Modeling and optimizing electro-persulfate processes using Fe and Al electrodes for paper industry wastewater treatment

Gamze Varank, Senem Yazici Guvenc, Ahmet Demir, Nihal Kavan, Nurten Donmez and Zeynep Tugce Onen

ABSTRACT

In this study, the treatment of paper industry wastewaters by the electrocoagulation (EC) process with a strong oxidant, persulfate addition, was investigated. Persulfate was activated by dissolution of Fe and Al from electrodes during the process. Central composite design method, being one of the response surface methods, was applied for the optimization of process parameters and the development of a mathematical model for chemical oxygen demand (COD) removal from paper industry wastewaters. The effects of S$_2$O$_8^{2-}$/COD ratio, current, pH, and reaction time, being the variables of process, were assessed on the efficiency of contaminant removal. For COD removal in EC processes in which Fe and Al electrodes were used, the model’s correlation coefficients ($R^2$) were determined as 90.14% and 87.46%, respectively. As the result of experimental study actualized under optimum conditions determined by the model in order to obtain maximum contaminant removal, COD removal efficiencies were determined as 63.5% and 72.8% respectively for the Fe electrode (S$_2$O$_8^{2-}$/COD ratio: 1.25, current: 4.14 A, pH: 6, and reaction time: 5 minutes), and the Al electrode (S$_2$O$_8^{2-}$/COD ratio: 0.5, current: 4.25 A, pH: 7.25, and reaction time: 25 minutes). Electro-activated persulfate process is an appropriate treatment alternative for COD removal from paper industry wastewaters.

Key words | central composite design, electrocoagulation, paper industry wastewaters, persulfate, response surface method

INTRODUCTION

The paper industry is one of the industries in which a high rate of water consumption and wastewater generation is present. The amount of water consumed per ton of paper produced varies between 5 and 300 m$^3$, which leads to about 2,000 m$^3$ wastewater generation per day during production. The paper industry wastewaters have a ratio of biochemical oxygen demand/chemical oxygen demand (BOD/COD) in between 0.02 and 0.07, representing low biodegradability, and include organic compounds with resistant lignin derivative (Rodrigues et al. 2008). These wastewaters are also characterized by high COD and total organic carbon (TOC) concentrations and cannot be decomposed easily through natural processes due to the strong covalent bonds in their molecular structure. In addition, the treatment of this type of wastewater is problematic due to the heavy metals, toxic and resistant organic contaminants in their contents (Zodi et al. 2011). The primary treatment (thereafter settling, or flotation), and secondary treatment (activated sludge, or anaerobic digestion) processes are able to be applied in the treatment of paper industry wastewaters. However, complex compounds in the content of paper industry wastewaters cannot be removed by biological processes, and the efficiency of the processes is low. Degradation of lignin by microorganisms is particularly hard. After biological treatment, the paper industry wastewaters contain COD, TOC, color and lignin in significant concentrations. For this reason, advanced treatment processes such as ultra-nanofiltration, ion exchange, and adsorption are required following biological treatment (Ciputra et al. 2010). Aerobic biological treatment systems are not economical and the anaerobic treatment processes cannot tolerate shock loads, while physical/
chemical methods cause secondary contamination, and are also unable to attain the required removal efficiencies. In the removal and detoxification of industrial sourced toxic and inert contaminants, the implementation of advanced oxidation processes, based on oxidative treatment of organic substances by free radicals arising as the result of chain reactions, is gradually gaining importance.

Advanced oxidation processes can be defined as oxidation methods based on hydroxyl radical generation in principle. In advanced oxidation processes, the quite reactive free radicals generated react randomly with many organic contaminants, and as a result of these reactions the contaminant is either transformed to a less toxic and easily biodegradable intermediate and/or end products through partial oxidation, or mineralization of the contaminant is ensured. Most of these systems are conducted by the combination of strong oxidants, transition metal ions and beams. The hydroxyl radical (HO·) generated during the Fenton process is commonly used in the oxidation of organic substances due to its strong oxidation potential (2.80 V). But the disadvantages of the instability of the chemicals used in the Fenton process, limited operational conditions like the necessity of an acidic pH and the possibility of corrosion problems because of hydrogen peroxide limit the use hydroxyl radicals. Besides, advanced oxidation ensured by the sulfate radicals generated as the result of the activation of peroxysulfate, which has recently started to be used as an oxidant, by different activation methods (thermal, alkali activation, catalysis of transition metal, photocatalysis) is one of the promising treatment processes.

SO₄²⁻ radical is a very strong oxidant with very high oxidation potential. The half-life of sulfate radical is longer compared to the hydroxyl radical; in other words, while HO· contributes to electron transfer reactions at the same time as the hydrogen – atom breakaway reaction, the sulfate radical only contributes to electron transfer reactions, and this explains the longer half-life of the sulfate radical compared to the hydroxyl radical (Laat & Le 2005). In the literature, it is also concluded that the high reactivity of the SO₄²⁻ radical may arise from the capacity to be the diverging group of bisulfate/sulfate ions which are the redox partner of the radicals (Dogliotti & Hayon 1977).

Oxidants commonly being used in the sulfate radical based treatment processes are peroxymonosulfate or peroxydisulfate (Govindan et al. 2014). Sulfate radicals are obtained by the activation of peroxymonosulfate or peroxydisulfate. For the activation, methods such as the addition of transition metals, heat, UV, and ultrasound can be used alone, or in combinations of some of them (Equations (1)–(6)).

\[
\begin{align*}
S_2O_8^{2-} + Mn^{n+} & \rightarrow SO_4^{-} + M^{(n+1)} & (1) \\
HSO_5^{-} + Mn^{n+} & \rightarrow SO_4^{-} + OH^- + M^{(n+1)} & (2) \\
S_2O_8^{2-} + \text{heat/UV/Ultrasound} & \rightarrow 2SO_4^- & (3) \\
HSO_5^{-} + \text{heat/UV/Ultrasound} & \rightarrow 2SO_4^- + OH^- & (4) \\
Fe^{+2} + S_2O_8^{2-} & \rightarrow Fe^{+3} + SO_4^{2-} + SO_4^- & (5) \\
HSO_5^{-} + Fe^{+2} & \rightarrow Fe^{+3} + SO_4^{-} + OH^- & (6)
\end{align*}
\]

In order to obtain sulfate radicals, iron, which is cost efficient and non-toxic, is commonly used as a transition metal. But slow regeneration after transformation of Fe³⁺ ion to Fe²⁺ is the disadvantage of this process (Zhang et al. 2014). This problem was solved by the cathodic reduction of Fe²⁺ ions in the electro-regeneration process (Equation (7)).

\[
Fe^{+3} + e^- \rightarrow Fe^{+2}
\] (7)

Iron, which is the transition metal used in the activation of persulfate, can be obtained by the electrocoagulation (EC) process using iron electrodes. In an electrolytic reactor not only does the EC process provide contaminant removal but also the iron ions released from the electrodes activate persulfate oxidant, ensuring sulfate radical generation and contaminant removal.

Reaction of sulfate radicals with the organic substance in the wastewater is given in Equation (8).

\[
SO_4^{-} + \text{organic substance} \rightarrow \text{intermediate products} + CO_2 + H_2O
\] (8)

In an electrochemical reaction, the charge is transferred in the interface between the electrode and the conductive liquid. An electrochemical reactor consists of a power supply, a conductive electrolyte, an anode and a cathode. In the anode charge increases oxidation as it is transferred from reactive species to electrode, while the cathode decreases oxidation as it is transferred from the electrode to the species in the reaction. Variation in oxidation results with the change in the forms and chemical quality of the species (Ochando-Pulido et al. 2015). This method is commonly applied for removal of organic and inorganic.
contaminants from industrial wastewaters. In the electrochemical process, oxidation process can be performed in two ways: direct and indirect oxidation. While direct oxidation occurs on anodic surfaces, indirect oxidation occurs by strong oxidant substances arising in electrochemical processes.

Since the direct oxidation process occurs on the surface of electrodes (anode–cathode) used in the system and organic substances are removed by oxidation reactions, the important part of the electro-chemical process is the anode. Here, Ti/IrO2, Pb/PbO2, IrO2, TiO2, glass carbon, porous carbon, fiber carbon, Fe, Al, Pt, and Ti electrodes are being used as the anode material whereas Pt, Ti and steel electrodes are generally used as the cathode material (Ochando-Pulido et al. 2015a). In this type of oxidation, the hydrolysis of water is ensured by the assistance of anodes with high catalytic activity, and the hydroxyl radicals form as given in Equation (9). Degradation of organic contaminants is ensured through the absorption of these radicals by organic substances (Ochando-Pulido et al. 2015a, 2015b).

\[ 2H_2O \rightarrow 2OH^- + 2H^+ - 2e^- \] (9)

An indirect oxidation mechanism is observed as a result of high electrocatalytic activity at the anode at high chloride concentrations. Hypochlorous acid (ClO\textsubscript{2}) and H\textsuperscript{+} ions form by the reaction of free chloride and water at the surface of the anode. Hypochlorous acid (ClO\textsubscript{2}) has an important role in degradation of organic matter (Cassano et al. 2011; Ochando-Pulido et al. 2015a). The parameters affecting the direct oxidation rate are the type of organic contamination, current density and diffusion ratio (Ochando-Pulido et al. 2015a). Indirect oxidation occurs not on the surface of the electrode, or not in its proximity, but in the water present in between the electrodes (Zireh-pour et al. 2014). In indirect oxidation, the decomposition of organic substances to smaller components occurs by the diffusion of primary (such as O\textsubscript{2} and Cl\textsubscript{2}) and secondary (such as H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3} and ClO\textsubscript{2}) oxidants, which arise by the degradation of radicals arising in direct oxidation, into the water. The strength of indirect oxidation depends on pH, temperature and diffusion rate (Cassano et al. 2011; Ochando-Pulido et al. 2015a).

EC is a common process used in electrochemical treatment. The EC process is based on the principle of destabilization of particles by passing electrical energy through wastewater under controlled conditions, and thus contaminants are removed from wastewater by the formation of a stabilized solution (Ozturk et al. 2005). Electrofloation and electrooxidation processes also occur together along with EC. These three important mechanisms acting together positively affect the removal efficiency. While the coagulation process is actualized by the addition of Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Al\textsuperscript{3+} ions as chemical substances, in EC Fe or Al metals dissolve from the anode material during electrolysis (Kurt 2007). In the EC process, the contaminants in suspended, colloidal or dissolved form in aqueous medium are removed by coagulation, adsorption, absorption, settling or flotation mechanisms (Aygun 2012).

EC process occurs in three consecutive stages:

- Formation of coagulants by the electrolytic oxidation of exhaustible electrodes,
- Destabilization of contaminants, suspension of particles, and break down of emulsions,
- Collection of flocs in destabilized phases.

Iron and aluminum electrodes are widely used in EC. Besides the proven applicability of these electrodes, their cheapness and ease of procurement are causes for their preference (Chen et al. 2000).

When iron is used as the anode, Fe(OH)\textsubscript{n} (n = 2 or 3) iron hydroxide forms in the electrolytic system. The formation of metal hydroxides is shown as two mechanisms in Equations (10)–(17).

1. Mechanism:

Anode: \[ 4Fe_{(k)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \] (10)
\[ 4Fe^{2+}_{(aq)} + 10H_2O_{(s)} + O_2_{(g)} \rightarrow 4Fe(OH)_3_{(k)} + 8H^+ \] (11)
Cathode: \[ 8H^+_{(aq)} + 8e^- \rightarrow 4H_2(g) \] (12)
Ultimately: \[ 4Fe_{(k)} + 10H_2O_{(s)} + O_2_{(g)} \rightarrow 4Fe(OH)_3_{(k)} + 4H_2(g) \] (13)

2. Mechanism:

Anode: \[ Fe_{(k)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \] (14)
\[ Fe^{2+}_{(aq)} \rightarrow 2OH^-_{(aq)} \rightarrow Fe(OH)_2_{(s)} \] (15)
Cathode: \[ 2H_2O_{(s)} + 2e^- \rightarrow H_2(g) + 2OH^-_{(aq)} \] (16)
Ultimately: \[ Fe_{(k)} + 2H_2O_{(s)} \rightarrow Fe(OH)_2_{(s)} + H_2(g) \] (17)

Fe(OH)\textsubscript{n(s)}, which removes the contaminants from wastewater through electrostatic attraction, or complexation,
and subsequent coagulation, forms a jellylike suspension in the flow. In complexation mode at the surface, the contaminant acts as a ligand chemically attached to Fe(OH)₃(s) (Equation (18)).

\[ L - H_{(aq)}(OH)OFe_{(s)} \rightarrow L - OFe_{(aq)} + H₂O_{(s)} \]  

(18)

H₂S generated as the result of the redox reaction, can remove the dissolved organics or suspended solids through flocculation. For this reason, (Equations (19)–(21)) Fe³⁺ ions may form Fe(OH)₂⁺, Fe(OH)²⁻, and Fe(OH)₃⁻ compounds under acidic conditions because of hydration (Mollah et al. 2001).

\[ Fe^{3+}_{(aq)} + H₂O_{(s)} \rightarrow Fe(OH)^{2+}_{(aq)} + 2H^{+}_{(aq)} \]  

(19)

\[ Fe^{3+}_{(aq)} + H₂O_{(s)} \rightarrow Fe(OH)^{2+}_{(aq)} + 2H^{+}_{(aq)} \]  

(20)

\[ Fe^{3+}_{(aq)} + H₂O_{(s)} \rightarrow Fe(OH)₃⁻_{(aq)} + 3H^{+}_{(aq)} \]  

(21)

The type of metal hydroxides, which will form in the EC process and which will have an effective role in the removal of contaminants, depends on the pH of the medium. By the use of iron electrodes, monomeric Fe(OH)₃ forms at the range of pH 7–10, and the complexes forming in the range of pH 3.5–7 tend to polymerize, and polymeric types of Fe(OH)³⁻, Fe(OH)²⁻, Fe(OH)⁻, Fe₃(OH)₄OH⁻², Fe₃(OH)₄(OH)²⁻, Fe₃(OH)₆(OH)₄⁻, Fe₃(OH)₆(OH)₄²⁻, and Fe(OH)₅ form, being polymeric over pH 10 (Aygun 2012).

When aluminium is used as the electrode material, Al dissolves at the anode, Equation (22), and hydrogen gas, Equation (23), is released at the cathode. The dissolution of aluminium in water electrolytically through oxidation forms the aqueous Al¹⁻³ species. H₂ gas, formed during the hydrolysis reaction, moves towards the surface of the water, and thus the flocculation process accelerates. The Al(OH)₃ precipitates formation reaction from Al¹⁻³ ions under alkaline and acidic conditions is shown in Equations (24) and (25) (Aygun 2012).

Anode: \[ Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \]  

(22)

Cathode: \[ 3H₂O_{(s)} + 3e^- \rightarrow 3/2H₂_{(g)} + 3OH^-_{(aq)} \]  

(23)

Under alkali conditions: \[ Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)₃_{(s)} \]  

(24)

Under acidic conditions: \[ Al^{3+}_{(aq)} + 3H₂O_{(s)} \rightarrow Al(OH)₃_{(s)} + 3H^{+}_{(aq)} \]  

(25)

By the hydrolysis of Al¹⁻³ ions, Al(H₂O)₆³⁻, Al(H₂O)₅OH⁻², Al(H₂O)₄(OH)⁻², Al(H₂O)₃OH⁻², Al(H₂O)₂(OH)⁺⁺, Al(OH)⁺⁺, and Al(OH)⁺, and polymeric types such as Al₆(OH)₁₅³⁻, Al₅(OH)₁₅⁺⁺, Al₄(OH)₂₀⁺⁺, Al₁₃O₄(OH)₂₄⁺⁺, Al₁₃(OH)₂₄⁺⁺ at a wide pH range (Mollah et al. 2004).

There are numerous studies relevant to the electrochemical treatment of paper industry wastewater (Katal & Pahlavanzadeh 2011; Jaafarzadeh et al. 2016; Camcioglu et al. 2017; Yuliani et al. 2017; Jaafarzadeh et al. 2017; Yazici-Guven et al. 2017). To the best of our knowledge, the application of electrochemically activated persulfate for treatment of paper industry wastewater is limited in the literature, and also few works on electrochemically activated persulfate process carried out for industrial wastewater treatment using modeling tools have been reported (Mehralipour et al. 2018; Gormez et al. 2020). Most of the studies in the literature on electrochemical treatment of paper industry wastewater focused on the classical optimization technique. Due to the complexity of AOP, application of appropriate modeling is essential. Under given circumstances, the developed empirical models for AOPs can directly predict their performance in terms of removal efficiency. The design of the working conditions can be implemented as the result of efficient prediction. Consequently, the costs of treatment processes are reduced by controlling the number of trials. In the present study, the advanced EC method, in which a strong oxidant (persulfate) was added to the electrolytic system using Fe and Al electrodes, was applied, and response surface methodology (RSM), empirical kinetics modeling, was used to efficiently optimize the electrochemical-activated persulfate processes.

The main objectives of the study were determined as:

- investigating electro-persulfate treatment of paper industry wastewaters by using iron and aluminum electrodes,
- revealing the process optimization by the use of the response surface method,
- evaluating the effect of operational parameters (oxidant dosage, current density, pH and reaction time) on COD removal efficiency, being the responses of the system.

**MATERIAL AND METHOD**

**Characterization and analytic method**

Samples of paper industry wastewaters were stored at +4 °C in order to prevent biological and chemical reactions, and
wastewater characterization was performed according to the methods provided in APHA (2005). The pH and conductivity values were measured using the WTW Multi 9620 IDS device, and turbidity values were measured using the WTW TURB 550 IR device. COD and total suspended solids (TSS) concentrations were determined according to the APHA 5220-C method and APHA 2540-D method, respectively. Characterization of paper industry wastewaters is given in Table 1.

### Experimental study

Experimental studies were performed in a laboratory-scale Plexiglas reactor with a diameter of 9 cm and height of 13 cm. Four monopolar (MP) electrode sets (two anode and two cathode electrodes) comprised of four parallel iron or aluminum sheets each having dimensions of 6 cm width, 12 cm height and 0.1 cm thickness. The electrodes were placed 1.5 cm distance from each other. A 500 mL wastewater sample was used for each test. The schematic diagram of the reactor used in the study is seen in Figure 1.

As the conductivity level of wastewater was not sufficient to provide the required electric current, 1 g of NaCl was added prior to each set. Prior to each study, electrodes were washed with acetone, and the impurities on the surfaces of the iron electrodes were removed by washing with a solution prepared by mixing 100 cm$^3$ HCl solution, and 200 cm$^3$ aqueous hexamethyltetramine solution (Gengec et al. 2012). The ranges of operational parameters of the processes were determined as the result of a prestudy that was performed. In the processes, the pH of the solution was adjusted prior to experimental studies, and a magnetic stirrer (200 rpm) was used for the stirring operation. A determined amount of oxidant was added to the wastewater sample in the electrolytic reactor prior to being exposed to electric current. Prior to analysis, all samples were filtered through a filter having a mesh diameter of 0.45 μm, and they were stored and analyzed according to the methods recommended by APHA.

### Response surface methodology and experimental design

Response surface methodology (RSM) can be defined as an optimization system performing mathematical modeling and statistical data analysis, enabling the correlation of independent variables and experimental results. The RSM method is a multivariate approach indicating the system’s responses as the result of concurrent variation of multiple independent variables (Ghaedi et al. 2016; Mosleh et al. 2016).

Central composite design (CCD), being a sub model of RSM, is an extensively used experimental design to analyze the second-order model in wastewater treatment requiring a lower number of experimental sets. Moreover, it is a method for estimating the effects of linear and quadratic interaction for the applied treatment technology. CCD includes three

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### Table 1 | Characterization of wastewater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.2–6.1</td>
<td>6.15</td>
</tr>
<tr>
<td>Conductivity, mS/cm</td>
<td>5.7–5.1</td>
<td>5.4</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>12.500–10.900</td>
<td>11.700</td>
</tr>
<tr>
<td>TSS, mg/L</td>
<td>84–74</td>
<td>79</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>405–395</td>
<td>400</td>
</tr>
</tbody>
</table>

---

Figure 1 | Schematic diagram of electrochemical reactor.

1. DC power supply
2. Electrical current and potential volt dashboard
3. Anode connection cable
4. Cathode connection cable
5. Electrochemical reactor
6. Plate electrodes
7. Magnetic stirrer

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types of points: cube, center and axial points derived from factorial design. Thus, the number of total experiment sets is determined by the following Equation (26) (Karimifard & Moghaddam 2018):

\[ Run = 2^n + 2n + N \]  \hspace{1cm} (26)

where \( n \) indicates the number of factors; \( 2^n \) indicates the cubic runs; \( 2n \) indicates the axial runs; and \( N \) indicates the center point's runs.

In this study, a full factorial CCD model, having four independent variables and five different levels, was used for each process. COD removal was selected as the response of the system (target). The system’s performance was assessed by analyzing the yield of COD removal. By Equation (26), six center points were selected, and the number of experiments for CCD, having four independent variables, was calculated as 30. Model codes and levels applied for the 30 experiments were determined by preliminary studies, and are shown in Table 2. Experimental values and predicted values, obtained by response surface model analyses, are given in Table 3 for each set.

To determine the presence of a relationship between the factors and the response variables investigated, the collected data must be analyzed in a statistical manner by the use of regression. A regression design is usually employed for modeling a response as a mathematical function (either known, or empirical) of a few continuous factors, and estimates of good model parameters are desired. In forming the regression equation, the test factors were coded according to Equation (27) (Salahi et al. 2013):

\[ X_i = X_i - \frac{X_i^c}{\Delta X_i} \]  \hspace{1cm} (27)

where \( X_i \) is the coded value of the \( i \)th independent variable; \( X_i \) is the natural value of the \( i \)th independent variable; \( X_i^c \) is the natural value of the \( i \)th independent variable at the center point; and \( X_i \) is the value of step change.

The dynamics of the model’s responses may be explained by the second-quadratic model in Equation (28) (Gasemloo et al. 2019).

\[ Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i<j}^{n} \beta_{ij} X_i X_j + \varepsilon \]  \hspace{1cm} (28)

where \( Y \) indicates the estimated quadratic model’s response; \( \beta_0 \) indicates the constant coefficient; \( \beta_i \) indicates the coefficient of the linear variable; \( \beta_{ii} \) indicates the coefficient of the chi-squared variable; \( \beta_{ij} \) indicates the coefficient of interactions of the variables; and variables \( X_i \) and \( X_j \) and \( \varepsilon \) indicate the error.

Numerical optimization was used to identify the specific point that maximizes the desirability function. The experimental design, statistical analysis, response surface plots, and optimization were performed using the Statgraphics Centurion XVI.I software program. In order to analyze which factors and relevant effects are significant for the responses, the coefficients in the model's equation were subject to a significance test by analysis of variance (ANOVA) (Popović et al. 2019). Statistical significance of the quadratic model has been assessed by the coefficient of determination \((R^2)\), the adjusted coefficient of determination \((R_{adj}^2)\) between the predicted and experimental values, and the F value (Fisher variation ratio).

A high F value indicates the importance of the relevant term. And whether the F value is sufficiently high or not is assessed by the \( p \) value (Prob > F). While a low \( p \) value indicates the rejection of the hypothesis, it also indicates the significance of the variable. \( p \) values with a value lower than 0.05 verify that the regression model is statistically significant (Amani-Ghadima et al. 2013). In addition, sum of squares should definitely be considered while making an assessment regarding whether the variable is significant or not. The significance of the variables also increases along with the increase of the sum of squares (Jing et al. 2011; Bajpai et al. 2012). Where the value of \( p \) has a value lower than 0.0001, it may be assessed that the model is statistically very significant, and that the terms of the model are significant at a probability level of 95%.

### RESULTS AND DISCUSSION

A second-degree polynomial response surface model was applied in order to analyze the conformity of the experimental results with the estimated values. The regression equations covering the coded variables based on the experimental results obtained for COD removal from paper industry wastewater through the electro active persulfate process using iron and aluminum electrodes are given

### Table 2: Experimental design codes, and their levels

<table>
<thead>
<tr>
<th>Factor</th>
<th>Original factor (X)</th>
<th>Factor codes</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{S}_2\text{O}_8 )/COD</td>
<td>( X_1 )</td>
<td></td>
<td>0.5</td>
<td>2</td>
<td>3.5</td>
<td>5</td>
<td>6.5</td>
</tr>
<tr>
<td>Current (A)</td>
<td>( X_2 )</td>
<td></td>
<td>0.25</td>
<td>1.25</td>
<td>2.25</td>
<td>3.25</td>
<td>4.25</td>
</tr>
<tr>
<td>pH</td>
<td>( X_3 )</td>
<td></td>
<td>6</td>
<td>7.5</td>
<td>9</td>
<td>10.5</td>
<td>12</td>
</tr>
<tr>
<td>Reaction time (minute)</td>
<td>( X_4 )</td>
<td></td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>
below Equations (29) and (30).

COD removal\textsubscript{Fe electrodes} \( \% \)
\[
= 46,581 - 2,59155 \times X_1 + 6,1276 \times X_2 - 0,880903 \times X_3
- 1,0501 \times X_4 - 0,41715 \times X_1^2 + 0,829167 \times X_1 \times X_2
+ 0,025 \times X_1 \times X_3 + 0,130833 \times X_1 \times X_4 + 0,686458 \times X_2^2
- 0,220833 \times X_2 \times X_3 - 0,37625 \times X_2 \times X_4 - 0,11715 \times X_3^2
+ 0,230833 \times X_3 \times X_4 - 0,0150417 \times X_4^2
\]

COD removal\textsubscript{Al electrodes} \( \% \)
\[
= 81,0982 + 1,45961 \times X_1 + 10,6443 \times X_2 - 5,96771 \times X_3
- 3,4724 \times X_4 + 0,136574 \times X_1^2 - 1,27917 \times X_1 \times X_2
+ 0,625 \times X_1 \times X_3 - 0,715833 \times X_1 \times X_4 + 1,56979 \times X_2^2
- 2,9625 \times X_2 \times X_3 + 1,10625 \times X_2 \times X_4 + 0,325463 \times X_3^2
+ 0,260833 \times X_3 \times X_4 + 0,0662917 \times X_4^2
\]

In Equations (29) and (30), the positive mark of the coefficients is the indicator of synergic effect, and their negative
mark is the indicator of antagonistic effect (Bajpai et al. 2012). The removal efficiencies ensured by the use of the iron electrode are estimated in Equation (29). In the process performed by using Fe electrodes, the initial pH, S2O8^2-/COD ratio and reaction time has a distinct negative effect on COD removal, and the applied electric current has a distinct positive effect on the same. According to Equation (30), the S2O8^2-/COD ratio and applied current have a positive effect on COD removal by Al electrodes whereas the initial pH and reaction time have a negative effect. As the coefficient values of the independent operating parameters whose coefficient marks are positive increase, the COD removal efficiencies also increase, and as the coefficient values of the independent operating parameters, whose coefficient marks are negative, decrease, removal efficiencies also decrease.

In Table 4, ANOVA results for the regression parameters of the response surface model are given. The model’s correlation coefficients (R²) for COD removal by electro active persulfate process using Fe and Al electrodes were determined as 90.14% and 87.46%, respectively. These values are expressing that only 9.86% and 12.54% of the total variation cannot be explained with the empirical model. In order to refer to conformity to the model, it is sufficient for the correlation coefficient to have a value higher than 0.80 (Olmez 2009). High correlation coefficient values obtained indicate that the conformity of the model with experimental data is satisfactory (Table 4). The values of the model obtained for Fe electrodes, whose F value is determined as 9.79 and p value is determined as 0.0000376, reveal that the obtained results are significant, and it reveals the explainability of the relation among the variables and responses for COD removal by means of the model. For Al electrodes, the model’s F value was determined as 7.47, and the relevant p value was determined as 0.000196. When the F value, p value and sum of high squares are assessed together for the use of Al electrodes, it is concluded that the model is significant, and that the relation between the independent variables and responses for COD removal is explainable by the use of the model.

By using conventional experimental design methods, the effect of each parameter on the system’s performance can be determined but the effect of interaction among the factors cannot be determined in multi-variable systems. Thus it is not possible to reach the real optimum by classical optimization methods (Mohajeri et al. 2010). To obtain the real optimum conditions for maximum COD removal by electrocoagulation process using Fe and Al electrodes, response surface methodology was used in the present study. It can be seen from the ANOVA results (Tables 5 and 6) that the interactive effect of a significant linear parameter and insignificant linear parameter can be significant or insignificant. In here, although X2 had a highly significant effect, X3 and X4 had an insignificant effect, the interactive effect of X2X4 and X3X4 factors were found to be significant for COD removal by using Fe electrodes. Similarly (Table 6), X1, X2 and X4 had a significant effect whereas X3 had an insignificant effect on COD removal using Al electrodes. As interactive parameters were evaluated, it can be seen that interactive factors of X1X4, X2X3 and X2X4 were determined as significant with the help of the model. In the electrocoagulation process using Fe electrodes, the effect of the linear X1 and X2 parameters was found to be significant for COD removal using Fe electrodes. As interactive parameters were evaluated, it can be seen that interactive factors of X1X4, X2X3 and X2X4 were determined as significant with the help of the model.

**Table 4 | ANOVA results of regression parameters of response surface model**

<table>
<thead>
<tr>
<th>Model</th>
<th>R²</th>
<th>Adjusted R²</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.90</td>
<td>0.80</td>
<td>813.4755</td>
<td>58.10539</td>
<td>9.79</td>
<td>0.0000376</td>
</tr>
<tr>
<td>Al</td>
<td>0.87</td>
<td>0.75</td>
<td>3921.039</td>
<td>280.0742</td>
<td>7.47</td>
<td>0.000196</td>
</tr>
</tbody>
</table>
with initial COD concentration of 1,537 mg/L and 61%, 40% and 50% COD removal efficiencies were obtained through EC, UV-PS and UV-PMS processes, respectively. Camcioglu and his co-workers (2014) investigated COD removal from paper industry wastewater (COD = 1,068.7 mg/L) by EC using Al and Fe electrodes and obtained 42.2% COD removal by using Al electrodes, whereas 30.2% COD removal was achieved by using Fe electrodes. Jaafarzadeh et al. (2017) compared the results of coagulation using FeCl₃ and electro-activated PMS processes.

### Table 5 | ANOVA results of the process using Fe electrodes

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>X₁</td>
<td>114.844</td>
<td>1</td>
<td>114.844</td>
<td>19.36</td>
<td>0.0005</td>
<td>Significant</td>
</tr>
<tr>
<td>X₂</td>
<td>483.304</td>
<td>1</td>
<td>483.304</td>
<td>81.49</td>
<td>&lt;0.0001</td>
<td>Highly significant</td>
</tr>
<tr>
<td>X₃</td>
<td>0.220417</td>
<td>1</td>
<td>0.220417</td>
<td>0.04</td>
<td>0.8497</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₄</td>
<td>21.0938</td>
<td>1</td>
<td>21.0938</td>
<td>3.56</td>
<td>0.0788</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₁</td>
<td>24.1607</td>
<td>1</td>
<td>24.1607</td>
<td>4.07</td>
<td>0.0618</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₂</td>
<td>24.7506</td>
<td>1</td>
<td>24.7506</td>
<td>4.17</td>
<td>0.0590</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₃</td>
<td>0.050625</td>
<td>1</td>
<td>0.050625</td>
<td>0.01</td>
<td>0.9276</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₄</td>
<td>15.4056</td>
<td>1</td>
<td>15.4056</td>
<td>2.60</td>
<td>0.1279</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₂X₂</td>
<td>12.925</td>
<td>1</td>
<td>12.925</td>
<td>2.18</td>
<td>0.1606</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₂X₃</td>
<td>1.75562</td>
<td>1</td>
<td>1.75562</td>
<td>0.30</td>
<td>0.5944</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₂X₄</td>
<td>56.6256</td>
<td>1</td>
<td>56.6256</td>
<td>9.55</td>
<td>0.0075</td>
<td>Significant</td>
</tr>
<tr>
<td>X₃X₃</td>
<td>1.90503</td>
<td>1</td>
<td>1.90503</td>
<td>0.32</td>
<td>0.5793</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₃X₄</td>
<td>47.9556</td>
<td>1</td>
<td>47.9556</td>
<td>8.09</td>
<td>0.0123</td>
<td>Significant</td>
</tr>
<tr>
<td>X₄X₄</td>
<td>3.8786</td>
<td>1</td>
<td>3.8786</td>
<td>0.65</td>
<td>0.4313</td>
<td>Not significant</td>
</tr>
<tr>
<td>Total error</td>
<td>88.9592</td>
<td>15</td>
<td>5.93061</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>902.435</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6 | ANOVA results of the process using Al electrodes

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>P-value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>X₁</td>
<td>1,678.35</td>
<td>1</td>
<td>1,678.35</td>
<td>44.79</td>
<td>&lt;0.0001</td>
<td>Highly significant</td>
</tr>
<tr>
<td>X₂</td>
<td>240.034</td>
<td>1</td>
<td>240.034</td>
<td>6.41</td>
<td>0.0231</td>
<td>Significant</td>
</tr>
<tr>
<td>X₃</td>
<td>24.6038</td>
<td>1</td>
<td>24.6038</td>
<td>0.66</td>
<td>0.4304</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₄</td>
<td>430.954</td>
<td>1</td>
<td>430.954</td>
<td>11.50</td>
<td>0.0040</td>
<td>Significant</td>
</tr>
<tr>
<td>X₁X₁</td>
<td>2.59003</td>
<td>1</td>
<td>2.59003</td>
<td>0.07</td>
<td>0.7962</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₂</td>
<td>58.9056</td>
<td>1</td>
<td>58.9056</td>
<td>1.57</td>
<td>0.2291</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₃</td>
<td>31.6406</td>
<td>1</td>
<td>31.6406</td>
<td>0.84</td>
<td>0.3727</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₁X₄</td>
<td>461.176</td>
<td>1</td>
<td>461.176</td>
<td>12.31</td>
<td>0.0032</td>
<td>Significant</td>
</tr>
<tr>
<td>X₂X₂</td>
<td>67.5907</td>
<td>1</td>
<td>67.5907</td>
<td>1.80</td>
<td>0.1992</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₂X₃</td>
<td>315.951</td>
<td>1</td>
<td>315.951</td>
<td>8.43</td>
<td>0.0109</td>
<td>Significant</td>
</tr>
<tr>
<td>X₂X₄</td>
<td>489.516</td>
<td>1</td>
<td>489.516</td>
<td>13.06</td>
<td>0.0026</td>
<td>Significant</td>
</tr>
<tr>
<td>X₃X₃</td>
<td>14.7086</td>
<td>1</td>
<td>14.7086</td>
<td>0.39</td>
<td>0.5404</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₃X₄</td>
<td>61.2306</td>
<td>1</td>
<td>61.2306</td>
<td>1.63</td>
<td>0.2206</td>
<td>Not significant</td>
</tr>
<tr>
<td>X₄X₄</td>
<td>75.3357</td>
<td>1</td>
<td>75.3357</td>
<td>2.01</td>
<td>0.1767</td>
<td>Not significant</td>
</tr>
<tr>
<td>Total error</td>
<td>562.111</td>
<td>15</td>
<td>37.4741</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>4,483.15</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
for paper industry wastewater (COD = 1,300 mg/L) treatment and obtained similar COD removal efficiencies. COD removal efficiencies of coagulation and electro-activated PMS processes were determined to be 55% and 53%, respectively. Yuliani and his co-workers (Yuliani et al. 2017) concluded 37% COD removal efficiencies for paper industry wastewater with initial COD concentration of 824 mg/L by EC processes using both Al and Fe electrodes. In our previous work (Yazici-Guvenc et al. 2014), we applied EC and electro-Fenton (EF) processes for paper industry wastewater having initial COD concentration of 12,717 mg/L and obtained 34.7% and 74.3% COD removal ratios by EC and EF processes, respectively. It can be seen that the initial COD concentration of the wastewater treated in this work has been nearly ten times that of the others reported in literature. In this study, 63.5% and 72.8% COD removal efficiencies were obtained by advanced EC process using Fe and Al electrodes with peroxydisulfate addition. The results were found to be consistent with the ones obtained for EF process in the previous work (Yazici-Guvenc et al. 2017). In our previous work 4,413 mg/L and 9,450 mg/L COD concentration was removed by EC and EF processes respectively whereas 7,430 mg/l and 8,518 mg/L COD removal was obtained by electroactivated persulfate processes using Fe and Al electrodes, respectively.

The three dimensional graphs indicating the interactions of four independent variables on COD removal obtained for advanced EC processes using Fe and Al electrodes are shown in Figures 2 and 3 respectively. Figure 2(a)–2(c) indicate that the highest COD removal efficiencies were obtained at lower S2O82−/COD ratios. As the S2O82−/COD ratio increases, the amount of sulfate radicals in the solution increases. Akbari et al. (2014) concluded that sulfate radicals react with each other, forming persulfate instead of reacting with organic matter, at high S2O82−/COD ratios (Equations (33) and (34)). This phenomenon is the scavenging effect of an excessive amount of persulfate. Persulfate is a weaker oxidant in

| Table 7 | Optimum operational conditions of process variables |
|---------|-----------------|-----------------|
| Factor  | Fe electrode    | Al electrode    |
| S2O82−/COD | 1.25 | 0.5 |
| Current (A) | 4.1 | 4.25 |
| pH      | 6.0 | 7.25 |
| Reaction time (min) | 5 | 25 |

Figure 2 | Response surface model graphs of EP process using Fe electrodes for COD removal from paper industry wastewaters. (a) Effect of S2O82−/COD and current, (b) effect of S2O82−/COD and pH, (c) effect of S2O82−/COD and reaction time, (d) effect of pH and reaction time.
comparison with sulfate radicals. Since excessive persulfate concentration has a negative effect on the degradability of organic matter, the desired oxidation level could not be obtained at high persulfate concentrations. Similar results were obtained by Rao et al. (2014) and Jaafarzadeh et al. (2016).

$H^+ + S_2O_8^{2-} \rightarrow HS_2O_8^-$

(31)

$HS_2O_8^- \rightarrow H^+ + SO_4^- + SO_4^{2-}$

(32)

$SO_4^- + SO_4^- \rightarrow S_2O_8^{2-}$

(33)

$S_2O_8^{2-} + SO_4^- \rightarrow S_2O_8^- + SO_4^{2-}$

(34)

Electrical current is a parameter with critical significance for the degradation of contaminants in the electro-chemical processes. Especially, it is the primary factor that controls the amount of the catalysts (Fe, Al, etc.) generated from the electrodes in the system as per Faraday’s Law (Equation (5)). Higher amount of the catalyst increases the formation of sulfate radicals by activating more persulfate (Kattel & Dulova 2017). Figure 2(a) reveals that COD removal increases as the applied electrical current increases. In advanced oxidation processes, pH is a parameter with a significant effect on the degradability of organic contaminants. Akbari et al. (2016) had specified that more sulfate radicals form at higher $H^+$ ion concentrations, as given in Equations (31) and (32). Asha et al. (2017) concluded that sulfate radicals and Fe$^{2+}$ ions are able to react under acidic conditions. Figure 2(d) shows that higher COD removal is ensured at pH levels of 6-7. The increase in reaction period has increased COD removal efficiency as expected (Figure 2(d)). As per Faraday's Law, Fe$^{2+}$ concentration increases as the electrolysis period increases, enabling a high rate of organic matter decomposition (Moradi et al. 2015). Moreover, the increase in reaction period results in higher organic matter decomposition by the way increasing the contact period of sulfate radicals with organic matter as shown in Equation (8). It can be seen from Figures 2 and 3 that COD removal efficiencies increase as pH level decreases, applied electrical current increases, reaction period increases and $S_2O_8^{2-}/COD$ ratio decreases.

**CONCLUSION**

In this study, the treatability of paper industry wastewaters by the electro-activated persulfate process using iron and
aluminum electrodes was investigated, and the response surface method and central composite design were applied to determine optimum operational conditions, ensuring that the maximum COD removal efficiencies are reached and the relations among independent variables are assessed. The process optimization was obtained in three analytical steps (determination of factors and variables by means of pre-studies, drawing variance analysis and response surface graphs, actualization of optimization within the frame of the appropriate model). Statgraphics Centurion XVI.I software was used for the statistical design of the experiments and data analyses. According to the results obtained by the application of the response surface method, correlation coefficients (R²) of second degree polynomial equation were determined to be 90.14% and 87.46% for Fe and Al electrodes, respectively. High R² values indicate that the experimental data are in conformity with the model’s results. COD removal efficiencies under optimum conditions determined by the model were found to be 63.5% and 72.8% respectively for Fe electrodes (S₂O₈²⁻/COD ratio: 1.25, current: 4.14 A, pH: 6 and reaction period: 5 minutes) and Al electrodes (S₂O₈²⁻/COD ratio: 0.5, current: 4.25 A, pH: 7.25 and reaction period: 25 minutes). It can be concluded that higher COD removal efficiencies are obtained as pH level decreases, applied electrical current increases, reaction period increases and S₂O₈²⁻/COD ratio decreases for both of the processes. By this study not only were higher COD concentrations removed from paper industry wastewater through the addition of persulfate in the EC process compared to other studies in the literature, but also contributed novelty by modelling the results of the advanced EC process.

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