Process optimization via response surface methodology in the treatment of metal working industry wastewater with electrocoagulation

Senem Yazici Guvenc, Yusuf Okut, Mert Ozak, Birsu Haktanir and Mehmet Sinan Bilgili

ABSTRACT

In this study, process parameters in chemical oxygen demand (COD) and turbidity removal from metal working industry (MWI) wastewater were optimized by electrocoagulation (EC) using aluminum, iron and steel electrodes. The effects of process variables on COD and turbidity were investigated by developing a mathematical model using central composite design method, which is one of the response surface methodologies. Variance analysis was conducted to identify the interaction between process variables and model responses and the optimum conditions for the COD and turbidity removal. Second-order regression models were developed via the Statgraphics Centurion XVI.I software program to predict COD and turbidity removal efficiencies. Under the optimum conditions, removal efficiencies obtained from aluminum electrodes were found to be 76.72% for COD and 99.97% for turbidity, while the removal efficiencies obtained from iron electrodes were found to be 76.55% for COD and 99.9% for turbidity and the removal efficiencies obtained from steel electrodes were found to be 65.75% for COD and 99.25% for turbidity. Operational costs at optimum conditions were found to be 4.83, 1.91 and 2.91 €/m³ for aluminum, iron and steel electrodes, respectively. Iron electrode was found to be more suitable for MWI wastewater treatment in terms of operational cost and treatment efficiency.

Key words | aluminum-iron-steel electrodes, cost analysis, electrocoagulation, response surface methodology

NOMENCLATURE

MWI | metal working industry
EC | electrocoagulation
J | current density, mA/cm²
COD | chemical oxygen demand, mg/L
RSM | response surface methodology
CCD | central composite design
ANOVA | variance analyses
ENC | electrical energy consumption, kWh/m³
ELC | electrode material consumption, kg/m³
MW | molecular weight, g/mole

INTRODUCTION

Metal working industry (MWI) wastewater is generated as a result of bath washing and infiltration of the metal material produced at the end of procedures such as material lubrication, corrosion prevention, surface cleaning, sandpapering, acid cleaning, cooling and polishing (Canizares et al. 2004; Machado et al. 2016). Wastewaters emerging at the end of the manufacturing processes can contain chemically complex and specially formulated components, metal components, permanent and highly resoluble organics, detergents, heavy metals, cyanide and other chemicals (Gast et al. 2011; Gabaldon et al. 2007; Machado et al. 2010). As a result of serious environmental problems owing to their high pollutant potential (Cheng et al. 2005; Grijalbo et al. 2016), the discharge of these wastewaters to the sewer system without treatment has been prohibited according to the Water Pollution Control Regulation (Ministry of Environment and Urbanisation 2004).

Physical, chemical and biological treatment processes are being widely used for the treatment of MWI wastewater...
Electrocoagulation (EC) is a suitable method for the removal of high chemical oxygen demand (COD) and turbidity of these wastewaters (Tir & Moulai-Mostefa 2009; Kobya et al. 2008). Recently, EC has been commonly preferred in wastewater treatment due to simplicity, low energy consumption, short operation time, no additional reagent, low sludge production and high pollutant removal (Varank et al. 2016; Zodi et al. 2010).

In the EC process, an electric current related to the chemical coagulant is applied to the anode and cathode. While electrodes are dissolved via electrolysis and coagulant types and metal hydroxides are formed on the one hand, dissolved pollutants within wastewater and colloidal particles become destabilized and aggregates emerge (Thirugnanasambandham et al. 2015) on the other hand. While the wastewater is treated via the EC process, the following four successful reactions take place.

(i) During the electrolytic reactions of electrodes, as M, where \( n = 2 \) or 3 (aluminum, iron or steel), coagulants are formed:

\[
M_{n} \rightarrow M_{(aq)}^{n+} + ne^- \quad (1)
\]

(ii) Electrolysis of water occurs on the anode and the cathode:

\[
\begin{align*}
2H_2O + 2e^- & \rightarrow H_2 + 2OH^- \quad \text{Cathodic reaction} \quad (2) \\
2H_2O & \rightarrow 4H^+ + O_2 + 4e^- \quad \text{Anodic reaction} \quad (3)
\end{align*}
\]

(iii) Destabilization of pollutants, particle suspensions and emulsions:

\[
\begin{align*}
M^{+n} + ne^- & \rightarrow nM \quad (4) \\
M^{+n} + nOH^- & \rightarrow nM(OH)_n \quad (5)
\end{align*}
\]

(iv) Aggregation of destabilized phase for the formation of flocs.

Various multi-variate statistical models have been used to optimize wastewater treatment processes in recent years (Karichappan et al. 2014; Varank et al. 2014; Pakravan et al. 2015; Akarsu et al. 2016; Šereš et al. 2016). Among these multi-variate statistical models, response surface methodology (RSM) is a useful and a highly preferred technique to minimize the amount of time needed and the cost of experimental sets. This mathematical model is a technique that utilizes modeling and analysis of a problem and is dependent on numerous variables, provides estimated answers to this problem, and checks the accuracy of the model (Thirungnanasambandham et al. 2013). RSM designs an optimum multi-factor model for EC processes by evaluating the interactions between multiple explanatory variables and one or more response variables, thus reducing the experimental set numbers (Chavalparit & Ongwandee 2009). Central composite design (CCD) is the most commonly used sub-design model of RSM. CCD is a flexible method demonstrating the interaction between variables using a minimized experimental set.

In this study, EC experiments were performed for MWI wastewater treatment, using aluminum, iron and steel electrodes. The main objective of the study was to investigate and optimize the variable parameters such as pH, current density (J) and electrolysis time (t) for the removal of COD and turbidity from MWI wastewater via RSM. EC process operational cost (OC) analyses were also conducted under optimum experimental conditions.

**EXPERIMENTAL METHOD**

**MWI wastewater**

The MWI wastewater used in the study was supplied from a facility in Gebze-Kocaeli (Turkey). The wastewater samples obtained from the input of the wastewater treatment plant were preserved at +4 °C in order to prevent microbial activity before the study was conducted. The characterization of the real wastewater used in the study is given in **Table 1**. All the analyses performed on the wastewater before and after the EC process were conducted according to **Standard Methods** (APHA 2005).

**Experimental setup and procedure**

Experimental studies were carried out in a laboratory-scale plexiglass reactor with 9 cm diameter and 15 cm length. A schematic view of the reactor used in the experimental studies is shown in **Figure 1**. Electrode sets consisting of anode and cathode electrodes are made up of two single-pole parallel plates (6 cm width \( \times \) 11.5 cm length and...
0.1 cm thickness) and the effective area of each plate is 42.5 cm². Electrodes are placed together at 3 cm intervals.

A 500 mL wastewater sample was used for each test. Due to the low conductivity of the wastewater content, 2,000 mg/L sodium chloride solution was added as electrolyte solution before each set. Before each experimental set, electrodes were washed with acetone and the impurities on the electrodes were removed by dipping in the solution prepared by mixing 100 mL hydrochloric acid solution (35% (v/v)) and 200 mL hexamethylenetetramine aqueous solution (2.80% (v/v)) for 5 minutes. EC experiments were performed at the ranges of pH 6–10, 10–30 minutes electrolysis time and 11–55 mA/cm² current density provided by the power supply. Analyses were conducted by taking samples from the supernatant at the end of the precipitation time (60 minutes) after each experimental step.

**Experimental design and model development**

In this study, EC process optimization for COD and turbidity removal from MWI wastewater was achieved in three analytical steps (i.e. determination of factors and variables with the help of preliminary studies, variance analysis and drawing of response surface graphs, realization of optimization of model suitability). For statistical calculations, levels of three parameters as X₁ (pH), X₂ (J), X₃ (t) were coded as Xᵢ depending on Equation (6). The graphical perspective of the mathematical model resulted in the creation of the response surface method term. The relationship between answers and variables is illustrated in Equation (6). For the statistical design of the experiments and data analysis, Statgraphics Centurion XVI.I software was used. In this study, a full factorial CCD model with three independent variables and three different levels was employed and a total of 15 experimental sets were used. Operation parameters of pH: 6–10, J: 11–55 mA/cm², t: 10–30 minutes were the independent variables; COD and turbidity removal rates were determined as system responses (Y). Independent variables and their levels are given in Table 2, while the experimental design matrix is shown in Table 3.

\[
y = f(x_1, x_2, \ldots, x_n) \pm \epsilon
\]

In Equation (6), y represents the observable response variable, f represents the function response, x₁, x₂, x₃, ..., xₙ represent independent variables, n represents the number of the independent variables and ε represents statistical errors. After the selection of the design, the model equation becomes definable, and model equation coefficients become predictable. Selected independent variables are coded according to Equation (7).

\[
X_i = \frac{X_i - X_{avg}}{\Delta X}
\]

In this equation, \(x_i\) represents the real value of factor i, \(X_{avg}\) represents the mean of high and low values of factor i, \(\Delta x\) represents the value of change (Bajpai et al. 2012). To correlate the relationship between independent variables and responses,

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.89</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1,270</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>190</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>1,485</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>1,820</td>
</tr>
<tr>
<td>Copper (mg/L)</td>
<td>0.120</td>
</tr>
<tr>
<td>Chromium (mg/L)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Nickel (mg/L)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>0.1200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original factor (X)</td>
<td>-1</td>
</tr>
<tr>
<td>pH</td>
<td>X₁</td>
</tr>
<tr>
<td>Current density (mA/cm²)</td>
<td>X₂</td>
</tr>
<tr>
<td>Time (min)</td>
<td>X₃</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Factors</th>
<th>Coded factors</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
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<td>Current density (mA/cm²)</td>
<td>X₂</td>
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<tr>
<td>Time (min)</td>
<td>X₃</td>
</tr>
</tbody>
</table>
the second-order polynomial model was selected for further analysis. The generalized mathematical form of the second-order polynomial equation is shown below:

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3
\]

(8)

where \( Y \) is the response in coded units, \( \beta_0 \) is a constant, and \( \beta_{11}, \beta_{22}, \beta_{33}, \beta_{12}, \beta_{13}, \beta_{23} \) are the linear, interactive, and quadratic coefficients respectively. The adequacy of the developed mathematical model was tested by variance analysis (ANOVA). The effectiveness of the fit of the model was expressed by the determination coefficient (R²) and its statistical significance was checked by the Fisher F-test. Model terms were determined by the P-value and the F-value.

### RESULTS AND DISCUSSION

#### Statistical analysis

A second-order polynomial response surface model was applied in order to analyze the match of the experimental results obtained via CCD with the predicted values. In order to explain COD and turbidity removal from MWI wastewater via the EC process, which is conducted by using aluminum, iron and steel electrodes, the regression equation, which includes coded variables created based on the experimental results provided in Table 3, is given below:

when aluminum electrode is used:

\[
\text{COD removal, } \% = -17.122 + 2.91435 X_1 + 1.50467 X_2 + 3.97284 X_3 - 0.0784903 X_1^2 - 0.0371618 X_1 X_2 - 0.0618132 X_1 X_3 - 0.00222787 X_2^2 - 0.0213745 X_2 X_3 - 0.0556854 X_3^2
\]

(9)

\[
\text{Turbidity removal, } \% = 100.582 - 0.0233805 X_1 + 0.00352079 X_2 - 0.129693 X_3 + 0.0068495 X_1^2 - 0.00208979 X_1 X_2 + 0.00185048 X_1 X_3 + 0.0000293424 X_2^2 - 0.000016958 X_2 X_3 + 0.00288787 X_3^2
\]

(10)

when iron electrode is used:

\[
\text{COD removal, } \% = 148.677 - 14.1358 X_1 + 0.0259116 X_2 - 2.49107 X_3 + 0.448146 X_1^2 + 0.0853313 X_1 X_2 + 0.156364 X_1 X_3 - 0.00650391 X_2^2 - 0.00561938 X_2 X_3 + 0.0316621 X_3^2
\]

(11)

<table>
<thead>
<tr>
<th>Run</th>
<th>X₁</th>
<th>X₂</th>
<th>X₃</th>
<th>Sludge volume mL/0.5 L of wastewater</th>
<th>Final ph</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Aluminum</td>
<td>Iron</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>10</td>
<td>11</td>
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<tr>
<td>3</td>
<td>-1</td>
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<td>0</td>
<td>6</td>
<td>55</td>
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<tr>
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<td>0</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>6</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>10</td>
<td>33</td>
</tr>
<tr>
<td>7</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>33</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
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<td>33</td>
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<tr>
<td>9</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>8</td>
<td>11</td>
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<tr>
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<td>8</td>
<td>33</td>
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<tr>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>33</td>
</tr>
</tbody>
</table>
In Equations (9)–(14), a positive sign of the coefficients represents synergic impact and a negative sign is representative of antagonistic effect (Bajpai et al. 2012). When the independent operation variables are taken into account, it is seen that for Equation (9), there is a significantly positive impact of pH of solution, current density and electrolysis time on COD removal. For Equation (10), however, pH of solution and electrolysis time had significant negative effect on turbidity removal but current density had a positive effect. In Equation (11), pH of solution and electrolysis time had a significantly negative effect on COD removal efficiency, whereas current density had a significantly positive effect. In Equation (12), while pH of solution and electrolysis time had a positive effect on turbidity removal, current density had a negative effect. In Equations (13) and (14), it is seen that all three variables had significantly positive effects on COD and turbidity removal. The higher the coefficient values of the independent operation parameters with positive coefficient signs, the higher the COD and turbidity removal efficiency; and the smaller the coefficient values of the independent operation parameters with negative coefficient signs, the smaller the removal efficiency. Removal efficiency rates obtained using aluminum, iron and steel electrodes were predicted via Equations (9)–(14).

The statistical analysis of the model was conducted via ANOVA and the ANOVA results of model are given in Table 4. High value of F represents the significance of the relevant term. The larger the F-value, the more significant is the corresponding term. Furthermore, the P-value related to the F-value could be used to show whether the F-value is large enough or not. P-values smaller than 0.05 prove that the regression model is statistically significant (Kumar et al. 2009; Amani-Ghadima et al. 2013). Additionally, besides the evaluation of whether or not the variable is significant, the sum of squares must be taken into account. As the sum of squares value grows, the significance of the variables grows at the same time (Ravikumar et al. 2007; Jing et al. 2011). In the case that the ‘Prob > F’ value is smaller than 0.0001, it can be accepted that the model is statistically highly significant and model terms are significant at the percentage of 95% probability. In the case that ‘Prob > F’ values are smaller than 0.05, model terms are significant (Zhang et al. 2010).

### Table 4 | ANOVA results of regression parameters of the predicted response surface quadratic model

<table>
<thead>
<tr>
<th>Model</th>
<th>R²</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum electrodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>0.94</td>
<td>1.205.580</td>
<td>133.9533</td>
<td>8.288877</td>
<td>0.015698</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.93</td>
<td>0.626425</td>
<td>0.069603</td>
<td>8.412312</td>
<td>0.015198</td>
</tr>
<tr>
<td>Iron electrodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>0.93</td>
<td>354.9039</td>
<td>39.43377</td>
<td>7.943527</td>
<td>0.017229</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.98</td>
<td>72.52459</td>
<td>8.058288</td>
<td>30.15499</td>
<td>0.000783</td>
</tr>
<tr>
<td>Steel electrodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>0.93</td>
<td>65.35961</td>
<td>7.262179</td>
<td>7.910522</td>
<td>0.017385</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.98</td>
<td>99.61293</td>
<td>11.06810</td>
<td>28.72289</td>
<td>0.000881</td>
</tr>
</tbody>
</table>

Turbidity removal, % = 47.8613 + 10.2701\*X₁ − 0.0589286\*X₂ + 0.65413\*X₃ − 0.545043\*X₁\(^2\) + 0.0260052\*X₁\*X₂ − 0.0662363\*X₁\*X₃ − 0.00194569\*X₂\(^2\) − 0.000716575\*X₃\(^2\) (12)

when steel electrode is used:

COD removal, % = 35.2969 + 5.17554\*X₁ + 0.17098\*X₂ + 1.13664\*X₃ − 0.285618\*X₁\(^2\) − 0.0104065\*X₁\*X₂ − 0.0571658\*X₁\*X₃ − 0.00174526\*X₂\(^2\) + 0.00017341\*X₁\*X₂\*X₃ − 0.0202007\*X₃\(^2\) (13)

Turbidity removal, % = 51.3016 + 4.87856\*X₁ + 0.725284\*X₂ + 0.97073\*X₃ − 0.103611\*X₁\(^2\) − 0.0420923\*X₁\*X₂ − 0.0390316\*X₁\*X₃ − 0.00205169\*X₂\(^2\) − 0.00940872\*X₂\*X₃ − 0.0059549\*X₃\(^2\) (14)
In ANOVA results of the EC study conducted with aluminum electrode (Table 4), 8.288877 and 8.412312 F-values of the model and P-values 0.015698 and 0.015198, respectively, for COD and turbidity removal indicate that the results obtained are significant and the relationship between variables and targets can be explained by the model for COD and turbidity removal. As can be seen in Table 4, when iron electrode was used, for COD and turbidity removal, F-values 7.943327 and 30.15499 and P-values 0.017229 and 0.000783, respectively, indicate that the results obtained are significant and the relationship between variables and targets can be explained by the model for COD and turbidity removal.

According to the ANOVA results obtained via the EC process carried out using steel electrodes, in Table 4 the F- and P-values of the effect of the model on the COD removal efficiency were found to be 7.910522 and 0.017385, respectively, whereas the F- and P-values of the effect of the model on the turbidity removal efficiency were found to be 28.72289 and 0.000881, respectively. These values demonstrate that the results are significant and the relationship between the variables and targets for COD and turbidity removal can be explained via this model.

According to the ANOVA results in Table 4, for the COD removal in EC processes in which aluminum, iron and steel electrodes are used, model correlation coefficients (R²) were found to be 0.94, 0.93 and 0.93, respectively. These values demonstrate that only 6.28%, 6.54% and 6.57% of the total variance cannot be explained by the empirical model for the EC process in which aluminum, iron and steel are used. In order to achieve compliance with the model, it is enough to have a correlation coefficient above 0.80 (Olmez 2009). For turbidity removal in EC processes in which aluminum, iron and steel electrodes are used, model correlation coefficients were found as 0.93, 0.98 and 0.98, respectively. For turbidity removal, 6.2%, 1.81% and 1.9% of the total variance cannot be explained by the empirical model in EC processes in which aluminum, iron and steel are used. That all R² values are above 0.80 indicates that the process can be explained via the regression model.

Table 5 shows the predicted response surface model regression parameters variance analysis results obtained using experimental results for COD removal via the EC process using aluminum electrodes. According to the ANOVA results in Table 5, while current density and electrolysis time independent variables X3X3 quadratic coefficients had a significant effect on COD removal efficiency, it is seen that solution pH, all interactive coefficients, X1X1 and X2X2 quadratic coefficients did not have a significant effect.

The ANOVA results of the predicted response surface model regression parameters for COD removal by the EC process using iron electrodes are given in Table 6. According to the ANOVA results in Table 6, pH of solution and current density, which are independent variables, had significant effects on COD removal efficiency. It is seen that X2X2 and X3X3 quadratic coefficients and X1X2 and X1X3 interactive coefficients had significant effects on COD removal.

### Table 5 | ANOVA results of the response surface quadratic model of COD removal using aluminum electrodes

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
<th>Remark</th>
</tr>
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<tbody>
<tr>
<td>Model</td>
<td>1,205.58</td>
<td>9</td>
<td>133.9533</td>
<td>8.288</td>
<td>0.0157</td>
<td>S</td>
</tr>
<tr>
<td>X1</td>
<td>20.6238</td>
<td>1</td>
<td>20.62380</td>
<td>1.280</td>
<td>0.3099</td>
<td>NS</td>
</tr>
<tr>
<td>X2</td>
<td>725.432</td>
<td>1</td>
<td>725.4320</td>
<td>44.89</td>
<td>0.0011</td>
<td>S</td>
</tr>
<tr>
<td>X3</td>
<td>238.107</td>
<td>1</td>
<td>238.1070</td>
<td>14.73</td>
<td>0.0121</td>
<td>S</td>
</tr>
<tr>
<td>X1X1</td>
<td>0.36321</td>
<td>1</td>
<td>0.363206</td>
<td>0.020</td>
<td>0.8867</td>
<td>NS</td>
</tr>
<tr>
<td>X1X2</td>
<td>10.6945</td>
<td>1</td>
<td>10.69450</td>
<td>0.660</td>
<td>0.4529</td>
<td>NS</td>
</tr>
<tr>
<td>X1X3</td>
<td>6.11339</td>
<td>1</td>
<td>6.113390</td>
<td>0.380</td>
<td>0.5654</td>
<td>NS</td>
</tr>
<tr>
<td>X2X2</td>
<td>4.29307</td>
<td>1</td>
<td>4.293070</td>
<td>0.270</td>
<td>0.6282</td>
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</tr>
<tr>
<td>X2X3</td>
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<td>1</td>
<td>88.44950</td>
<td>5.470</td>
<td>0.0664</td>
<td>NS</td>
</tr>
<tr>
<td>X3X3</td>
<td>114.493</td>
<td>1</td>
<td>114.4930</td>
<td>7.080</td>
<td>0.0448</td>
<td>S</td>
</tr>
<tr>
<td>Total error</td>
<td>80.803</td>
<td>5</td>
<td>16.16060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>1,286.38</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>93.72%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S: Significant.
NS: Not significant.
efficiency. Also, the electrolysis time, an independent variable, $X_1X_1$ quadratic coefficient and $X_2X_3$ interactive coefficient did not have significant effects on COD removal efficiency.

Table 7 shows the ANOVA results of the predicted response surface model regression parameters for COD removal by the EC process using steel electrodes. As can be seen from Table 7, the pH of solution, electrolysis time linear coefficients and $X_2X_3$ quadratic coefficients had a significant effect on COD removal, whereas current density, all interactive coefficients and $X_1X_1$ and $X_2X_2$ coefficients did not.

Table 8 shows the predicted response surface model regression parameters variance analysis results obtained using experimental results for turbidity removal via the EC process using aluminum electrodes. In Table 8, it is seen
that solution pH and current density independent variables and $X_2X_3$ and $X_3X_3$ quadratic coefficients had a significant effect on turbidity removal efficiency, whereas electrolysis time, all interactive coefficients and $X_1X_1$ quadratic coefficient did not. Since the coefficients found to be non-significant, depending on the F- and P-values as a result of the ANOVA analysis, do not have a significant impact on removal efficiency, they are ignored in the RSM equation. Removal of these coefficients from the equation makes the operations simpler and makes it easier according to obtained results.

The ANOVA results of the predicted response surface model regression parameters for turbidity removal by the EC process using iron electrodes are given in Table 9. The results in Table 9 demonstrate that among the independent variables, pH of solution had the greatest effect on turbidity removal efficiency.

### Table 8 | ANOVA results of the response surface quadratic model of turbidity removal using aluminum electrodes

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.626425</td>
<td>9</td>
<td>0.069603</td>
<td>8.412</td>
<td>0.01519</td>
<td>S</td>
</tr>
<tr>
<td>$X_1$</td>
<td>0.094210</td>
<td>1</td>
<td>0.094210</td>
<td>11.39</td>
<td>0.01980</td>
<td>S</td>
</tr>
<tr>
<td>$X_2$</td>
<td>0.131574</td>
<td>1</td>
<td>0.131574</td>
<td>15.90</td>
<td>0.01040</td>
<td>S</td>
</tr>
<tr>
<td>$X_3$</td>
<td>0.000003</td>
<td>1</td>
<td>0.000003</td>
<td>0.000</td>
<td>0.98450</td>
<td>NS</td>
</tr>
<tr>
<td>$X_1X_1$</td>
<td>0.002771</td>
<td>1</td>
<td>0.002771</td>
<td>0.330</td>
<td>0.58780</td>
<td>NS</td>
</tr>
<tr>
<td>$X_1X_2$</td>
<td>0.033819</td>
<td>1</td>
<td>0.033819</td>
<td>4.090</td>
<td>0.09910</td>
<td>NS</td>
</tr>
<tr>
<td>$X_1X_3$</td>
<td>0.005478</td>
<td>1</td>
<td>0.005478</td>
<td>0.660</td>
<td>0.45280</td>
<td>NS</td>
</tr>
<tr>
<td>$X_2X_2$</td>
<td>0.074469</td>
<td>1</td>
<td>0.074469</td>
<td>9.000</td>
<td>0.03010</td>
<td>S</td>
</tr>
<tr>
<td>$X_2X_3$</td>
<td>0.000055</td>
<td>1</td>
<td>0.000055</td>
<td>0.010</td>
<td>0.93780</td>
<td>NS</td>
</tr>
<tr>
<td>$X_3X_3$</td>
<td>0.307930</td>
<td>1</td>
<td>0.307930</td>
<td>37.22</td>
<td>0.00170</td>
<td>S</td>
</tr>
<tr>
<td>Total error</td>
<td>0.0413696</td>
<td>5</td>
<td>0.008273</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>0.667794</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>93.8%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S: Significant.  
NS: Not significant.

### Table 9 | ANOVA results of the response surface quadratic model of turbidity removal using iron electrodes

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>72.5245</td>
<td>8</td>
<td>8.058288</td>
<td>30.15</td>
<td>0.00078</td>
<td>S</td>
</tr>
<tr>
<td>$X_1$</td>
<td>37.5254</td>
<td>1</td>
<td>37.52540</td>
<td>140.4</td>
<td>&lt;0.0001</td>
<td>HS</td>
</tr>
<tr>
<td>$X_2$</td>
<td>0.02989</td>
<td>1</td>
<td>0.029891</td>
<td>0.110</td>
<td>0.75160</td>
<td>NS</td>
</tr>
<tr>
<td>$X_3$</td>
<td>2.58469</td>
<td>1</td>
<td>2.584690</td>
<td>9.670</td>
<td>0.02660</td>
<td>S</td>
</tr>
<tr>
<td>$X_1X_1$</td>
<td>17.5501</td>
<td>1</td>
<td>17.55010</td>
<td>65.67</td>
<td>0.00050</td>
<td>S</td>
</tr>
<tr>
<td>$X_1X_2$</td>
<td>5.23706</td>
<td>1</td>
<td>5.237060</td>
<td>19.60</td>
<td>0.00680</td>
<td>S</td>
</tr>
<tr>
<td>$X_1X_3$</td>
<td>7.01959</td>
<td>1</td>
<td>7.019590</td>
<td>26.27</td>
<td>0.00370</td>
<td>S</td>
</tr>
<tr>
<td>$X_2X_2$</td>
<td>3.27442</td>
<td>1</td>
<td>3.274420</td>
<td>12.25</td>
<td>0.01730</td>
<td>S</td>
</tr>
<tr>
<td>$X_2X_3$</td>
<td>0.26675</td>
<td>1</td>
<td>0.266755</td>
<td>1.000</td>
<td>0.36360</td>
<td>NS</td>
</tr>
<tr>
<td>$X_3X_3$</td>
<td>0.01895</td>
<td>1</td>
<td>0.018959</td>
<td>0.070</td>
<td>0.80060</td>
<td>NS</td>
</tr>
<tr>
<td>Total error</td>
<td>1.33618</td>
<td>5</td>
<td>0.267235</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>73.8604</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>98.19%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S: Significant.  
NS: Not significant.  
HS: Highly significant.
removal. Electrolysis time, $X_1X_1$ and $X_2X_2$ quadratic coefficients and $X_1X_2$ and $X_2X_3$ interactive coefficients had significant effects on turbidity removal. However, the current density independent variable and $X_2X_3$ interactive coefficient and $X_3X_3$ quadratic coefficient did not have a significant effect on turbidity removal.

Table 10 shows the ANOVA results of the predicted response surface model regression parameters for turbidity removal by the EC process using steel electrodes. The results presented in Table 10 indicate that pH of solution, current density and electrolysis time independent variables had significant effects on turbidity removal. It is seen that $X_1X_1$ and $X_2X_2$ quadratic coefficients had significant effects on turbidity removal, whereas $X_3X_3$ coefficients did not. It is clear from the results in the table that while $X_1X_2$ and $X_2X_3$ interactive coefficients had significant effects on turbidity removal, $X_1X_3$ coefficient did not.

As can be seen from Figure 2, there is a high level of match between the data obtained experimentally in COD and turbidity removal and the values that are predicted via the model for all three processes applied. Table 11 presents the optimized process conditions. Under the optimized conditions determined with the help of the model, for the EC processes in which aluminum, iron and steel electrodes are used, maximum COD removal efficiency values were found to be 76.72%, 76.55% and 65.75%, respectively, and turbidity removal efficiency values were found to be 99.97%, 99.99% and 99.99%, respectively.

In response surface model graphs given in Figures 3–5, while a variable is held fixed in the center, the other two variables get values between the contours determined. The response surface and contour graph is a function of the variable held fixed and two variables that have values between the contours.

### Cost analysis

The energy consumption and the amount of electrode material are two important parameters in the OC analysis of the EC process. The OC at optimum conditions was calculated by the following equation:

$$ OC = aENC + bELC + SDC $$  \hspace{1cm} (15)

where $aENC$ ($\text{kWh/m}^3$) denotes the electrical energy consumed and $bELC$ ($\text{kg/m}^3$) estimates the material cost. The electrical energy consumption was calculated using the following equation (El-Ashtoukhy et al. 2009):

$$ ENC = \frac{UisEC}{v} $$  \hspace{1cm} (16)

where $U$ is the applied voltage (V), $i$ is the current (A), $t_{EC}$ is the operating time (s) and $v$ is the volume ($\text{m}^3$) of the wastewater.

### Table 10

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>99.6129</td>
<td>9</td>
<td>11.0681</td>
<td>28.72</td>
<td>0.00088</td>
<td>S</td>
</tr>
<tr>
<td>$X_1$</td>
<td>35.3539</td>
<td>1</td>
<td>35.3539</td>
<td>91.75</td>
<td>0.00020</td>
<td>S</td>
</tr>
<tr>
<td>$X_2$</td>
<td>16.3391</td>
<td>1</td>
<td>16.3391</td>
<td>42.40</td>
<td>0.00130</td>
<td>S</td>
</tr>
<tr>
<td>$X_3$</td>
<td>9.64377</td>
<td>1</td>
<td>9.64377</td>
<td>25.03</td>
<td>0.00410</td>
<td>S</td>
</tr>
<tr>
<td>$X_1X_1$</td>
<td>0.63421</td>
<td>1</td>
<td>0.63421</td>
<td>1.650</td>
<td>0.25580</td>
<td>NS</td>
</tr>
<tr>
<td>$X_1X_2$</td>
<td>13.7205</td>
<td>1</td>
<td>13.7205</td>
<td>35.61</td>
<td>0.00190</td>
<td>S</td>
</tr>
<tr>
<td>$X_1X_3$</td>
<td>2.43754</td>
<td>1</td>
<td>2.43754</td>
<td>6.330</td>
<td>0.05350</td>
<td>NS</td>
</tr>
<tr>
<td>$X_2X_2$</td>
<td>3.64092</td>
<td>1</td>
<td>3.64092</td>
<td>9.450</td>
<td>0.02770</td>
<td>S</td>
</tr>
<tr>
<td>$X_2X_3$</td>
<td>17.1382</td>
<td>1</td>
<td>17.1382</td>
<td>44.48</td>
<td>0.00110</td>
<td>S</td>
</tr>
<tr>
<td>$X_3X_3$</td>
<td>1.30932</td>
<td>1</td>
<td>1.30932</td>
<td>3.400</td>
<td>0.12460</td>
<td>NS</td>
</tr>
<tr>
<td>Total error</td>
<td>1.92664</td>
<td>5</td>
<td>0.38532</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>101.54</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$S$: Significant.

NS: Not significant.
Figure 2 | Predicted versus actual plots for the removal of COD and turbidity (a) and (b) for aluminum electrodes; (c) and (d) for iron electrodes; (e) and (f) for steel electrodes.

Table 11 | Optimum operating conditions of the process variables

<table>
<thead>
<tr>
<th>Factor</th>
<th>Aluminum electrodes</th>
<th>Iron electrodes</th>
<th>Steel electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.000</td>
<td>6.000</td>
<td>6.000</td>
</tr>
<tr>
<td>Current density (mA/cm²)</td>
<td>55.00</td>
<td>37.00</td>
<td>30.18</td>
</tr>
<tr>
<td>Time (min)</td>
<td>21.78</td>
<td>10.00</td>
<td>18.89</td>
</tr>
<tr>
<td>Sludge volume (mL)</td>
<td>185.0</td>
<td>100.0</td>
<td>75.00</td>
</tr>
</tbody>
</table>
Electrode material consumption was calculated using the following equation:

\[
ELC = \frac{i t_{EC} MW}{z F v}
\]  

(17)

where \(i\) is the current (A), \(t_{EC}\) is the operating time (s) and \(v\) is the volume (m\(^3\)) of the wastewater, \(MW\) is the molecular mass of aluminium (26.98 g/mol) or iron (55.84 g/mol), \(z\) is the number of electrons transferred (\(z = 3\) for aluminium and iron electrodes) and \(F\) is the Faraday constant (96,487 C/mol). Cost of chemicals for adjustment of a desired pH is ignored.

In Equation (15), SDC is the sludge disposal cost. According to Turkish regulations, the generated sludge by EC is classified as hazardous. Therefore, the incineration process must be chosen as the sludge disposal method. The hazardous sludge disposal cost is about 240 €/ton.

Figure 3 | Three-dimensional response surface graphs for the effects of variables on the COD and turbidity removals (aluminum electrodes).

Figure 4 | Three-dimensional response surface graphs for the effects of variables on the COD and turbidity removals (iron electrodes).
The sludge disposal cost is calculated as 1.8, 0.96 and 0.72 €/m$^3$ and 2, 1.1 and 0.85 $/m^3$ for sludge volume generated in the EC process using aluminum, iron and steel electrodes at the optimum conditions, respectively.

At the optimum conditions, OC of the EC process using aluminum, iron and steel electrodes applied on MWI wastewater for COD removal was found to be 4.83, 1.91 and 2.91 €/m$^3$ and 5.40, 2.14 and 3.26 $/m^3$ respectively. In comparison with the OC of the EC process using aluminum, iron and steel electrodes, the OC of the EC process using iron electrodes was lower than the others.

CONCLUSIONS

In the present study, treatment of MWI wastewaters via the EC process using aluminum, iron and steel electrodes was investigated. The results of the study indicated that the EC process is a suitable treatment alternative in order to achieve high pollutant removal from MWI wastewater and low energy consumption. Pollutant removal efficiency is a function of solution pH, current density and electrolysis time. Response surface method has been successfully conducted in applying the EC process in MWI wastewater. The impacts of solution pH, current density and electrolysis time on COD and turbidity removal were investigated. Three operational parameters were determined, pH: 6–10, J: 11–55 mA/cm$^2$, t: t 10–30 min intervals, as independent parameters, while COD and turbidity removal rates were identified as system targets. The model applied in the study indicated that there was a high level of correlation ($R^2 > 0.80$) between the experimental data and the values predicted via the model. High correlation coefficient values obtained from variance analysis indicate that the second-order model sufficiently matches with experimental data. Under optimum conditions, removal efficiency rates achieved using iron electrodes were found to be 76.55% for COD and 99.9% for turbidity, removal efficiency rates obtained using aluminum electrodes were found to be 76.72% for COD and 99.97% for turbidity, and removal efficiency rates achieved using steel electrodes were found to be 65.75% for COD and 99.9% for turbidity. Under optimum conditions, operational cost that includes both electricity and electrode consumption was found to be 1.91 €/m$^3$ for iron electrode, 4.83 €/m$^3$ for aluminum electrode and 2.91 €/m$^3$ for steel electrode. Response surface graphs and low error rates in experimental and predictable values are the indicators of the match between the values obtained from the models and the real data. The results demonstrate that response surface method is an efficient method for optimizing the operational conditions of MWI wastewater treatment by the EC process.

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