*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2022.29010

278 (2022) 93–101
December

# Modeling and optimization of electrocoagulation process for removal of Cr(VI) and total suspended solids from tannery effluent

Deepesh Singh[a], Vikas Shende[b], Sushil Kumar Agrahari[a], G.L. Devnani[c], Yash Jaiswal[d,*], Sunder Lal Pal[d,*]

[a]*Department of Civil Engineering, HBTU, Kanpur, India*
[b]*Department of Energy Centre, MANIT, Bhopal, India*
[c]*Department of Chemical Engineering, HBTU, Kanpur, India*
[d]*Department of Chemical Engineering, MANIT, Bhopal, India, Tel. +91-755-405-1802; +919479961203;*
*emails: yash.jaiswal28@gmail.com (Y. Jaiswal), Sunderlalin@gmail.com/sunderp@manit.ac.in (S. Lal Pal)*
*http://orcid.org/0000-0002-3787-9085*

Received 21 April 2022; Accepted 4 October 2022

**ABSTRACT**

Hexavalent chromium [Cr(VI)] is one of the toxic heavy metals and total suspended solids both present in different industrial effluents. The key objective is to adopt best and design suitable methods either to reduce or to prevent heavy metals from wastewater. This present study concerns with EC (electrocoagulation) technique which was a robust technique used to treat polluted tannery effluent without using any chemicals and easy to operate and generate less by-products after wastewater treatment. In electro coagulation electric current is applied to both electrodes (anodes and cathodes) whereby sacrificial anodes corrode to create free ions for coagulations in the solution. This study also optimize process variables like current density, operating time and initial pH for electro coagulation for removal of Cr(VI) and total suspended solids (TSS). The response surface methodology (RSM) with central composite design (CCD) used in the development of modelling and statistical analysis of tannery wastewater by EC where RSM is a best mathematical and statistical tool for optimizing the solutions and identify the best solution and artificial neural network which is a robust technique of optimization, validate the RSM prediction. A CCD was executed for suitable and adequate measurement and predicted two factor interaction model were design for %Cr(VI) removal efficiency for both aluminium and iron electrode. The most significant model for %TSS removal efficiency for aluminium and iron electrode, respectively, was quadratic and linear. These models gave coefficient of determination *R*-squared value, adjusted *R*-squared value and predicted *R*-squared values for Cr(VI) and TSS for both Al and Fe electrode, respectively. The optimum condition for predicted maximum Cr(VI) removal was found to be 53.93% and 57.72% for Al and Fe electrodes, respectively, similarly 89% and 86% for %TSS removal.

*Keywords:* Cr(VI) and total suspended solids (TSS) removal; Response surface methodology (RSM); Central composite design (CCD); Statistical modeling; Artificial neural network (ANN); Analysis of variance (ANOVA); Design-Expert software

* Corresponding authors.

1944-3994/1944-3986 

## 1. Introduction

Industrial waste are usually generated from different industrial processes, the amount and toxicity of waste released from industrial varies with the industrial processes, among all the industrial wastes tannery effluents are highest pollutant [1]. Other industries like electroplating, dairy, textile, oil and oil in water emulsion etc. also generate toxic wastewater [2]. Electroplating industry, leather tanning and textile mill generate a high concentration of chromium (Cr(VI)) in its effluents 140, 10–15 and 5–20 mg/L of Cr(VI), respectively [3,4]. Various treatment are used for tannery effluent like physico-chemical methods, sedimentation, electroflotation, coagulation, filtration, adsorption, reverse osmosis, chemical precipitation etc. [5–7]. Cr(VI) is naturally soluble in aqueous solution [8]. Approximately, 90% of tanneries in the world use Cr salt as tanning material and at least 60% of the Cr is used up in tanning process rest remain in the tanning effluent [9].

The electrocoagulation (EC) technology is highly acceptable for wastewater treatment, due to the need for simple and easy operation, good settling ability of the sludge, lower sludge production, bigger flocks and reducing the secondary pollution without using chemicals and also being safe and environmentally friendly [10,11]. EC is a treatment process of applying electrical current to treat contaminated wastewater and capable of removing small particles with direct current applied, setting them into motion [12,13].

## 2. Experimental setup and working process

### *2.1. Apparatus required*

The electrocoagulation unit was used 2-L glass reactor for treatment of 1.5 L of tannery effluent. The reactor having an area of 4 $cm^2$ × 6 $cm^2$ and height of 12 cm, contains six Al or Fe electrodes with magnetic stirrer. Al and Fe electrodes were having thickness of 5 mm, length and width of 5 and 10 cm, respectively. The whole process was connected by D.C. power supply through connecting wire. Tannery effluent which was collected from tanneries treated by EC reactor at maintain initial pH (3, 6.5, and 10), current density (15, 30, and 45 mA/$cm^2$) and operating time (30, 60, and 120 min) [14]. U.V. double beam spectrophotometer, pH-meter and I.R.-30 were used for measuring Cr(VI), pH of solution and total suspended solids of samples [15].

### *2.2. Experiment processes and analytical approach*

For experiment, tannery effluent was collected and segregated it into nine other sample for experiment for both Al and Fe electrodes and maintained initial pH at 3, 6.5 and 10 as required for experiment [16,17]. In these samples, took one sample and maintain initial pH-3 (more acidic) by using acids and treated it for 120 min at 15 mA/$cm^2$ current density [18,19]. In that treated sample picked out the treated samples at 30, 60 and 120 min for checking Cr(VI) and total suspended solids (TSS) concentration in treated sample. Similarly took other samples and maintained parameters (initial pH, current density, operating time) like (3, 15, 120), (3, 30, 120), (3, 45, 120), (6.5, 15, 120), (6.5, 30, 120), (6.5, 45, 120), (10, 15, 120), (10, 30, 120), (10, 45, 120) and picked treated sample at 30 and 60 min also for both electrodes (Table 1).

The calculation of %Cr(VI) removal efficiency and %TSS removal efficiency after electrocoagulation process were performed using the following formula [20,21].

$$\%C_R = \left[\frac{\left(C_0 - C\right)}{C_0}\right] \times 100 \tag{1}$$

where $C_R$-contaminant removal, $C_o$ and $C$ are concentration of wastewater before and after electrocoagulation.

## 3. Methodology

Response surface methodology is a collection of mathematical and statistical techniques useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [20,22,23].

A central composite design (CCD) is very effective design tool for fitting second-order model was pointed out in this study. The number of tests required for CCD include: $2^k$ factorial points, $2k$ axial points fixed at a distance and $n_c$ central points where $k$ is the number of factors [20] then total number of design points in a CCD is $N = 2^k + 2k + n_c$.

The value of alpha (the axial points, $\alpha$) and $n_c$ are chosen so that the CCD can acquire certain desirable properties causes the CCD to be rotatable. A CCD for 3 factors (operating time, current density, pH) have 8 design points ($2^k = 8$), 6 axial points ($2k = 6$), and 6 central points and total 8 + 6 + 6 = 20 runs, with alpha to be 1.

The data obtained from the experiment was analyzed using Design-Expert trial version software (Stat-Ease Inc., Minneapolis) for three analytical steps: various model test, analysis of variance (ANOVA) and the response surface plotting were performed to establish an optimal condition [24,25]. The optimum operating time and current density, two dependent factors were analysed as response; Cr(VI) and TSS removal. A regression model was employed for predicting the optimum conditions. The response can be expressed as polynomial model [20,22,26].

$$Y = \beta_o + \sum_{i=1}^{n}\beta_i X_i + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{ij}X_iX_j + \sum_{i=1}^{n}\beta_{ii}X_i^2 \tag{2}$$

where $Y$ is the predicted response; $n$ is the number of independent factor, $X_{ij}$ the controlling factors, $\beta_0$ constant coefficient.

Response surface plots were developed from model equation. These response surface plots are helpful in locating the optimized condition [3,13]. In numerical optimization each parameter is set at a desired goal (maximum,

Table 1
Input variable factors and initial ranges

| Factor | Variables | Range of initial variables | | |
|---|---|---|---|---|
| *A* | pH | 3 | 6.5 | 10 |
| *B* | Current density (mA/$cm^2$) | 15 | 30 | 45 |
| *C* | Treatment time (min) | 30 | 60 | 120 |

minimum, target, within range and none) along with upper and lower limits for each variable (Fig. 1).

*3.1. Artificial neural network modeling*

Artificial neural network (ANN) is a parallel computing model, which can map almost any function of practical use [3]. In it normalized CCD data (with range –1 to +1) were used to train the ANN model in visual gene developer 1.7 neural network tool platform. In this case six neurons were chosen for the hidden layer. The sigmoidal, hyperbolic and Gaussian transfer functions were used for input to hidden layer mapping and predicted, which transfer function gave best $R^2$-value for data and compared with models, which was selected through response surface methodology (RSM) technique. The Bayesian regulation based function 'TRAINBR' was applied in the feed-forward back propagation framework to train the network in working platform [27]. The ANN model used to validate the optimum RSM predictions.

## 4. Results and discussion

*4.1. Statistical result and analysis*

The three factor variable and two response for both aluminium and iron electrode for electrocoagulation was analyzed using RSM, respectively. The CCD Tables 2 and 3 developed the mathematical equations where ANOVA and ANN predicted response was analysed as a function of current density, pH and operating time.

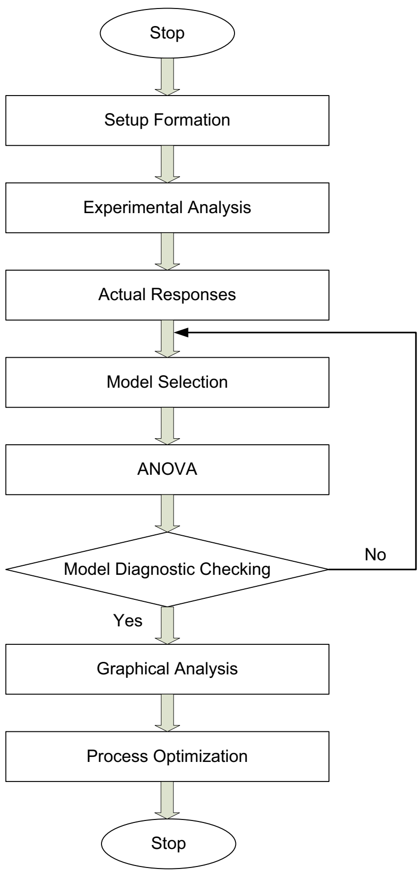


Fig. 1. Schematic representation of methodology.

*4.2. Model selection and validation*

Predicted responses were formed to develop models using RSM [3,20]. The responses were correlated with three factors variable (pH, current density, operating time) according to three factor variable RSM predicted four model (linear, two factor interaction, quadratic and cubic). To determine a most significant model following parameters must follow:

- The model $F$-value must be high.
- The value of Prob. > $F$ must less then 0.05 indicate terms are significant [28].
- The predicted $R^2$-value is close to the Adj.-$R^2$ value or difference not more than 20% [20].
- Adeq. precision measures the signal to noise ratio. A ratio greater than 4 is desirable [3].

*4.2.1. Model selection for %Cr(VI) removal efficiency for Al and Fe electrode*

To develop a response surface regression model for %Cr(VI) for Al electrode a two factor interaction model was most significant and polynomial model as shown in Eq. (3) and Table 4.

$$\begin{aligned}\%\ \mathrm{Cr}(\mathrm{VI})\ \text{removal efficiency} &= +39.39 - 0.633\times\mathrm{pH} \\ &+ 0.133\times\text{current density} + 0.075\times\text{Operating time} \\ &- 0.013\times\mathrm{pH}\times\text{current density} - 9.95\times\mathrm{pH}\times\text{time} \\ &+ 1.44\times\text{current density}\times\text{time}\end{aligned} \quad (3)$$

To develop a response surface regression model for %Cr(VI) for Fe electrode a two factor interaction model was most significant and polynomial model as shown in Eq. (4) and Table 5.

$$\begin{aligned}\%\ \mathrm{Cr}(\mathrm{VI})\ \text{removal efficiency} &= +46.14 - 2.33\times\mathrm{pH} \\ &+ 0.231\times\text{current density} + 0.066\times\text{Operating time} \\ &- 0.019\times\mathrm{pH}\times\text{current density} - 7.613\times\mathrm{pH}\times\text{time} \\ &+ 1.042\times\text{current density}\times\text{time}\end{aligned} \quad (4)$$

*4.2.2. Validation of model for %Cr(VI) removal efficiency*

The response surface model was selected for higher $R^2$-value like 0.9621 and 0.99 for Al and Fe electrode, respectively. However $R^2_{adj}$ value likely close to the $R^2$-value insure a satisfactory result. For validation of model graphical method were used and characterize the residue of the models. A residual is a difference between experimental value and its predicted value [20,26]. If the model is valid, the residue should be structure less, it should be unrelated to any other variable like predicted response. The graphical representation of residue vs predicted response for

Table 2
CCD with experimental and predicted responses for Cr(VI) removal efficiency

| S. No. | Actual value | | | %Cr(VI) removal efficiency for Al | | | %Cr(VI) removal efficiency for Fe | | |
|---|---|---|---|---|---|---|---|---|---|
| | pH | Current density ($mA/cm^2$) | Operating time (min) | Exp. | ANOVA pred. | ANN pred. | Exp. | ANOVA pred. | ANN pred. |
| 1 | 3 | 15 | 30 | 40.25 | 39.90 | 40.39 | 45.01 | 43.49 | 44.15 |
| 2 | 3 | 45 | 120 | 54.63 | 53.93 | 52.08 | 59.01 | 57.72 | 56.11 |
| 3 | 6.5 | 30 | 60 | 40.30 | 38.88 | 38.55 | 36.32 | 36.93 | 36.50 |
| 4 | 6.5 | 30 | 60 | 38.50 | 38.88 | 38.55 | 35.72 | 36.93 | 36.50 |
| 5 | 10 | 15 | 30 | 31.45 | 31.96 | 30.96 | 22.65 | 23.45 | 23.08 |
| 6 | 10 | 15 | 120 | 33.01 | 31.73 | 32.80 | 25.03 | 23.97 | 24.32 |
| 7 | 6.5 | 30 | 60 | 39.30 | 38.88 | 38.55 | 37.31 | 36.93 | 36.40 |
| 8 | 6.5 | 30 | 60 | 40.01 | 38.88 | 38.55 | 36.65 | 36.93 | 36.40 |
| 9 | 3 | 30 | 60 | 46.47 | 44.61 | 45.05 | 48.72 | 48.78 | 49.28 |
| 10 | 6.5 | 30 | 60 | 39.40 | 38.88 | 38.55 | 37.02 | 36.93 | 36.40 |
| 11 | 10 | 45 | 30 | 33.65 | 33.19 | 34.16 | 27.23 | 25.41 | 27.10 |
| 12 | 3 | 15 | 120 | 45.42 | 45.95 | 46.54 | 47.65 | 48.80 | 50.31 |
| 13 | 6.5 | 30 | 30 | 36.40 | 37.26 | 37.11 | 35.43 | 35.49 | 36.16 |
| 14 | 10 | 45 | 120 | 36.40 | 36.87 | 37.34 | 27.74 | 28.75 | 29.33 |
| 15 | 6.5 | 30 | 60 | 38.50 | 38.88 | 38.55 | 36.96 | 36.93 | 36.40 |
| 16 | 6.5 | 45 | 60 | 41.03 | 40.86 | 40.44 | 40.67 | 39.41 | 38.96 |
| 17 | 6.5 | 30 | 120 | 40.03 | 42.12 | 41.90 | 40.67 | 39.81 | 39.67 |
| 18 | 6.5 | 15 | 60 | 35.50 | 36.90 | 36.22 | 34.14 | 34.44 | 33.71 |
| 19 | 10 | 30 | 60 | 33.12 | 33.15 | 33.35 | 25.23 | 25.07 | 25.22 |
| 20 | 3 | 45 | 30 | 42.32 | 43.98 | 45.90 | 49.24 | 49.60 | 50.76 |

Table 3
CCD with experimental and predicted responses for TSS removal efficiency

| S. No. | Actual value | | | %TSS removal efficiency for Al | | | %TSS removal efficiency for Fe | | |
|---|---|---|---|---|---|---|---|---|---|
| | pH | Current density ($mA/cm^2$) | Operating time (min) | Exp. | ANOVA pred. | ANN pred. | Exp. | ANOVA pred. | ANN pred. |
| 1 | 10 | 15 | 120 | 76.3 | 77.84 | 79.08 | 76.8 | 76.50 | 79.14 |
| 2 | 6.5 | 30 | 60 | 86.2 | 84.59 | 85.39 | 87.3 | 86.85 | 81.68 |
| 3 | 3 | 15 | 120 | 94.6 | 94.98 | 92.50 | 76.4 | 75.75 | 80.56 |
| 4 | 6.5 | 30 | 60 | 85.2 | 84.59 | 85.39 | 88.3 | 86.85 | 81.68 |
| 5 | 10 | 45 | 30 | 75.4 | 75.65 | 75.12 | 78.9 | 79.19 | 83.64 |
| 6 | 6.5 | 30 | 60 | 84.2 | 84.59 | 85.39 | 87.5 | 86.85 | 81.68 |
| 7 | 10 | 15 | 30 | 72.3 | 73.51 | 73.15 | 74.2 | 73.64 | 78.48 |
| 8 | 6.5 | 30 | 120 | 89.4 | 87.48 | 88.92 | 87.5 | 88.91 | 82.02 |
| 9 | 6.5 | 15 | 60 | 82.8 | 83.52 | 84.19 | 81.5 | 83.23 | 79.57 |
| 10 | 3 | 30 | 60 | 93.5 | 93.16 | 90.31 | 75.2 | 76.17 | 82.19 |
| 11 | 10 | 45 | 120 | 77.2 | 79.98 | 80.95 | 80.3 | 79.90 | 83.90 |
| 12 | 6.5 | 30 | 60 | 85.6 | 84.59 | 85.39 | 86.4 | 86.85 | 81.68 |
| 13 | 6.5 | 45 | 60 | 91.4 | 85.66 | 86.36 | 89 | 89.21 | 84.44 |
| 14 | 3 | 15 | 30 | 90.3 | 90.65 | 88.31 | 70.1 | 69.89 | 80.00 |
| 15 | 10 | 30 | 60 | 74.5 | 76.02 | 75.90 | 76.8 | 77.77 | 80.83 |
| 16 | 6.5 | 30 | 30 | 85.3 | 83.15 | 84.32 | 85.1 | 85.63 | 81.57 |
| 17 | 6.5 | 30 | 60 | 86.4 | 84.59 | 85.39 | 88.3 | 86.85 | 81.68 |
| 18 | 6.5 | 30 | 60 | 85.5 | 84.59 | 85.39 | 87.2 | 86.85 | 81.68 |
| 19 | 3 | 45 | 30 | 86.2 | 92.79 | 90.29 | 77.8 | 77.74 | 84.83 |
| 20 | 3 | 45 | 120 | 96.8 | 97.12 | 93.54 | 81.5 | 81.45 | 85.00 |

Table 4
Model selection for Al electrode

| Model | $R^2$-value | Adj.-$R^2$ value | Pred.-$R^2$ value | Adeq. precision | $F$-value | Prob. > $F$ | Model condition |
|---|---|---|---|---|---|---|---|
| Linear | 0.9033 | 0.8852 | 0.7945 | 26.707 | 49.81 | <0.0001 | Significant |
| Two factor interaction | 0.9621 | 0.9446 | 0.8104 | 29.828 | 55.01 | <0.0001 | Most significant |
| Quadratic | 0.9738 | 0.9503 | 0.7063 | 26.334 | 41.33 | <0.0001 | More significant |
| Cubic | 0.9925 | 0.9763 | –3.1438 | 33.773 | 61.25 | <0.0001 | Aliased |

Table 5
Model selection for Fe electrode

| Model | $R^2$-value | Adj.-$R^2$ value | Pred.-$R^2$ value | Adeq. precision | $F$-value | Prob. > $F$ | Model condition |
|---|---|---|---|---|---|---|---|
| Linear | 0.9752 | 0.9705 | 0.9420 | 47.62 | 209.47 | <0.0001 | Significant |
| Two factor interaction | 0.9900 | 0.9854 | 0.8982 | 51.58 | 215.03 | <0.0001 | Most significant |
| Quadratic | 0.9919 | 0.9845 | 0.8429 | 41.62 | 135.30 | <0.0001 | More significant |
| Cubic | 0.9990 | 0.9967 | 0.9232 | 81.39 | 442.82 | <0.0001 | Aliased |

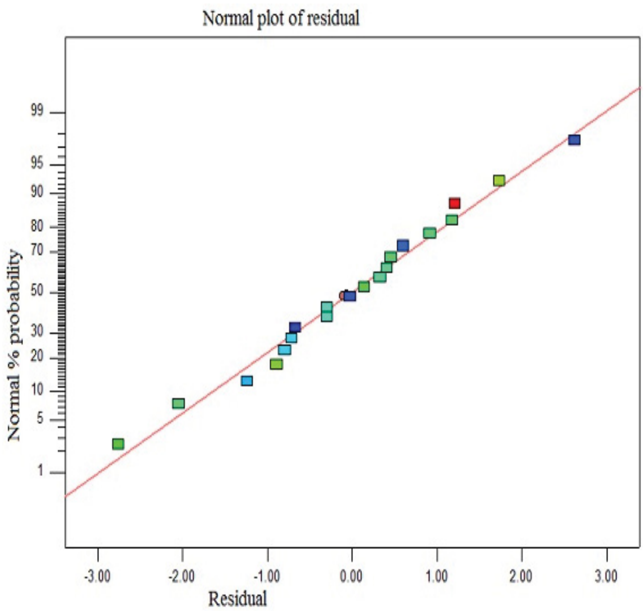


Fig. 2. Normal % probability vs. residual of %Cr(VI) removal for 2F interaction model for Al electrode.

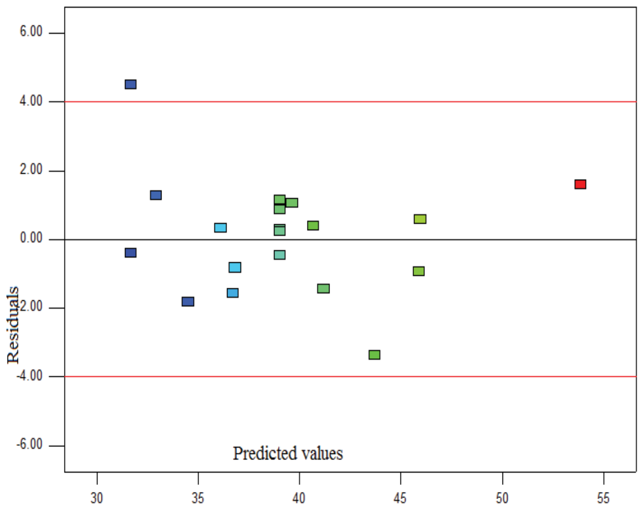


Fig. 3. Residual vs. predicted value of %Cr(VI) removal for 2F interaction model for Al electrode.

Al and Fe electrode were shown in Figs. 3 and 5 which was not in a particular structure and normal % probability plot also show the normal distribution of residues for responses in Figs. 2 and 4.

*4.2.3. Model selection for %TSS removal efficiency for Al and Fe electrodes*

To develop a response surface regression model for %TSS for Al electrode a linear model was most significant and polynomial model as shown in Eq. (5) and Table 6.

$$\%\ \text{TSS removal by Al electrode} = +95.48 - 2.45 \times \text{pH} + 0.07 \times \text{current density} + 0.048 \times \text{Operating time} \quad (5)$$

To develop a response surface regression model for %TSS for Fe electrode a quadratic model was most significant and polynomial model as shown in Eq. (6) and Table 7.

$$\begin{aligned}\%\ \text{TSS removal by Fe electrode} = {} & +34.77 - 11.32 \times \text{pH} \\ & + 0.49 \times \text{current density} + 0.102 \times \text{time} \\ & - 0.0109 \times \text{pH} \times \text{current density} - 4.76 \times \text{pH} \times \text{time} \\ & - 7.97 \times \text{current density} \times \text{time} - 0.80 \times \text{pH}^2 \\ & - 2.808 \times \text{current density}^2 - 7.138 \times \text{time}^2 \quad (6)\end{aligned}$$

*4.2.4. Validation of model for %TSS removal efficiency*

The response surface model was selected for higher $R^2$-value like 0.88 and 0.97 for Al and Fe electrode, respectively (Figs. 6–9).

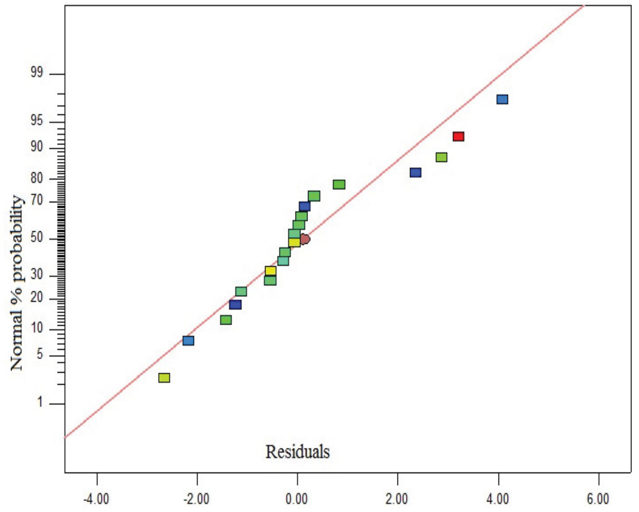


Fig. 4. Normal % probability vs. residual graph for %Cr(VI) removal for 2F interaction model for Fe electrode.

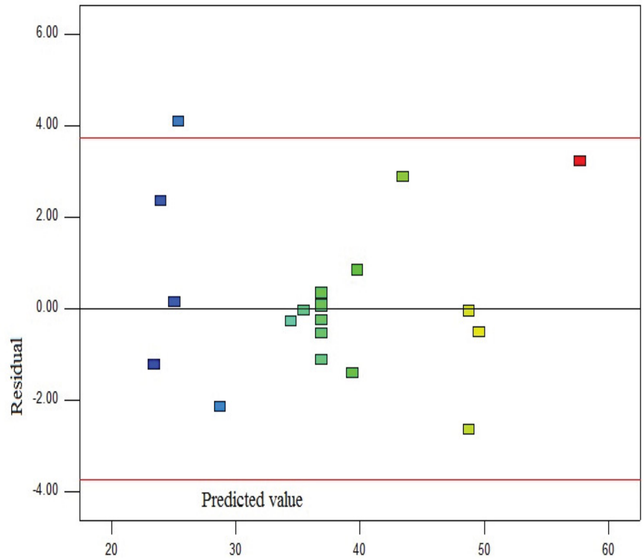


Fig. 5. Residual vs. actual value graph of %Cr(VI) removal for 2F interaction model for Fe electrode.

### *4.3. Analysis of variance for %Cr(VI) and %TSS removal for Al and Fe electrodes*

The *p*-value was used as a tool to check the significant factors. The factors, which show the major effect for %Cr(VI) removal by Al and Fe electrodes were the linear effect of pH, current density and operating time, Having *p*-value of <0.0001 significant for each factor as shown in Table 8 and others interaction terms pH × operating time and current density × operating time are significant with *p*-value 0.0035 and 0.0449, respectively for Al electrode and significant interaction terms for Fe electrode is pH × current density and pH × operating time with p value 0.0215 and 0.0092, respectively. The lack of fit F-test predicts the variation in the data around the fitted model. If the model does not fit the data means, the lack of fit will be significant. Here for %Cr(VI) removal by Al and Fe electrode the *p*-value for the lack of fit equals 0.0721 and 0.0367, respectively, shows that for Al electrode lack of fit was insignificant. It implies that the significant model correlation between the factor variables and process response.

%TSS removal by Al and Fe electrode show in Table 9 in which the *p*-value for the lack of fit equals 0.0037 and 0.0727, respectively, shows that for Fe electrode lack of fit was insignificant.

### *4.4. Optimization analysis of responses*

Table 10 shows the optimal parameters suggested by RSM. These optimized values was obtained at pH = 3, current density = 45 mA/cm$^2$ and operating time 120 min which produced overall desirability (*D*) 0.970 and 0.965 for Al and Fe electrode, respectively, for giving 53.930% by Al and 57.724% by Fe electrode. Table 11 show the optimal condition for %TSS removal efficiency.

Table 6
Model selection for Al electrode

| Model | $R^2$-value | Adj.-$R^2$ value | Pred.-$R^2$ value | Adeq. precision | *F*-value | Prob. > *F* | Model condition |
|---|---|---|---|---|---|---|---|
| Linear | 0.8807 | 0.8583 | 0.7857 | 20.34 | 39.36 | <0.0001 | Most significant |
| Two factor interaction | 0.8957 | 0.8476 | 0.3774 | 14.94 | 18.61 | <0.0001 | significant |
| Quadratic | 0.9444 | 0.8943 | 0.4659 | 15.40 | 18.86 | <0.0001 | More significant |
| Cubic | 0.9892 | 0.9659 | –1.19686 | 22.87 | 42.41 | <0.0001 | Aliased |

Table 7
Model selection for Fe electrode

| Model | $R^2$-value | Adj.-$R^2$ value | Pred.-$R^2$ value | Adeq. precision | *F*-value | Prob. > *F* | Model condition |
|---|---|---|---|---|---|---|---|
| Linear | 0.1396 | –0.0217 | –0.4026 | 3.113 | 0.87 | 0.4792 | Not significant |
| Two factor interaction | 0.1547 | –0.2354 | –3.4621 | 2.502 | 0.40 | 0.8683 | Not significant |
| Quadratic | 0.9789 | 0.9599 | 0.8996 | 23.56 | 51.50 | <0.0001 | Significant |
| Cubic | 0.9838 | 0.9486 | –20.3653 | 18.31 | 28.00 | <0.0001 | Aliased |

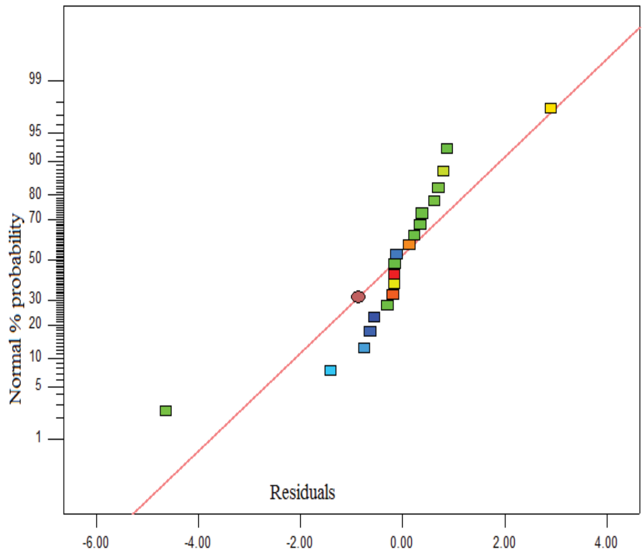


Fig. 6. Normal % probability vs. residual graph for linear model for Al electrode.

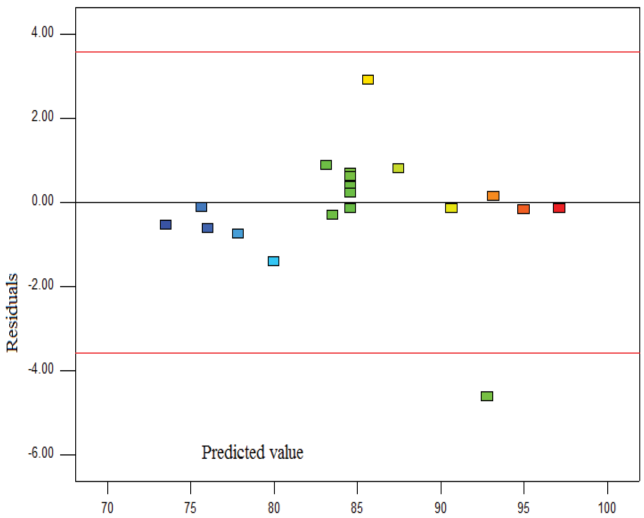


Fig. 7. Predicted value vs. residual graph of for linear model for Fe electrode.

These optimized value was obtain at pH = 3, current density = 45 mA/cm$^2$ and operating time = 120 min, which gives overall desirability ($D$) = 0.991 for Al electrode and for pH = 6.964, current density = 32.096 mA/cm$^2$, operating time 119.922 min gave desirability ($D$) = 1.000 for Fe electrode.

## 5. Summary and conclusions

Electrocoagulation is a best technique for tannery wastewater treatment or removal of heavy metals from contaminated water and produced less sludge, no chemical used in the processes. A central composite design (CCD) was executed for suitable and adequate measurement and predicted two factor interaction model was most significant for

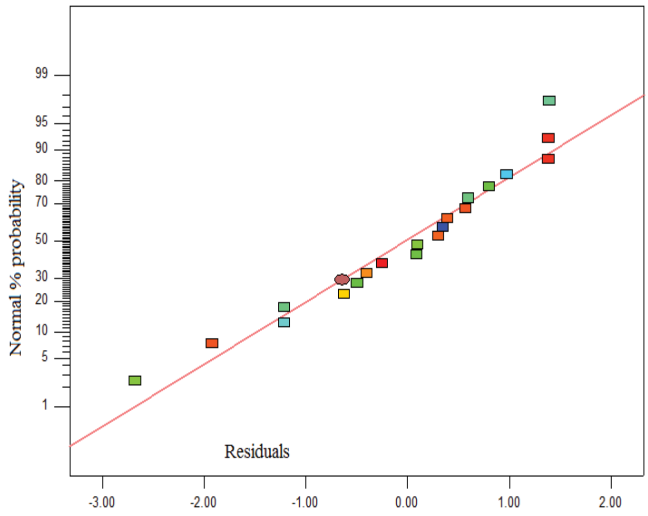


Fig. 8. Normal % probability vs. residual graph of quadratic model for Fe electrode.

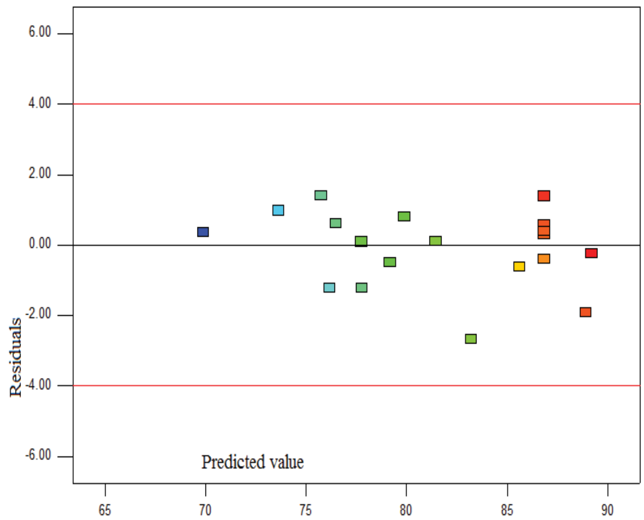


Fig. 9. Predicted values vs. residual graph of for quadratic model for Fe electrode.

%Cr(VI) removal efficiency for both aluminium and iron electrode and for %TSS removal efficiency, quadratic model was found suitable for Fe electrode and linear model for Al electrode. These models gave coefficient of determination $R$-squared value, adjusted $R$-squared value and predicted $R$-squared values (0.9621, 0.9446, 0.8104), (0.9900, 0.8583, 0.8982), (0.8857, 0.8583, 0.7857), (0.9789, 0.9599, 0.8996) for %Cr(VI) removal efficiency for Al and Fe electrodes and %TSS removal efficiency for Al and Fe electrodes, respectively, and $F$-value was 55.01, 215.03, 39.36 and 51.50, which was high enough. In multiple optimization for %Cr(VI) removal efficiency was found 53.930% and 57.724% for Al and Fe electrode, respectively, and for %TSS removal efficiency was found 96.586% and 89.004%, respectively.

Finally, this study concluded that Al electrode was best fitted for Cr(VI) removal efficiency over to Fe electrode in

Table 8
ANOVA prediction of 2FI model for %Cr(VI) removal for Al and Fe electrode

| Source | %Cr(VI) removal efficiency for Al | | %Cr(VI) removal efficiency for Fe | |
|---|---|---|---|---|
| | *F*-value | Prob. > *F* | *F*-value | Prob. > *F* |
| Model (2FI) | 55.01 | <0.0001* | 215.03 | <0.0001* |
| *A*-pH | 245.58 | <0.0001* | 1,184.10 | <0.0001* |
| *B*-current density | 33.40 | <0.0001* | 58.41 | <0.0001* |
| *C*-operating time | 39.42 | <0.0001* | 39.05 | <0.0001* |
| *AB* | 2.56 | 0.1338 | 6.83 | 0.0215* |
| *AC* | 12.70 | 0.0035* | 9.32 | 0.0092* |
| *BC* | 4.92 | 0.0449* | 3.21 | 0.0965 |
| Residual | | | | |
| Lack of fit | 3.99 | 0.0721(NS) | 5.62 | 0.0367* |

*significant at $p \leq 0.05$; NS = Not significant

Table 9
ANOVA prediction of linear and quadratic model for %TSS removal for Al and Fe electrode, respectively

| Source | %TSS removal efficiency for Al | | %TSS removal efficiency for Fe | |
|---|---|---|---|---|
| | *F*-value | Prob. > *F* | *F*-value | Prob. > *F* |
| Model | 39.36 | <0.0001* | 51.50 | <0.0001* |
| *A*-pH | 109.01 | <0.0001* | 2.24 | 0.1657 |
| *B*-current density | 1.70 | 0.2108 | 58.55 | <0.0001* |
| *C*-operating time | 7.36 | 0.0153* | 19.99 | 0.0012* |
| *AB* | | | 1.97 | 0.1911 |
| *AC* | | | 3.42 | 0.0942 |
| *BC* | | | 1.76 | 0.2141 |
| $A^2$ | | | 199.62 | <0.0001* |
| $B^2$ | | | 0.82 | 0.3876 |
| $C^2$ | | | 0.033 | 00.8600 |
| Residual | | | | |
| Lack of fit | 15.41 | 0.0037* | 4.13 | 0.0727 (NS) |

*significant at $p \leq 0.05$; NS = Not significant

Table 10
Multiple response optimization with RSM and ANN prediction for %Cr(VI)

| S. No. | Parameters | Goal | Upper limit | | Lower limit |
|---|---|---|---|---|---|
| 1 | pH | In range | 10 | | 3 |
| 2 | Current density | In range | 45 | | 15 |
| 3 | Operating time | In range | 120 | | 30 |
| 4 | %Cr(VI) removal by Al | Maximize | 54.63 | | 31.45 |
| 5 | %Cr(VI) removal by Fe | Maximize | 59.01 | | 22.65 |
| Validation experiment | pH | Current density (mA/cm²) | Operating time (min) | %Cr(VI) removal efficiency by Al | %Cr(VI) removal efficiency by Fe |
| Validation at optimize condition | 3 | 45 | 120 | 53.930 | 57.724 |
| ANN prediction | 3 | 45 | 120 | 52.08 | 56.11 |

Table 11
Multiple response optimizations with RSM and ANN prediction for %TSS

| S. No. | Parameters | Goal | Upper limit | Lower limit |
|---|---|---|---|---|
| 1 | pH | In range | 10 | 3 |
| 2 | Current density | In range | 45 | 15 |
| 3 | Operating time | In range | 120 | 30 |
| 4 | %TSS removal by Al | Maximize | 96.80 | 72.30 |
| 5 | %TSS removal by Fe | Maximize | 89.00 | 70.10 |
| Validation experiment | pH | Current density (mA/cm²) | Operating time (min) | %TSS removal efficiency by Al |
| Validation at optimize condition | 3 | 45 | 120 | 96.586 |
| ANN prediction | 3 | 45 | 120 | 94.33 |
| Validation experiment | pH | Current density (mA/cm²) | Operating time (min) | %TSS removal efficiency by Fe |
| Validation at optimize condition | 6.964 | 32.096 | 119.922 | 89.004 |
| ANN prediction | 6.964 | 32.096 | 119.922 | 86.025 |

all pH range but in acidic medium Fe electrode performed better than Al. For TSS removal Fe electrode was best fitted and gave better removal efficiency.

## References


[1] S. Banuraman, T.P. Meikandaan, Treatability study of tannery effluent by enhanced primary treatment, Engineering (Semantic Scholar), 3 (2013) 119–122.
[2] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.
[3] M.S. Bhatti, A.S. Reddy, R.K. Kalia, A.K. Thukral, Modeling and optimization of voltage and treatment time for electrocoagulation removal of hexavalent chromium, Desalination, 269 (2011) 157–162.
[4] A. Deghles, U. Kurt, Treatment of tannery wastewater by a hybrid electrocoagulation/electrodialysis process, Chem. Eng. Process. Process Intensif., 104 (2016) 43–50.
[5] I. Ilou, S. Souabi, K. Digua, Quantification of pollution discharges from tannery wastewater and pollution reduction by pre-treatment station, Int. J. Sci. Res., 3 (2014) 1706–1715.
[6] C.A. Igwegbe, O.D. Onukwuli, J.O. Ighalo, C.J. Umembamalu, The process partially fitted to the theory of flocculation proposed by von Smoluchowski, Chem. Eng. J. Adv., (2021) 100107, doi: 10.1016/j.ceja.2021.100107.
[7] J.-w. Feng, Y.-b. Sun, Z. Zheng, J.-b. Zhang, S. Li, Y.-c. Tian, Treatment of tannery wastewater by electrocoagulation, J. Environ. Sci., 19 (2007) 1409–1415.
[8] S.S. Hamdan, M.H. El-Naas, Characterization of the removal of chromium(VI) from groundwater by electrocoagulation, J. Ind. Eng. Chem., 20 (2014) 2775–2781.
[9] L. Szpyrkowicz, S.N. Kaul, R.N. Neti, S. Satyanarayan, Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater, Water Res., 39 (2005) 1601–1613.
[10] M. Dehghani, S. Seresht, H. Hashemi, Treatment of hospital wastewater by electrocoagulation using aluminum and iron electrodes, Int. J. Environ. Health Eng., 3 (2014) 15, doi: 10.4103/2277-9183.132687.
[11] H. Zheng, G. Zhu, S. Jiang, T. Tshukudu, X. Xiang, P. Zhang, Q. He, Investigations of coagulation-flocculation process by performance optimization, model prediction and fractal structure of flocs, Desalination, 269 (2011) 148–156.
[12] V. Kuokkanen, T. Kuokkanen, J. Rämö, U. Lassi, Recent applications of electrocoagulation in treatment of water and wastewater—a review, Green Sustainable Chem., 3 (2013) 89–121.
[13] E.Ü. Deveci, C. Akarsu, Ç. Gönen, Y. Özay, Enhancing treatability of tannery wastewater by integrated process of electrocoagulation and fungal via using RSM in an economic perspective, Process Biochem., 84 (2019) 124–133.
[14] L.S. Thakur, P. Mondal, Simultaneous arsenic and fluoride removal from synthetic and real groundwater by electrocoagulation process: parametric and cost evaluation, J. Environ. Manage., 190 (2017) 102–112.
[15] S. Vasudevan, J. Lakshmi, G. Sozhan, Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water, J. Hazard. Mater., 192 (2011) 26–34.
[16] S. Aoudj, A. Khelifa, N. Drouiche, R. Belkada, D. Miroud, Simultaneous removal of chromium(VI) and fluoride by electrocoagulation–electroflotation: application of a hybrid Fe-Al anode, Chem. Eng. J., 267 (2015) 153–162.
[17] S. Elabbas, N. Ouazzani, L. Mandi, F. Berrekhis, M. Perdicakis, S. Pontvianne, M.N. Pons, F. Lapicque, J.P. Leclerc, Treatment of highly concentrated tannery wastewater using electrocoagulation: influence of the quality of aluminium used for the electrode, J. Hazard. Mater., 319 (2016) 69–77.
[18] N. Galvão, J.B. de Souza, C.M. de Sousa Vidal, Landfill leachate treatment by electrocoagulation: effects of current density and electrolysis time, J. Environ. Chem. Eng., 8 (2020) 104368, doi: 10.1016/j.jece.2020.104368.
[19] Y.A. El-Taweel, E.M. Nassef, I. Elkheriany, D. Sayed, Removal of Cr(VI) ions from waste water by electrocoagulation using iron electrode, Egypt. J. Pet., 24 (2015) 183–192.
[20] A.N. Ghanim, Optimization of Pollutants Removal from Textile Wastewater by Electrocoagulation Through RSM, J. Babylon Univ., 2014.
[21] A.D. Villalobos-Lara, F. Álvarez, Z. Gamiño-Arroyo, R. Navarro, J.M. Peralta-Hernández, R. Fuentes, T. Pérez, Electrocoagulation treatment of industrial tannery wastewater employing a modified rotating cylinder electrode reactor, Chemosphere, 264 (2021) 128491, doi: 10.1016/j.chemosphere.2020.128491.
[22] A.I. Khuri, S. Mukhopadhyay, Response surface methodology, WIREs Comput. Stat., 2 (2010) 128–149.
[23] Y. Ait Ouaissa, M. Chabani, A. Amrane, A. Bensmaili, Integration of electro coagulation and adsorption for the treatment of tannery wastewater – the case of an Algerian factory, Rouiba, Procedia Eng., 33 (2012) 98–101.
[24] J.N. Hakizimana, B. Gourich, M. Chafi, Y. Stiriba, C. Vial, P. Drogui, J. Naja, Electrocoagulation process in water treatment: a review of electrocoagulation modeling approaches, Desalination, 404 (2017) 1–21.
[25] J. Lu, Z. Wang, X. Ma, Q. Tang, Y. Li, Modeling of the electrocoagulation process: a study on the mass transfer of electrolysis and hydrolysis products, Chem. Eng. Sci., 165 (2017) 165–176.
[26] C. Lalanne, R Companion to Montgomery's Design and Analysis of Experiments, Cpdee. Ufmg. Br., 2005. Available at: http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:R+Companion+to+Montgomery's+Design+and+Analysis+of+Experiments#0
[27] M. Zakaria, M. Al-Shebany, S. Sarhan, Artificial neural network: a brief overview, Int. J. Eng. Res. Appl., 4 (2014) 7–12.
[28] Z. He, X-t. Zhang, G.-q. Xie, Product Quality Improvement Through Response Surface Methodology: A Case Study, Diversity, Technology, and Innovation for Operational Competitiveness: Proceedings of the 2013 International Conference on Technology Innovation and Industrial Management, 2013, pp. 120–130.