Optimum conditions for the 4th scenario.

Table 5. The optimal conditions for the different scenarios.

Scenario	COD	E.C.	pH	C.D. (A/m²)	E.T. (min.)	COD rem. (%)	Energy Cons. (kWh/m³)	Des.	E. S.P Overcast Weather (kWh/m³)	F.P. (%)	E. S.P Sunny Weather (kWh/m³)	F.P. (%)	Ref.
1	Max.	none	5.09	79.71	58.1	85.03	55.52	1	2.77	5	58.33	105	P.S.
Reason	To determine the maximum COD removal efficiency of the process												
2	Max.	Min.	5	80	22.15	75.23	18.33	0.812		15		318	
Reason	To determine the maximum COD removal with a minimum energy consumption												
3	None	Max.	5.01	80	60	85.77	57.56	0.857		4.8		101	
Reason	Determining whether the energy obtained with the solar panel can fulfill the maximum energy required in the EO reactor												
4	Max.	Max.	5	80	57	86.09	55.04	0.904		5		106	
Reason	To determine the maximum COD removal with a maximum energy consumption												

LITERATURE

Pollutant/Wastewater	pH	C.D.-Current	E.T. (min.)	COD rem. (%)	Energy Cons. (kWh/m³)	Electrode Anode-Cathode	Ref.
Tricyclazole	5.0	25 mA/m²	2.5 h	69.5	-	Ti/SnO_2–Sb/ PbO_2	[28]
Landfill leachate	8.2	2A	8 h.	35	240	$TiRuSnO_2$	[29]
				>99.9	250	PbO_2	
				>99.9	130	BDD	
Textile wastewater	4.0	800 A/m²	5 h.	62	-	Ti/RuO_2-IrO_2	[30]
Petroleum wastewater	7.5-9.0	3.5 mA/cm²	15 min.	49-60	0.79	Graphite-SS	[31]
Herbicide wastewater	4.0	4 A/dm²	2 h.	87	-	PbO_2 - Ti	[33]
Sugar beet industry process wastewater	5.0	49.1 mA/cm²	294 min.	75-COD 71-sCOD	28	BDD-SS	[34]

E.C. Energy Consumption, E.S.P: Energy supply of solar panel, F.P.: Fulfillment percentage, Des.: Desirability, P.S. Present Study

3.4 Effect of solar panel integration on energy consumption

EO process is effective for the degradation of organics, but it has an important disadvantage as energy consumption which effects the usage of this process.

In regions where the unit energy cost is high, the use of this process may not be appropriate. It is mentioned that this disadvantage can be minimize by using renewable energy or to combine directly with solar irradiation [32]. In this study, it is hypothesized that the usage of renewable energy option can be eliminate the energy consumption of EO process.

The E.C. of EO process was varied between 1.05 to 30.04 Wh. The voltage/current obtained from the solar panel was 4.95 V/0.272 A, and the obtained energy was 1.33 Wh in overcast weather. In case the weather is completely sunny and the sun comes at the desired angle, 34.62 V energy input value was determined from the solar panel. When current was applied to the electrodes, this value was determined as 4 V, 7 A. That is, it produces an energy of 28 Wh.

When the energy consumed for wastewater treated per m3 volume was calculated, 2.77 kWh/m³ energy was obtained from solar panels when the weather is overcast, while 58.33 kWh/m3 energy was obtained when the weather is sunny. According to the developed scenarios, 5%, 15%, 4.8% and 5% of the energy requirement of the EO process was fulfilled with the energy obtained by solar panels in overcast weather, respectively. In sunny weather, all of the energy requirements of the EO process were fulfilled by the photovoltaic solar panel.

4 Discussion and conclusion

In this study, the COD removal efficiency of the graphite/titanium electrode as anode/cathode connected EO process was determined by RSM with BBD. It was seen that the R^2 value of the COD removal efficiency response and E.C. response was appropriate for the quadratic model. Accordingly, ANOVA results showed that Box-Behnken statistical design is an important model in explaining the effective parameters of COD removal from metal cutting wastewater by EO process.

The study also tried to determine the optimum conditions for the treatment of metal processing wastewaters with EO process by developing some different scenarios. The scenario in which the energy requirement was 18.33 kWh/m^3 and the COD removal efficiency was 75.23%, i.e. the scenario that maximizes the COD removal efficiency and minimizes the E.C., is considered to be appropriate. In this case, the optimum pH for the EO process was 5, C.D. was 80 A/m^2, E.T. was 22.15 min. If the highest COD removal efficiency is desired, only the scenario that maximizes COD removal and maximizes the E.C. can be appropriate. In this scenario, the EO process, which has an E.C. of 55.04 kWh/m^3, showed about 3 times more E.C., but the COD removal efficiency was determined as 86.09%.

Graphite electrode was preferred as an active anode with low cost and high oxidation potential. Although this anode connection type cannot remove all of the dissolved COD, it is seen that high COD removal efficiency (86%) can be obtained. Although it is predicted that the performance can be improved with the use of inactive electrode types such as BDD and metal oxides, their use may be limited in terms of application due to the high costs of these electrode types with electrochemical processes. Therefore, it is necessary to develop cost-effective electrode types with high oxidation potential to be used with the electrooxidation process.

It has been determined that the energy obtained by the solar panel produces much more than the energy required for the EO process. Accordingly, it also shows that the energy to be obtained has the potential to be stored by integrating with battery systems, converter and inverters.

Generally, it is thought that the E.C., which determines the operating cost in the treatment of industrial wastewater, can be minimized with the solar panel to be integrated into the electrochemical processes, and the use of solar panel integrated electrochemical reactors in water/wastewater treatment will be very effective, especially in coastal areas that have the opportunity to benefit more from sunlight and it can be applied to real enterprises with scale-up studies.

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6 Author contribution statements

In present study, Murat SOLAK made contributions to the idea development, experimental design, data collection, analysis, literature review, writing, and evaluation of the results; Tuğba ARSLAN made contributions to the material supply and the experimental analysis; and Ahmet AKBURAK made contributions to the experimental analysis.

7 Ethics committee approval and conflict of interest statement

"The prepared article does not require approval from the ethics committee".

"The article was written with no conflict of interest with any individual or organization".

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