

## A Renewable Energy Application to the Electrochemical Reactor in the Treatment of Metal Cutting Wastewater: Double Criteria Optimization of Process

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### Keywords

Electrocoagulation,  
Metal cutting wastewater,  
Photovoltaic Solar Panel  
Al electrode,  
Box-Behnken Design,  
Renewable energy

**Abstract:** Electrochemical wastewater treatment methods are effectively used for all type of wastewaters and pollutants. One of the huge negative impact of these processes is the energy consumption of the process. Therefore, the goal of the study is to develop a minimal energy user Electrocoagulation (EC) option with an integration of a direct photovoltaic solar panel as a subsection of electrochemical processes for the degradation of low COD (Chemical Oxygen Demand) from metal cutting wastewater. To optimize the operating parameters of the EC process such as pH, current density (C.D.) and electrolysis time (E.T.) Box-Behnken Design by RSM was used with a double criterial optimization option. COD removal and energy consumption were evaluated as responses of the model and they were well-fitted with the quadratic model. Also, it was determined that all parameters are effective on EC process. Optimum conditions were found at a pH of 7.48, a C.D. of 30 A/m<sup>2</sup>, an E.T. of 65 min, an energy consumption of 3.9 kWh/m<sup>3</sup> and a desirability of 0.954. At the optimum conditions, the energy consumption of the EC process was fulfilled from solar panel in a ratio of 71% and 1495% in overcast and sunny weather, respectively. Especially, the energy obtained by the solar panel in the sunny weather produces much more than the energy required of the process.

## Metal Kesme Atıksularının Arıtılmasında Elektrokimyasal Reaktöre Yenilenebilir Enerji Uygulaması: Prosesin Çift Kriterli Optimizasyonu

### Anahtar Kelimeler

Elektrokoagülasyon,  
Metal kesme atıksuları,  
Fotovoltaik Güneş Paneli,  
Al elektrot,  
Box-Behnken Tasarımı,  
Yenilenebilir Enerji

**Öz:** Elektrokimyasal atıksu arıtma yöntemleri her türlü atıksu ve kirletici için etkin bir şekilde kullanılmaktadır. Bu proseslerin en büyük olumsuz etkilerinden biri prosesin enerji tüketimidir. Bu nedenle, çalışmanın amacı, metal kesme atıksuyundan KOİ'nin ayrıştırılması için elektrokimyasal proseslerin bir alt bölümü olarak doğrudan fotovoltaik güneş paneli entegrasyonu ile minimum enerji kullanan bir Elektrokoagülasyon (EK) seçeneği geliştirmek olarak belirlenmiştir. EC prosesinin pH, akım yoğunluğu (A.Y.) ve elektroliz süresi (E.S.) gibi işletme parametrelerini optimize etmek için çift kriterli optimizasyon seçeneği ile RSM ile Box-Behnken Tasarımı kullanılmıştır. KOİ giderimi ve enerji tüketimi modelin yanıtları olarak değerlendirilmiş ve kuadratik model ile iyi uyum göstermişlerdir. Ayrıca, tüm parametrelerin EC prosesi üzerinde etkili olduğu belirlenmiştir. Optimum koşullar pH 7,48, A.Y. 30 A/m<sup>2</sup>, E.S. 65 dakika, enerji tüketimi 3,9 kWh/m<sup>3</sup> ve arzu edilebilirlik 0,954 olarak bulunmuştur. Optimum koşullarda, EK sürecinin enerji tüketimi kapalı ve güneşli havalarda sırasıyla %71 ve %1495 oranında güneş panelinden karşılanmıştır. Özellikle güneşli havada güneş panelinden elde edilen enerji, proses için gerekli olan enerjiden çok daha fazlasını üretmektedir.

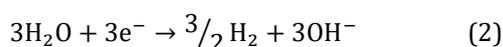
## 1. Introduction

Metal processing is one of the high waters consumed and produced high volume of wastewater. During metal processing, the water used to cool the metal materials. This procedure is the source of the wastewater. Such wastewater contains pollutants such as heavy metals, oil-grease, COD and color. Conventional wastewater treatment techniques as coagulation-flocculation, adsorption, sedimentation has some advantages as minimal cost, easy operation while there are some disadvantages as high sludge volume, transportation, usage and storage of chemicals. Today, new techniques are being developed to eliminate these disadvantages of existing techniques. There are different electrochemical processes such as electrocoagulation, electrooxidation, electroflotation, electrofenton, electrodialysis [1] and hybrid of these processes [2] that can be preferred depending on the type and character of wastewater. Because of the versatility, environmental compatibility [3], ease of operation, eco-friendly, low footprint, no chemical additions, decreased amount of sludge [4] and simultaneous multi-pollutant removal property usage of EC process has been increased in recent. The procedure of EC technique may occur as two steps: dissolving of the metal electrode to its ions and merging of the hydroxyl ions generated at the cathode with metal ions [1]. Aluminum (Al), ferric (Fe) and magnesium (Mg) electrodes are used as a sacrificial electrode in EC process [5,6]. However, Al and Fe electrodes can typically be preferred due to the efficient compression of the electrical double layer caused by the greater charge valency of Al and Fe ions in comparison to copper, zinc, and magnesium. In addition to that, Al electrode can prefer to Fe electrode. Due to Al electrode's excellent strength to weight ratio, corrosion-resistance, and high electrical conductivity [4], the discharge water is not colored like it is with Fe electrode [7]. Because of these reasons Al electrode was used in the study. During electrolysis using Al electrode anodic and cathodic reactions occur as Eq.1-3 [4].

Aluminum dissolution in anode electrode:



Water electrolysis at the cathode:



In the solution:



To optimize the operating parameters of the EC process some modeling programs as Box-Benhken, Central Composite, Taguchi can be used. These programs have some advantages as minimum experiment number, reliable results and multiple scenarios [8,9]. In the literature it was determined that the using of RSM was effective to explain the operating parameters of EC process [4]. Optimization of different treatment techniques for different wastewater types with Box-Behnken design has been studied by various researchers [10,11,12].

Metal cutting wastewaters can be treated as methods as coagulation, flocculation, electrocoagulation, electrooxidation [13,14,15]. The reuse of wastewater in production processes after treatment is possible with advanced treatment techniques as electrochemical methods i.e. EC. Although there are many articles on EC in the literature, studies on the usage of solar panel with EC process is limited. But in recent, it is shown that some researchers investigate the integration of solar panel on EC [3,16,17]. One of the most significant obstacles in the use of this approach [17] is energy consumption, particularly for lengthy treatment durations. In order to minimize the energy consumption of electrochemical processes, it is necessary to effectively determine the optimum values of parameters such as electrolysis time, current density, support electrolyte solution and integrate solar panels to provide electrical energy externally. These panels can be integrated into electrochemical systems in two ways: firstly, the energy from the sun is fed directly into the reactor, and secondly, the energy from the sun is stored in batteries and fed into the system when needed. This work hypothesized that the direct photovoltaic solar panel integration to the electrochemical process could be utilized to reduce energy consumption [18].

The study's main goal is to investigate the efficacy of the EC procedure for low COD removal from metal processing wastewaters, to optimize the energy consumption of the processes using an experimental design methodology and to establish whether the photovoltaic solar panel can fulfill the energy needs of the EC process during treatment.

## 2. Material and Method

### 2.1. Experiments and materials

In the study, the wastewater was collected from a metal cutting industry in Düzce / Türkiye. Wastewater was stored in refrigerator and was allowed to stand until it reached room temperature before using it in the experiments. Raw wastewater characterization was determined as a pH of 7.68, a conductivity of  $570 \pm 10$  mS/cm, a SS of  $122 \pm 5$  mg/L, a soluble COD of  $71 \pm 2$  mg/L, a color of RES ( $\text{m}^{-1}$ ) (436 nm) 11.8, (525 nm) 8.6, (620 nm) 6.7.

In experimental studies COD parameter was selected to determine the effectiveness of the EC process. Electrochemical reactor was performed in a batch mode (Figure 1a). Current and voltage was controlled by using DC Power Supply (0-30V, 0-3A- GPS-3303-Multi Output). The mixing process was carried out with the IKA RCT basic mixer. The reactor was designed with a plexiglass material and a volume of 500 mL. Four Al electrodes with a dimension of 35cm\*70cm\*2mm, an inter-electrode distance of 1 cm

and a parallel electrode connection system was used during electrolysis. In each experiment, all the electrodes are washed and cleaned with HCl solution after electrolysis. A photovoltaic solar panel with a dimension of 1650\*992\*40 mm was used. The photovoltaic solar panel is integrated to the EC reactor without batteries, inverter/converter or any energy storage equipment. Solar module type of the panel was SPE250, and the input voltage value was 38.00V (Figure 1b).



a)



b)

**Figure 1.** EC reactor a) only process b) solar panel integrated process

**2.2. Mathematical modeling**

Box Behnken Design (BBD) was used to examine the effect of pH, C.D. and E.T. parameters on COD removal from metal processing industry by EC model reactor. Based on a three-level Box-Behnken factorial design, this experimental design had 17 runs. For the statistical analysis, the Design Expert trial version was employed. It is seen in the Eq. 4 that COD removal and energy consumption responses are described with Y, while model coefficients are  $\beta_0\beta_i (i = 1,2,3), \beta_{ij}(i = 1,2,3; j = 1,2,3)$ , the coded independent variables are  $X_i$  and  $X_j$  and the error is  $\epsilon$ .

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j + \epsilon \tag{4}$$

The key variables influencing the COD removal efficiency (R.E.) and energy consumption of the EC process were pH ( $X_1$ ), current density ( $X_2$ ), and electrolysis time ( $X_3$ ). The process variables and levels are shown in Table 1.

**Table 1.** Process variables and levels for EC Process

Coded Variables ( $X_i$ )	Factors	Unit	Levels		
			Low (-1)	Center (0)	High (+1)
$(X_1)$	<b>pH</b>	-	5	7	9
$(X_2)$	<b>C.D.</b>	A/m <sup>2</sup>	30	45	60
$(X_3)$	<b>E.T.</b>	min.	10	25	50

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

**2.3. Chemical Analysis**

The parameters were analyzed using Standard Methods (SM) [19]. The inlet/outlet COD concentration of the EC process was evaluated using a UV-VIS spectrophotometer (WTW 6100) and the SM of 5220 D. The gravimetric technique of SM 2540-D was used to determine SS concentration levels. The pH was evaluated using a pH meter (Hanna) and the conductivity was measured by using a conductivity meter (Hach 7100e) (SM 2510-B).

**3. Results**

**3.1 Optimization and authentication of process parameters and responses**

To determine the quantitative data which shows the relationship between the input and output factors a mathematical model was developed by RSM. Three factors with three levels of the BBD were employed to optimize the effect of process variables on responses

such as COD removal and energy consumption. The total number of experiments for a 3-factor design at the design center was 17, with three repeats to evaluate the pure error. According to the statistical data, the quadratic model produced with RSM may explain the COD R.E. and process energy consumption responses.

Both the suitability and significance of the model must be evaluated in optimization studies using ANOVA. [20]. In present study, statistical analysis parameters which shows the adequacy of the model, R<sup>2</sup>, adjusted R<sup>2</sup> were checked (Table 2). For COD removal and energy consumption response R<sup>2</sup> values were 0.89 and 0.99 while Adj R<sup>2</sup> were 0.75 and 0.97, respectively.

The quadratic model had a high signal, which is thought to explain the operating parameters of the EC process for COD removal and energy consumption responses. The F-value of the model was 2.08 and 4.92 for COD removal and energy consumption, respectively, with a very low probability value (<0.0001). This shows that the model is essential. The

model's "lack fit p-value" for COD removal and energy consumption was 0.25 and 0.08, respectively, implying that there was no major error in the data. Adequacy of precision (A.P.) measures the signal to noise ratio which has to be greater than 4. In the study, the A.P. of COD removal and energy consumption responses was determined to be as 9.92 and 27.25, respectively. Additionally, A.P. was greater than 4 in all responses. To determine the fitting quality of the model at each point in the design, the PRESS value is used. PRESS was obtained as 3327 and 113, respectively. 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. A "Prob > F" less than 0.05 shows that the model terms are significant. X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>3</sub><sup>2</sup> are significant model terms for COD removal, while X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>2</sub>X<sub>3</sub> are significant model terms for energy consumption. The importance of the main parameters on the COD R.E. response was: pH > E.T > C.D., but in the energy consumption response, they were C.D.=E.T> pH.

**Table 2.** ANOVA and Statistical Parameters of the EC Process

Source	COD Rem. (%)		Energy Cons. (kWh/m <sup>3</sup> )		R <sup>2</sup>	COD Rem. (%)	Energy Cons. (kWh/m <sup>3</sup> )
	F Value	P Value	F Value	P Value			
<b>Model</b>	6.42	0.0114	51.87	< 0.0001			
<b>X<sub>1</sub>-pH</b>	14.93	0.0062	8.47	0.0226			
<b>X<sub>2</sub>-C.D.</b>	6.02	0.0438	171.87	< 0.0001		0.8920	0.9852
<b>X<sub>3</sub>-E.T.</b>	14.53	0.0066	235.41	< 0.0001		Adj R <sup>2</sup> 0.7530	0.9662
<b>X<sub>1</sub>X<sub>2</sub></b>	0.55	0.4843	0.032	0.8629		Pred. R <sup>2</sup> -0.1202	0.8091
<b>X<sub>1</sub>X<sub>3</sub></b>	1.07	0.3356	4.05	0.0842		Adeq. Prec. 9.917	27.247
<b>X<sub>2</sub>X<sub>3</sub></b>	1.23	0.3046	37.94	0.0005		Std. Dev. 6.77	1.12
<b>X<sub>1</sub><sup>2</sup></b>	3.12	0.1209	6.00	0.0442		Mean 49.82	9.28
<b>X<sub>2</sub><sup>2</sup></b>	1.80	0.2218	0.74	0.4181		C.V. % 13.59	12.02
<b>X<sub>3</sub><sup>2</sup></b>	14.52	0.0066	2.77	0.1399		PRESS 3327.63	112.69
<b>Lack of Fit</b>	2.08	0.2450	4.92	0.0790		Equation Type Quadratic	Quadratic

Table 3 shows the predicted and actual values for the COD R.E. and energy consumption responses.

As per the results, COD R.E. was varied from 11% to 65%, whereas energy consumption was in the range of 1.65-26.5 kWh/m<sup>3</sup>.

**Table 3.** Experimental results and prediction of the model

	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	COD Rem. (%)		Energy Cons. (kWh/m <sup>3</sup> )	
				Actual	Predicted	Actual	Predicted
<b>1</b>	9	30	30	61	67	4.76	4.48
<b>2</b>	5	30	30	56	54	3	2
<b>3</b>	5	45	50	38	41	11.71	12.62
<b>4</b>	5	45	10	11	16	2.93	2.76
<b>5</b>	9	45	10	45	41	3.72	2.8
<b>6</b>	7	30	10	52	48	1.65	2.84
<b>7</b>	7	45	30	52	56	8.31	9.26
<b>8</b>	7	60	10	28	29	6.43	6.31
<b>9</b>	7	30	50	61	60	7.97	8.08
<b>10</b>	7	45	30	52	56	8.79	9.26
<b>11</b>	7	45	30	54	56	9.9	9.26
<b>12</b>	5	60	30	44	38	12.24	12.52
<b>13</b>	7	60	50	52	55	26.5	25.31
<b>14</b>	7	45	30	59	56	9.6	9.26
<b>15</b>	9	60	30	59	55	13.6	14.62
<b>16</b>	7	45	30	65	61	9.72	9.26
<b>17</b>	9	45	50	58	53	16.99	17.16

The coded equations of the COD removal and energy consumption response for EC process are given in Eq. 5. and Eq. 6, respectively. The coded equation can be applied to predict the amount of response for the level of each variable. In this equation,  $Y_1$  represents the predicted COD R.E. in EC ( $0 < Y_1 \leq 100\%$ ),  $X_1$ ,  $X_2$ , and  $X_3$  presents the pH ( $5 \leq X_1 \leq 9$ ), current density ( $30 \text{ A/m}^2 \leq X_2 \leq 60 \text{ A/m}^2$ ), and electrolysis time ( $10 \text{ min.} \leq X_3 \leq 50 \text{ min.}$ ), respectively.

The sign of the coefficients in the equations indicates how the parameters affect the main output. It is seen in the Eq. 5 that pH and C.D. was positively affected the COD R.E., while electrolysis was negatively. In other words, increasing the pH and C.D. raises the COD R.E., whereas increasing the E.T. decreases it.

$$\text{COD rem. (EC)} - Y_1 = 56.4 + 9.25 \times A - 5.88 \times B + 9.13 \times C + 2.5 \times AB - 3.5 \times AC + 3.75 \times BC - 5.83A^2 + 4.43 \times B^2 - 12.58 \times C^2 \quad (5)$$

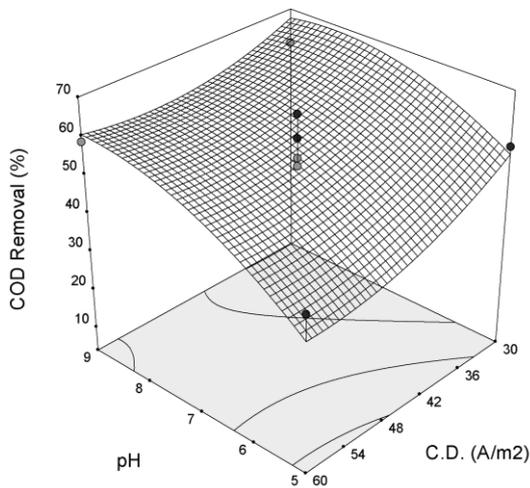
The quadratic model was used to predict the energy consumption response values. Eq. 6 depicts the response equations for energy consumption. Here,  $Y_2$  is the predicted energy consumption of EC process. It is seen from the Eq. 6 that all the coefficient of the parameters has positive sign that energy consumption varies directly proportional to pH, C.D. and E.T. The increase in these factors raises the COD R.E.

$$\text{E. C. } \left(\frac{\text{kWh}}{\text{m}^3}\right) - \text{EC} - Y_3 = 9.26 + 1.15 \times A + 5.17 \times B + 6.06 \times C - 0.1 \times AB + 1.12 \times AC + 3.44 \times BC - 1.33 \times A^2 + 0.47 \times B^2 + 0.91 \times C^2 \quad (6)$$

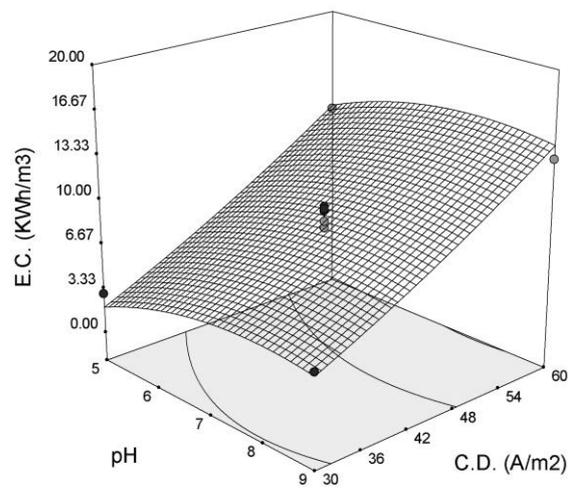
### 3.1. Evaluation of Interactive Effects of the Processes

Figure 2 (a) indicates that the influence of pH/CD on the EC process. According to Figure 2 (a), when the E.T. is constant (30 min.), the COD R.E. increases when the pH rises from 5 to 9. The increase in the C.D. increased the COD R.E. This can be due to the addition of excess chemical to the wastewater. During the electrolysis, pH presents a higher increase in the R.E. of COD was determined than C.D. At a low pH media when Al anode dissolved,  $\text{Al}^{3+}$  and  $\text{Al}(\text{OH})_2$  occurs, while at a high pH media,  $\text{Al}(\text{OH})_3$  occurs [21]. In high pH values OH ion accumulates in the solution that COD removal increases [10].

The interactive effect of pH/C.D. on energy consumption of the EC process is given in Figure 2 (b). When the E.T. is constant (30 min.), the energy consumption (3.33-16.7 kWh/m<sup>3</sup>) of the EC process increased with the increase of C.D. from 30 to 60 A/m<sup>2</sup>, while the pH did not affect the COD removal.



(a) COD removal (E.T. 30 min.)

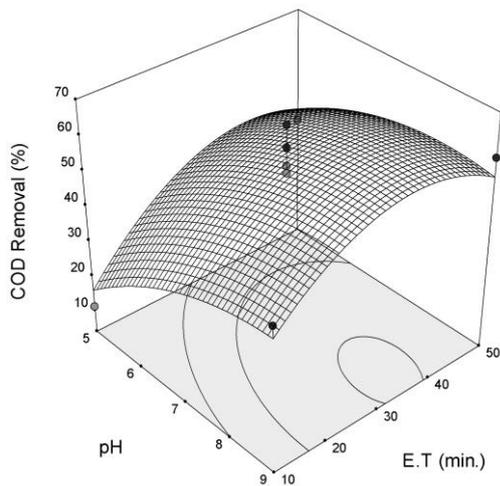


(b) Energy consumption (E.T. 30 min.)

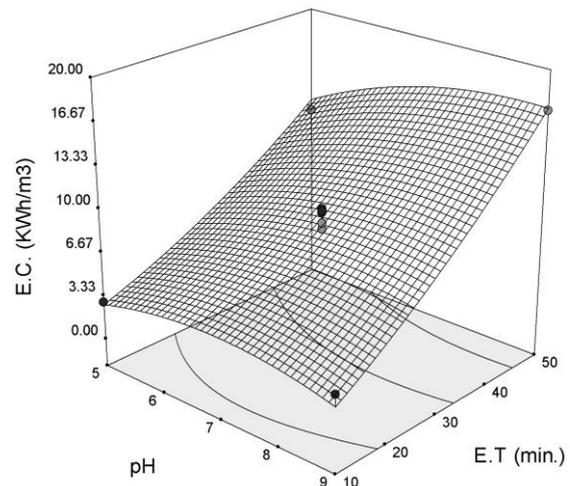
**Figure 2.** Effect of pH/C.D.

Effect of pH/E.T. on EC process is seen in Figure 3 (a). When the C.D. is constant ( $45 \text{ A/m}^2$ ), the COD R.E. increases with the increase of the pH 5 to 9. The increase in the E.T. decreased the COD R.E. This can be due to the secondary reactions which occur at the high C.D. and lead to colloid charge reversal thus results re-dispersion of the colloids [22,23].

The effect of pH/E.T. on COD removal is given in Figure 3 (b). When the C.D. is constant ( $45 \text{ A/m}^2$ ), the COD R.E. of the EO process increased with the increase of E.T., while the pH did not affect the COD removal. EC process is more effective at higher pH values while it is at lower pH values in EC process.



(a) COD removal (C.D. 45 A/m<sup>2</sup>)



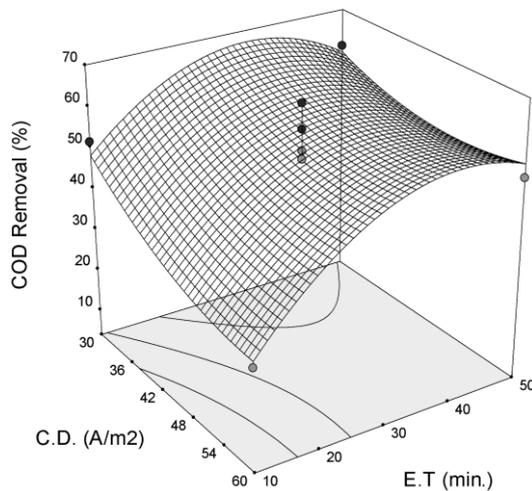
(b) Energy consumption (C.D. 45 A/m<sup>2</sup>)

**Figure 3.** Effect of pH/E.T.

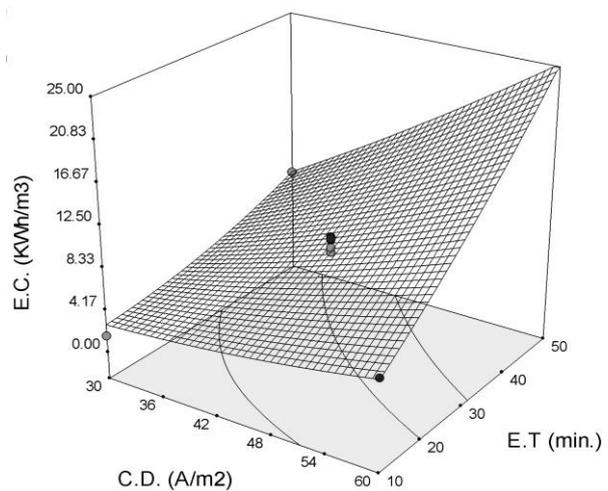
3D counter plots of C.D./E.T. for EO process is shown in Figure 4 (a). According to Figure 4 (a), when the pH is constant (pH 7), the COD R.E. increases with the increase of the E.T. 10 to 50 min. The efficacy of the EC process is due to the metal ion concentration occurred during electrolysis. With the increase of E.T. increases the metal ion concentration and hydroxide flocs. Therefore, pollutant removal efficiency increases [23]. The increase in the C.D. decreased the COD R.E. This can be explained as the excess of the applied C.D. causes the secondary reactions by the formation of colloidal charge reversal, shorten the electrode life

and thus decreases the pollutant R.E. of the EC process [4].

The interactive effect of C.D./E.T. COD removal is given in Figure 4 (b). When the pH is constant (pH 7), the energy consumption of the EC process increased with the increase of C.D. and E.T. During the electrolysis, E.T. presents a higher increase in the energy consumption was determined than C.D.



(a) COD removal (pH 7)



(b) Energy consumption (pH 7)

**Figure 4.** Effect of C.D./E.T.

The actual values obtained from the experiment were compatible with the expected values of the model response for the EC process, as shown in Figure 5 a-b.

impact on the resulting quadratic model. Thus, it is clearly seen that all the parameters are effective on COD removal and energy consumption of EC process as evaluated in the ANOVA analysis section.

Main effects of X<sub>1</sub> (A), X<sub>2</sub> (B), and X<sub>3</sub> (C) parameters for EC are given in Figure 6 a-b. As seen in Figure 6 a-b, the primary impacts of X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> have a significant

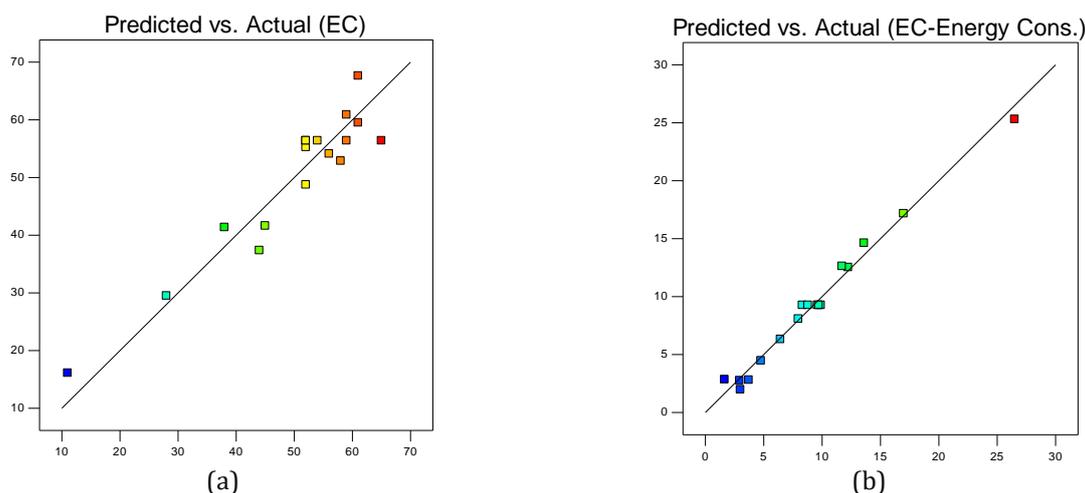


Figure 5. Regression graphs of the actual and predicted values describing COD R.E. and energy consumption

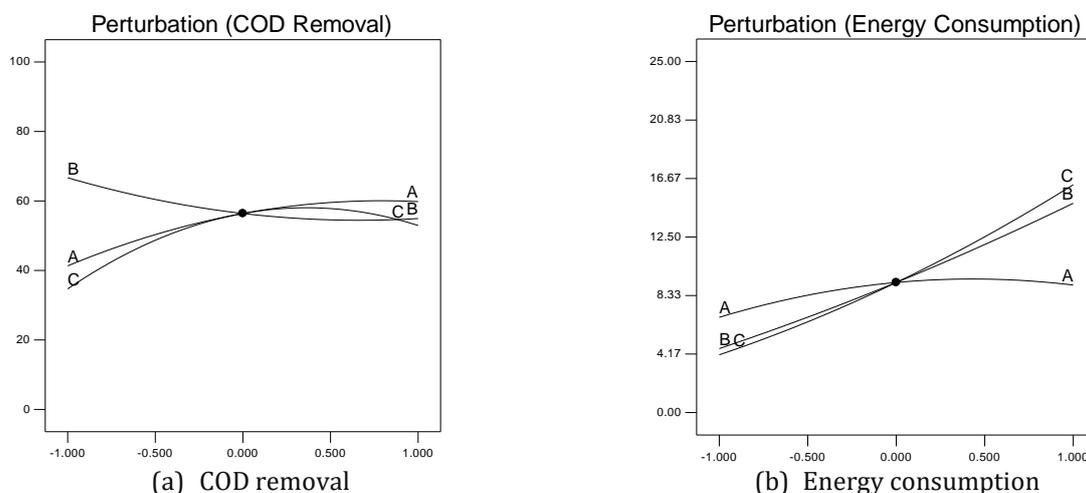


Figure 6. Perturbation of COD removal and Energy consumption

### 3.2. Optimization of process

Comparison of present study results with literature is given in Table 4. The optimization study was evaluated in three scenarios 1. the development of results that maximize COD R.E., 2. the development of optimum conditions that maximize COD R.E. and minimize energy consumption, 3. the development of optimum conditions that maximize COD R.E. and maximize energy consumption.

In first scenario, the optimum conditions for EC process were determined to be an initial pH of 7.48, a C.D. of 33 A/m<sup>2</sup>, a reaction time of 33 min in which COD removal of 66% with an energy consumption of 6.45 kWh/m<sup>3</sup> was achieved.

In second scenario, the optimum conditions for EC process were determined to be an initial pH of 7.48, a C.D. of 30 A/m<sup>2</sup>, a reaction time of 23 min in which COD removal of 65% with an energy consumption of 3.9 kWh/m<sup>3</sup> and with a desirability of 0.954 was achieved.

In third scenario, the optimum conditions for EC process were determined to be an initial pH of 8.48, a C.D. of 60 A/m<sup>2</sup>, a reaction time of 50 min in which COD removal of 58% with an energy consumption of 26.18 kWh/m<sup>3</sup> and with a desirability of 0.929 was achieved.

It is mentioned that neutral and higher pH values are effective in Al electrode connected EC process in the literature [24]. In the bulk solution, two removal mechanism realize as precipitation process at pH<4 and adsorption process at higher pH values [24]. In the study, it is thought that adsorption mechanism was occurred, because the optimal pH was varied from 7.91 to 8.48.

**Table 4.** Comparison of present study results with literature

Type of Wastewater	Electrode Type Anode/Cathode	pH	C.D.	E.T.	COD rem. (%)	Energy Cons.	Ref.
Metal cutting wastewater	Al/Al	7.91	33 A/m <sup>2</sup>	33.5 min.	66	6.43 kWh/m <sup>3</sup>	Present Study
		7.48	30 A/m <sup>2</sup>	23 min.	65	3.9 kWh/m <sup>3</sup>	
		8.48	60 A/m <sup>2</sup>	50 min.	58	26.18 kWh/m <sup>3</sup>	
Textile wastewater	Al/Al	7.6	11.55 20 mA/cm <sup>2</sup>	10 min.	79.7	-	[23]
Ayurveda pharmaceutical wastewater	Al/SS	6.0	99.89 A/m <sup>2</sup>	120 min.	58.35	27.13 kWh/kg COD	[25]
Machinery industry wastewater	Al/Al	-	20 mA/cm <sup>2</sup>	30 min.	68	0.88 kWh/kg-COD	[26]
Paint industry washing wastewater	Al/Fe	6.6-7.15	14.2 mA/cm <sup>2</sup>	32 min.	68	16.53 kWh/m <sup>3</sup>	[27]
Biodigester effluent	Al/Al	8.0	135 30 A/m <sup>2</sup>	93.4 min.	85.1	-	[28]
Metal cutting wastewater	Al/Al	5.0	60 A/m <sup>2</sup>	25 min.	93	-	[29]
Distillery wastewater treatment	Al/Fe	7.0	24.9 mA/cm <sup>2</sup>	60 min.	> 80	15 kWh/m <sup>3</sup> (solar driven EC)	[30]

### 3.3. Effect of solar panel integration on energy consumption

In the study, energy consumption of EC process was varied from 3.9 to 26.8 kWh/m<sup>3</sup> for different scenarios. Energy consumption of EC process which connected with Al electrode was determined as 16.53 kWh/m<sup>3</sup> [27]. The scenarios, the optimization results, contour plots and energy fulfillment ratio of EC process by solar panel are given in Table 5.

The EC process's operating costs are mostly comprised of the cost of energy usage [24]. Therefore, minimization of energy consumption of the EC process is significant for applicability. One of the theories which decrease the energy consumption of electrochemical process is solar panel integration. Also, a solar panel was integrated to the EC process in the study. In the measurements made in overcast air, the voltage/current obtained from the solar panel was 4.95 V/0.272 A, and the energy obtained was 1.33 Wh. In case the weather is completely sunny and the sun comes at the desired angle, 34.62 V energy input value is determined from the solar panel. When current was applied to the electrodes, this value was determined as 4 V, 7 A from the multimeter. That is, it produces an energy of 28 Wh. When the energy consumed for wastewater treated per m<sup>3</sup> volume is calculated, 2.77 kWh/m<sup>3</sup> energy is obtained from solar panels when the weather is overcast, while 58.33 kWh/m<sup>3</sup> energy is

obtained when the weather is sunny. According to the developed scenarios, 11% to 71% of the energy requirement for the EC process was fulfilled with the energy obtained by solar panels in overcast weather. In sunny weather, all the energy consumption of the process was fulfilled and more than consumption was obtained by solar energy. Generally, photovoltaic solar panel integrated EC is more suitable than DC power supplied EC process. The same results were determined by the researchers that compared to photovoltaic solar technology; conventional electric power consumption is higher. Thus, it may be said that traditional power sources needed longer time and a little bit greater voltage. While PV systems need lower voltage and shorter times to remove pollutants with the same effectiveness. Thus, makes the EC process cost-effective and destroys the limited usage of this process because of the energy consumption. However, the performance of a solar-powered system is affected by natural factors such as sun irradiation, temperature, and other meteorological circumstances [30]. Especially, industries in the coastal area will not be affected from these factors. Most EC systems are presently powered by conventional energy rather than solar energy [30]. Direct photovoltaic solar integrated EC systems will be an environmental-friendly/cost effective, thus, preferred technology to treat industrial wastewater in near future.

**Table 5.** The optimal conditions and effect of solar panel on EC process for the different scenarios

Scenario	COD	Energy Consumption	pH	C.D. (A/m <sup>2</sup> )	E.T. (min.)	COD rem. (%)	Energy Cons. (kWh/m <sup>3</sup> )	Des.	E. S.P. O.W. (kWh/m <sup>3</sup> )	F.P. (%)	E. S.P. S.W. (kWh/m <sup>3</sup> )	F.P. (%)
1	maximum	none	7.91	33	33.5	66	6.43	1	2.77	43	58.33	900
<p>Scenario 1 plots: Desirability (Prediction 1), COD Removal (%) (Prediction 66.0853), E.C. (KWh/m3) (Prediction 6.42941). X1: A: pH, X2: B: C.D. (A/m2).</p>												
2	maximum	minimum	7.48	30	23	65	3.9	0.95	2.77	71	58.33	1495
<p>Scenario 2 plots: Desirability (Prediction 0.953556), COD Removal (%) (Prediction 65.0003), E.C. (KWh/m3) (Prediction 3.90466). X1: A: pH, X2: B: C.D. (A/m2).</p>												
3	none	maximum	8.48	60	50	58	26.18	0.93	2.77	11	58.33	222
<p>Scenario 3 plots: Desirability (Prediction 0.987222), COD Removal (%) (Prediction 58.1622), E.C. (KWh/m3) (Prediction 26.1825). X1: A: pH, X2: B: C.D. (A/m2).</p>												

E.S.P. O.: Energy supply of solar panel Overcast, E.S.P. S.W.: Energy supply of solar panel Sunny weather F.P.: Fulfillment percentage, Des: Desirability

#### 4. Discussion and Conclusion

In this study, an experimental design of BBD for the COD R.E. and energy consumption responses were developed. It was determined from the statistical analysis that COD R.E. and energy consumption responses were well fitted with the quadratic model. It is considered that the scenario with an energy consumption of 3.9 kWh/m<sup>3</sup> and a COD R.E. of 65% is suitable for the EC process. In this case, the optimum pH for EC process was 7.48, C.D. was 30 A/m<sup>2</sup> and E.T. was 23 minutes. If the highest COD R.E. is desired, only the scenario that maximizes COD will be appropriate.

High SS concentration cause the scratching of the metal materials. Also, SS concentration of the metal cutting wastewater was determined as 0.5 mg/L after treatment in all scenarios. This means that the treated wastewater could be used in any other process in the production.

In all scenarios the energy consumption of the EC process was fulfilled from 11 to 71% in overcast and 222 to 1495 % in sunny weather from solar panel. Accordingly, it also shows that the energy to be obtained has a high potential to be stored by integrating with battery systems and converters. The incorporation of solar panels into the EC process can be viewed as a strategy that can remove energy costs and hence significantly lower the EC process's operational costs and it can be said that the energy obtained from direct photovoltaic solar panel is an effective alternative in comparison with the conventional energy.

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#### Declaration of Ethical Code

*In this study, we undertake that all the rules required to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" are complied with, and that none of the actions stated under the heading "Actions Against Scientific Research and Publication Ethics" are not carried out.*

#### References

- [1] AlJaberi, F. Y., Ahmed, S. A., Makki, H. F., Naje, A. S., Zwain, H. M., Salman, A. D., Juzsakova, T., Viktor, S., T. Van, B., Le, P. C., Duong La, D., Woong Chang, S., Um, M. J., Ngo, H. H., Nguyen, D. D. 2023. Recent advances and applicable flexibility potential of electrochemical processes for wastewater treatment Science of the Total Environment, 867, 161361.
- [2] Solak, M., 2019. Treatment of Denim Product Manufacturing Wastewater by Hybrid Electrocoagulation /Electrooxidation Processes, Süleyman Demirel University, Journal of Natural and Applied Sciences, 23, 3, pp. 780-786.
- [3] Nawarkar, C. J., Salkar, V. D., 2019. Solar powered Electrocoagulation system for municipal wastewater treatment, Fuel, 237, 222–226.
- [4] Das, P. P., Sharma, M., Purkait, M. K. 2022. Recent progress on electrocoagulation process for wastewater treatment: A review, Separation and Purification Technology, 292, 121058.
- [5] Gatsios, E., Hahladakis, J. N., Gidaracos, E. 2015. Optimization of electrocoagulation (EC) process for the purification of a real industrial wastewater from toxic metals, Journal of Environmental Management, 154, 117-127.
- [6] Oden M. K., Sarı Erkan H. 2018. Treatment of metal plating wastewater using iron electrode by electrocoagulation process: Optimization and process performance, Process Safety and Environmental Protection 119, 207–217.
- [7] Solak, M., Kılıç, M., Yazıcı, H., Baldan Pakdil, N. 2014. Economical Analysis of the Treatment of Marble Processing Wastewaters by Electrocoagulation and Chemical Coagulation Processes, Faculty of Engineering Engineering Sciences Journal, 16, 2, 13-26.
- [8] Wu, J., Zhang, H., Oturan, N., Wang, Y., Chen, L., Oturan, M. A. 2012. Application of response surface methodology to the removal of the antibiotic tetracycline by electrochemical process using carbon-felt cathode and DSA (Ti/RuO<sub>2</sub>-IrO<sub>2</sub>) anode. Chemosphere, 87, 6, 614-620.
- [9] Ghjair, A. Y., Abbar, A. H. 2023. Applications of advanced oxidation processes (Electro-Fenton and sono-electro-Fenton) for COD removal from hospital wastewater: Optimization using response surface methodology. Process Safety and Environmental Protection, 169, 481-492.
- [10] Tak, B., Tak, B., Kim, Y., Park, Y., Yoon, Y., Min., G. 2015. Optimization of color and COD removal from livestock wastewater by electrocoagulation process: Application of Box-Behnken design (BBD). J. Industrial and Engineering Chemistry, 28, 307-315.
- [11] Garg, K. K., Prasad, B. 2016. Development of Box Behnken design for treatment of terephthalic acid wastewater by electrocoagulation process: Optimization of process and analysis of sludge, Journal of Environmental Chemical Engineering, 4, 1, 178-190.
- [12] Solak, M. 2019. Optimization of the Electrocoagulation Process in the treatment of Chemical Spraying Wastewater: Box-Behnken

- Design, *Düzce Üniversitesi Bilim ve Teknoloji Dergisi*, 7, 1367-1377.
- [13] Elnenay, A. M. H. Nassef, E., Malasha, G. F., Magid, M. H. A. 2007. Treatment of drilling fluids wastewater by electrocoagulation, *Egyptian Journal of Petroleum*, 26, 203–208.
- [14] Demirbas, E., Kobya M. 2017. Operating cost and treatment of metalworking fluidwastewater by chemical coagulation and electrocoagulation processes, *Process Safety and Environmental Protection*, 105, 79–90.
- [15] Zini, L. P., Longhi, M., Jonko, E., Giovanela, M. 2020. Treatment of automotive industry wastewater by electrocoagulation using commercial aluminum electrodes, *Process Safety and Environmental Protection* 142, 272–284.
- [16] García-Orozco, V. M. Linares-Hernandez, I., Natividad, R., Balderas-Hernandez, P., Alanis-Ramírez, C., Barrera-Díaz, C. E., Roa-Morales, G. 2022. Solar-photovoltaic electrocoagulation of wastewater from a chocolate manufacturing industry: Anodic material effect (aluminium, copper and zinc) and life cycle assessment, *Journal of Environmental Chemical Engineering* 10, 107969.
- [17] Mohamad, Z., Razak, A. A., Krishnan, S., Singh, L., Zularisam, A. W., Nasrullah, M., 2022. Treatment of palm oil mill effluent using electrocoagulation powered by direct photovoltaic solar system *Chemical Engineering Research and Design* 177, 578–582
- [18] Solak, M. 2023. Cost-Effective Processes for Denim Production Wastewater: Dual Criterial Optimization of Techno-Economical Parameters by RSM and Minimization of Energy Consumption of Photo Assisted Fenton Processes via Direct Photovoltaic Solar Panel Integration, *Processes*, 11, 7 1903.
- [19] American Public Health Association (APHA), 2005. *Standard Methods for the Examination of Waste and Wastewater* (19th ed.), Washington.
- [20] Nasrullah, M., Ansar, S., Krishnan S., Singh, L., Peera, S. G., Zularisam, A. W. 2022. Electrocoagulation treatment of raw palm oil mill effluent: Optimization process using high current application, *Chemosphere* 299, 134387.
- [21] Mollah, M.Y.A., Schennach, R., Parga, J.R., Cocke D.L., 2001. Electrocoagulation (EC) Science and Applications. *Journal of Hazardous Materials*, 84, 29-41.
- [22] Lu, J., Zhang, P., Li, J. 2021. Electrocoagulation technology for water purification: an update review on reactor design and some newly concerned pollutants removal, *J. Environ. Manag.* 296 (2021), 113259.
- [23] Anuf, A. R., Ramaraj, K., Sivasankarapillai, V. S., Dhanusuraman, R., Maran, J. P., Rajeshkumar, G., Rahdare, A., Díez-Pascual, A M., 2022. Optimization of electrocoagulation process for treatment of rice mill effluent using response surface methodology, *Journal of Water Process Engineering*, 49, 103074.
- [24] Merzouk, B., Madani, K., Sekki, A. 2010. Using electrocoagulation – electroflotation technology to treat synthetic solution and textile wastewater, two case studies, *DES* 250, 573–577.
- [25] Singh, S., Singh, S., Lo, S. L., & Kumar, N. (2016). Electrochemical treatment of Ayurveda pharmaceuticals wastewater: optimization and characterization of sludge residue. *Journal of the Taiwan Institute of Chemical Engineers*, 67, 385-396.
- [26] Pantorlawn, W., Khanitchaidech W., Threrujirapapong T., Channei, D., Nakaruk, A. 2018. Electrocoagulation for spent coolant from machinery industry, *J Water Reuse, Desalination*, 8, 497–506.
- [27] Rajaniemi, K., Rauliob, M., Tuomikoskia, S., Lassia U. 2019. Comparison of batch and novel continuous electrocoagulation processes in the treatment of paint industry wash water, *Desalination and Water Treatment*, 170, 394–404.
- [28] Dubey, S., Joshi, A., Parmar, N., Amitesh, C. R., Prajapati, A K. 2023. Process optimization of electrocoagulation reactor for treatment of distillery effluent using aluminium electrode: Response surface methodology approach, *Chemical Data Collections* 45, 101023.
- [29] Kobya, M., Çiftçi, C., Bayramoğlu, M., Sensoy, M. T. 2008. Study on the treatment of waste metal cutting fluids using electrocoagulation, *Sep. Purif. Technol.*, 60 285–291.
- [30] Karmankar, S. B., Sharma, A., Ahirwar R. C., Mehra, S., Pal, D., Prajapati A. K. 2023. Cost cutting approach of distillery effluent treatment using solar photovoltaic cell driven electrocoagulation: Comparison with conventional electrocoagulation, *Journal of Water Process Engineering*, 54, 103982.