

# Hexavalent chromium removal by monopolar electrodes based electrocoagulation system: optimization through Box–Behnken design

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## ABSTRACT

The aim of the present study was to investigate the performance of the graphite and aluminum electrode in monopolar arrangement to assess chromium removal efficiency. The aluminum anode has been used for generation of metal coagulants species, while the cathode material was replaced with monopolar graphite cathode to accomplish a major challenge, i.e., reduce energy consumption and cost of treatment. Moreover, the process has been optimized through the Box–Behnken design application under response surface methodology by selecting process variables such as current density, pH, process time and a distance between electrodes. The optimized process variables found to be responsible for maximum removal are current density of 2.38 mA/cm<sup>2</sup>, pH of 7.29, process time 23 min, and electrode distance 3.5 cm. It has been found that the power consumed under the optimized condition was low for graphite cathode monopolar arrangement (0.194 kWh/m<sup>3</sup>) in comparison to aluminum cathode (0.425 kWh/m<sup>3</sup>) for approximate removal of the hexavalent chromium under similar optimized process variables as applied voltage reduced in the case of graphite cathode due to structural properties and hydrogen adsorption capacity of graphite cathode.

**Key words** | electrocoagulation, graphite electrode, hexavalent chromium, power consumption, response surface methodology

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## HIGHLIGHTS

- Performance of electrocoagulation process investigated in order to assess the removal efficiency of hexavalent chromium.
- Optimization of the process was carried out through Box–Behnken design under response surface methodology.
- Graphite cathode along with aluminum anode have shown outstanding performance in terms of power consumption.

$C$	Process time, minute
$D$	Distance between electrodes, cm
$R_E$	Removal efficiency, %
$C_0$	Initial concentration of hexavalent chromium, mg/L
$C_t$	Residual concentration of hexavalent chromium after t minute, mg/L
$E$	Electrical power consumed, kWh/m <sup>3</sup>
$U$	Applied voltage, Volt
$I$	Current, ampere
$T$	Electrocoagulation time, hours
$V$	Volume of solution, liters
$Al$	Aluminum
$Al/Al$	Aluminum anode and aluminum cathode
$Al/C$	Aluminum anode and graphite cathode

## NOMENCLATURE

$A$	Current density, mA/cm <sup>2</sup>
$B$	pH

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<i>EC</i>	Electrocoagulation
<i>BBD</i>	Box–Behnken design
<i>Df</i>	Degree of freedom
<i>2FI</i>	Two-factor interaction
<i>p-value</i>	Probal value
<i>ANOVA</i>	Analysis of variance
<i>PRESS</i>	Predicted residual error sum of squares

## INTRODUCTION

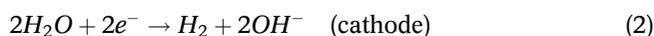
Due to urbanization and industrialization, the amount of waste generation increases day by day to a greater extent. Growing concern with respect to pure and safe water has led to more stringent rules for industries, which is likely to be more responsible for contaminating the natural water. Discharge of effluent from industries causes a serious threat to mankind as well as the environment as these effluents contain various organic compounds, heavy metals, color, etc. The release of heavy metals directly into water bodies has fatal effects on aquatic life as heavy metals are toxic, bioaccumulative and non-biodegradable and may cause chronic effects (Jaishankar *et al.* 2014).

Chromium is one of the heavy metals used in many industries, such as electroplating, metal finishing, tannery, leather industries, and fertilizer industries. In aqueous phase, chromium exists in two forms, namely, trivalent and hexavalent forms (Mohanty & Patra 2013). A trivalent form of chromium is essential for plants and animal metabolism while the hexavalent form is known to be carcinogenic and toxic, causing health problems such as liver damage, pulmonary congestions, vomiting, and severe diarrhea (Semary *et al.* 2016). Therefore, effluents containing chromium (VI) must be treated prior to discharge directly into water bodies. Chromium can be removed by a variety of methods, such as conventional chemical reduction followed by precipitation, adsorption, reverse osmosis, and ion exchange, all having their own limitations of huge sludge generation, high cost, and technical complications, respectively. Thus, a new method for heavy metal removal called electrocoagulation (EC) is emerging and is accomplished with the combined benefits of coagulation, flocculation, and electrochemistry. Being efficient in terms of simplicity, less chemical use, comparatively low

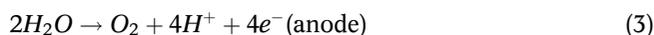
generation of sludge, technical feasibility, and removal efficiency of heavy metal has made EC a more feasible and economical method to remove heavy metals.

EC is the process of electrochemical production of destabilizing agents that neutralize the electric charges of the pollutants present in a solution. The basic EC setup consists of a solution with two electrodes (cathode and anode) immersed in the solution to be treated, an electrolytic cell and a DC (direct current) power supply. Generally, iron and aluminum electrodes are used commonly in the EC process for the electrolysis of water. These electrodes are dissolved by electrolysis and hydroxides as well as metal species being released which destabilizes the contaminant species and precipitates it out as oxidized anode and cathode is reduced. The oxidation reaction occurs at the anode and metal ions dissociate when DC current is passed through the cell while reduction and water electrolysis occurs at the cathode resulting in the formation of reduced precipitate of the contaminants (Aji *et al.* 2012).

A brief description of EC using an aluminum anode to parallel a graphite cathode as well as the aluminum material is discussed below by reactions occurring during electrolysis:



when anode potential is high, then a secondary reaction may occur, especially oxygen evolution at the anode surface (Equation (3)):



Aluminum ions ( $Al^{3+}$ ) produced by electrolytic dissolution of the anode (Equation (1)) immediately undergo spontaneous hydrolysis reactions which generate various monomeric species,  $Al(OH)^{2+}$ ,  $Al(OH)_2^{+}$ , and  $Al(OH)_3$  under acidic conditions, while hydrogen evolution at the cathode (Equation (2)) makes the electrode vicinity alkali. Polynuclear hydrolysis products of Al can also form during electrolysis of water. The EC process depends on various parameters such as electrode arrangement types of power supply, current density, pH, conductivity, electrode types, etc. All these influence the reactions occurring within the

bulk solution. For better efficiencies of the EC setup, optimization of factors like pH, current density, time and electrode distance has been optimized by using the Box–Behnken design (BBD) under a response surface methodology (RSM) tool.

Generally, any analytical process is optimized by selecting one variable at a time while other factors remain fixed or constant. Traditionally, one-factor optimization was being carried out at a time which does not include interactive effects of more than one factor consequently on the response of the process. To overcome this problem, a multivariate optimization for the analytical process should be adopted that includes mathematical multivariate optimization technique along with the explanation of the significance and fitting a polynomial equation for the experimental data set to run the best system evaluation by reducing cost as well as the time of the process. There are some requisite stages in the RSM technique which help to provide the complete optimization of the analytical process: the selection of variables, the choice of the experimental design matrix, statistical treatment of the obtained experimental data, evaluation of the fitted model, and obtaining optimal conditions (Bezerra *et al.* 2008; Witek-Krowiak *et al.* 2014). RSM is a multivariate effective means to accomplish such an optimization by analyzing and modeling the effects of multiple variables and their reactions and ultimately optimizing the operation. This method has been widely used for the optimization of various processes in food chemistry, material science, chemical engineering and biotechnology, pulp mill wastewater, livestock wastewater, industrial effluent, and synthetic wastewater (Granato *et al.* 2010; Singh *et al.* 2010; Hong *et al.* 2011; Wang *et al.* 2011; Liu *et al.* 2012; Asaithambi *et al.* 2016; Garg & Prasad 2016). The BBD provides comprehensive conclusions and detailed information even for a smaller number of experiments and interactive effects of working parameters on all responses.

The purpose of the present work was to examine the feasibility of the EC process using aluminum electrode as an anode for the reduction of hexavalent chromium. There are no studies available in the literature on cathode alteration with a graphite cathode and optimization evaluation through the RSM statistics tool. Therefore, recent research has focused on the development of an EC process by

changing the cathode material. Furthermore, the process optimization has been done through a process variable using the BBD (RSM) tool, which fulfilled the research gap of the EC technique, showing the effect of interchanging cathode material via graphite and aluminum for the removal of hexavalent chromium and optimization through a recent optimization tool. The main aim of optimization was to maximize the hexavalent chromium removal with selected cathode material and process variables such as interelectrode distance, pH, current density, and electrolysis time from synthetic water containing hexavalent chromium.

## MATERIALS AND METHODS

### Reagents and solutions

Reagents were prepared using demineralized distilled water from the Mili-Q water system. Titrisol Merck® standard solutions of 1,000 mg/L of chromium were used and solutions of different concentrations were obtained by adequate dilutions to calibrate the instrument. A stock solution of chromium (VI) of 1,000 ppm was prepared by dissolving an appropriate amount of chemical  $K_2Cr_2O_7$  of Merck quality ACS (American Chemical Society) Emparta grade, and chromium-based synthetic water was prepared to demonstrate the effect of initial concentration of 10 mg/L and the time required for quantitative removal. Solutions used in the reactor were prepared freshly for each experimental run from the stock solution of chromium. The pH of the solution was adjusted by 0.1 N HCl and 0.1 N NaOH solutions prepared from AR (analytical reagents) grade Merck chemicals.

### Experimental setup and procedure

A Perspex reactor (Table 1) having specific dimensions of 180 mm × 180 mm × 300 mm was used to carry out remediation of hexavalent chromium as a batch type to conduct the experiments. The distance between the anode and cathode was varied as per experimental requirement. This work has introduced the effect of cathode material using aluminum and graphite as the cathode material, whereas anode material was used of the same material, i.e., aluminum, for the removal of hexavalent chromium.

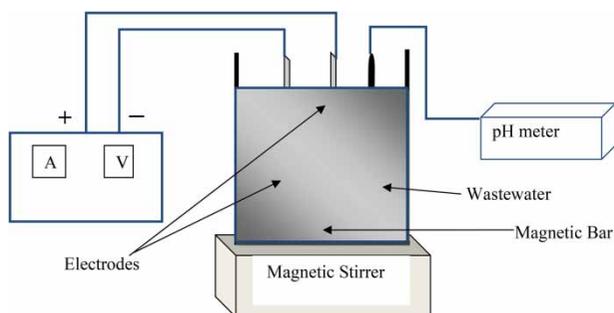
**Table 1** | Reactor and electrode characteristics

Reactor characteristics	Specification
Material	Plexiglass
Size	180 mm × 180 mm × 300 mm
Reactor mode	Batch
Volume	7 L
Working volume	5 L
<b>Electrode</b>	
Material and size	Aluminum: 300 mm × 150 mm × 2 mm Graphite: 300 mm × 150 mm × 4 mm
Anode surface area	113 cm <sup>2</sup>
Connection arrangement	Parallel type

The experimental setup is shown in Figure 1 for the EC experiments. Aluminum (Al) plates of 2 mm and graphite with 4 mm thickness were used, and the surface area in contact with the electrolyte was, in each case, 113 cm<sup>2</sup> per side. In each experiment, two plates were used in the electrochemical reactor and the distance between plates varied from 2 to 4 cm. The electrodes were placed using a monopolar configuration with a total anodic or cathodic surface area of 450 cm<sup>2</sup>.

The current values were selected from 150 to 450 mA corresponding to a current density from 1.3 to 5.3 mA/cm<sup>2</sup> using a precision DC power supply (PowerPac™ HC (high current) power supply Bio-Rad Laboratories, USA, model no. 164-5052). Before each experiment, the electrodes were cleaned with abrasive paper to get rid of an oxide film and then thoroughly rinsed with HCl of 1 M molarity.

To follow the progress during treatment, 10 mL samples were periodically taken from the container at predetermined time intervals (10 to 40 min) and were filtered using

**Figure 1** | Diagram of EC cell for removal of hexavalent chromium.

Whatman filter paper (grade 42) to get aliquot without any obstructing particles for smooth running of the instrument. The residual concentration of hexavalent chromium was determined using an atomic absorption spectrophotometer (FAAS-GBC Avanta, Australia) according to APHA (2012) standard. Morphological characteristics of electrode surface and floc agglomerates were performed using field emission surface scanning electron microscopy (FE-SEM, Zeiss, Germany).

The percentage removal efficiency of EC process was computed as a function of operating time by Equation (4):

$$R_E = \frac{C_0 - C_t}{C_0} \times 100 \quad (4)$$

where  $C_0$  and  $C_t$  are the initial and residual concentration of hexavalent chromium at times 0 and  $t$ .

The amount of electrical power consumed is an important economic parameter in the EC process. This parameter was computed by Equation (5) for the optimized EC process:

$$E = \frac{UIT}{V} \quad (5)$$

where  $E$  is the electrical energy consumed (in kWh/m<sup>3</sup>),  $U$  is the voltage applied (in V),  $I$  is the current (in A),  $T$  is the EC time in hours.  $V$  is the volumes in liters.

### The BBD

Experimental data were analyzed using Design Expert Software 10.0.3 and fitted to a second-order polynomial model to optimize the variables in the electrochemical process. The second-order model is generally found to be significant for RSM in a number of cases (Witek-Krowiak et al. 2014). Furthermore, fitting an appropriate response surface model requires the use of statistical fundamentals, regression modeling techniques, and optimization methods. The quality of the fit polynomial model has been explained with the coefficient of determination, i.e.,  $R^2$ . The  $R^2$  values provide a measure of how much variation in the observed response values can be explained by the experimental factors and their interactions. These analyses were done by means of Fisher's F test and  $p$ -value (probability). Model terms were

**Table 2** | Actual and coded variable with standard deviation

Actual variable	Unit	Coded variables		
		-1	0	+1
A: current density	mA/cm <sup>2</sup>	1.3	2.6	3.9
B: pH	–	6	7	8
C: time	minute	10	20	30
D: electrode distance	cm	2	3	4

evaluated by *p*-value with 95% confidence level (Moghadam *et al.* 2010). Finally, the optimal values of the critical parameters were obtained by analyzing the 3D surface plots and also by desirability function using Design Expert Software 10.0.3. Twenty-nine experiments were used to estimate the model coefficients. The corresponding four-variable BBD is shown in Table 2. The validation of the model was carried out by an appropriate analysis of variance (ANOVA). The model is considered adequate if the variance due to regression is significantly different from the total variance. Design Expert software has been employed for regression and graphical analysis of data obtained. The optimum study parameters (current density, pH, time, and electrode distance) were obtained by analyzing the response surface contour plots.

## RESULTS AND DISCUSSION

In order to assess the effect of the cathode material, i.e., aluminum and graphite for optimization of an electrochemical process in terms of power consumption, process variables such as current density, pH, electrode distance, and electrolysis time have been investigated. Generally, in order to reduce energy consumption for the EC process the following factors have influenced the electrolysis cell performance, including chemistry of water electrolysis, electrode kinetics (oxygen, hydrogen and cell overpotential), resistances in electrolysis systems (electrical, reactions, and transport-related resistances), oxygen and hydrogen evolution reaction, and hydrogen production.

The overpotential on the electrodes is directly related to the vicinity of the electrode. The amount of oxygen and hydrogen formation is related to anode and cathode vicinity, respectively. The formation of hydrogen is intrinsically

determined by the bond between hydrogen and the electrode surface (Zeng & Zhang 2010). The adsorption capacity of hydrogen atoms is greater on the graphite electrode surface due to its porous structure and bonding nature. The adsorption phenomenon by means of high-resolution electron-energy-loss spectroscopy and periodic first-principle density-functional theory has been reported, through which the adsorption occurred in clusters of four atoms and adsorption in pairs of atoms in contiguous carbon sites (Allouche *et al.* 2005). It gives alkali vicinity to the cathode electrode and solution pH in the reaction increases due to excess of hydroxide ions.

Furthermore, the performance of the EC process has been investigated by selecting process variables such as current density, pH, electrode distance, and process time to reveal the effect of the cathode material. Furthermore, four-factor with three-levels of BBD techniques were used to evaluate and optimize the effects of process variables of the EC process on the response of chromium removal efficiency. The predicted values of responses were obtained from quadratic model fitting techniques for the percentage reduction of chromium using Design Expert Software 10.0. The response functions with the determined coefficients for chromium are presented by Equations (6) and (7) in terms of coded factors. Equation (6) is obtained by analyzing the results of aluminum electrodes in which anode and cathode materials were the same, whereas Equation (7) represents cathode material of graphite for which the anode material was aluminum.

The final equations in terms of coded factors for the BBD model are as follows.

Chromium removal: Anode and cathode electrodes of aluminum (Al/Al)

$$Y_1 = +72.80 - 2.63^*A + 3.60^*B + 5.27^*C + 3.02^*D + 1.43^*AB + 10.48^*AC - 7.50^*AD + 1.23^*BC + 3.85^*BD + 0.25^*CD - 14.36^*A^2 - 15.91^*B^2 - 9.51^*C^2 - 13.34^*D^2 \quad (6)$$

Chromium removal: Anode of aluminum and cathode of graphite (Al/C)

$$Y_2 = +72.80 - 5.43^*A + 6.09^*B + 7.41^*C + 4.18^*D - 1.93^*AB + 9.40^*AC - 5.13^*AD + 0.33^*BC + 1.37^*BD + 0.70^*CD - 12.07^*A^2 - 5.68^*B^2 - 7.88^*C^2 - 29.44^*D^2 \quad (7)$$

A positive sign indicates the synergistic effects while a negative sign indicates antagonistic effects of the factors on the respective responses.

### Sequential model sum of squares and model summary statistics and ANOVA analysis

In the obtained BBD, experimental data have been analyzed by two different tests, namely, the sequential model sum of squares and model summary statistics in order to obtain effective regression models among various models such as linear, interactive, quadratic, and cubic. The removal efficiency of hexavalent chromium via different electrodes arrangement is shown in Tables 3 and 4 through BBD response. According to the results shown in Tables 3 and 4, it was found that the quadratic models exhibited higher  $R^2$ , adjusted  $R^2$ , and predicted  $R^2$  when compared to the other models like linear, cubic, etc. The cubic model was found to be aliased and the model had become inappropriate for further investigation since not enough experiments were run to independently estimate all the terms of that model. The sequential model sum of squares showed that the  $p$ -values were less than 0.0001 for the quadratic model of the design models. However, the model summary

statistics showed that after excluding the cubic model which was aliased, the quadratic model was found to have the maximum  $R^2$ , adjusted  $R^2$ , and predicted  $R^2$  values for hexavalent chromium for both the combinations used in this study. Therefore, the quadratic model was found to describe the significant effects of process variables on the treatment of synthetic water containing chromium (VI) through the EC process. The  $R^2$  value of the design models was 0.8724 when electrode materials were the same, i.e., aluminum, whereas a higher  $R^2$  value of 0.9096 was found when graphite electrode was introduced as the cathode material. The  $p$ -value of quadratic vs two-factor interaction (2FI) was found to be significant because the  $p$ -value <0.0001 shown in Tables 3 and 4 for both the model responses means two factors influence the process responses and have a significant contribution in the reduction of hexavalent chromium.

The agreement relationship between the predicted values from the model calculated by Equations (3) and (4) and the experimental values were analyzed by regression plots of the actual data against the predicted values from the response surface models describing hexavalent chromium removal efficiency, which described that the graphite cathode arrangement was found to be more reliable

**Table 3** | Sequential model sum of squares and model summary statistics for chromium reduction using aluminum electrodes

#### Sequential model sum of squares (Al/Al)

Source	Sum of squares	Df	Mean square	F-value	p-value	Prob > F
Mean vs total	74,889.37	1	74,889.37			
Linear vs mean	680.79	4	170.20	0.91	0.4748	
2FI vs linear	737.57	6	122.93	0.59	0.7351	
Quadratic vs 2FI	3,097.98	4	774.49	16.41	<0.0001	Suggested
Cubic vs quadratic	501.86	8	62.73	2.37	0.1544	Aliased
Residual	158.76	6	26.46			
Total	80,066.33	29	2,760.91			

#### Model summary statistics

Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Linear	13.69	0.1315	-0.0132	-0.1302	5,851.18	
2FI	14.45	0.2740	-0.1294	-0.3614	7,048.15	
Quadratic	6.87	0.8724	0.7448	0.2650	3,805.20	Suggested
Cubic	5.14	0.9693	0.8569	-3.4160	22,861.44	Aliased

Df = degree of freedom; 2FI = two-factor interaction; Al/Al = aluminum anode with aluminum cathode.

**Table 4** | Sequential model sum of squares and model summary statistics for chromium reduction using aluminum anode and graphite cathode**Sequential model sum of squares (Al/C)**

Source	Sum of squares	df	Mean square	F-value	p-value	Prob > F
Mean vs total	72,540.01	1	72,540.01			
Linear vs mean	1,668.16	4	417.04	1.39	0.2680	
2FI vs linear	483.27	6	80.54	0.22	0.9670	
Quadratic vs 2FI	5,926.23	4	1,481.56	25.84	<0.0001	Suggested
Cubic vs quadratic	370.45	8	46.31	0.64	0.7255	Aliased
Residual	432.39	6	72.06			
Total	81,420.50	29	2,807.60			

**Model summary statistics**

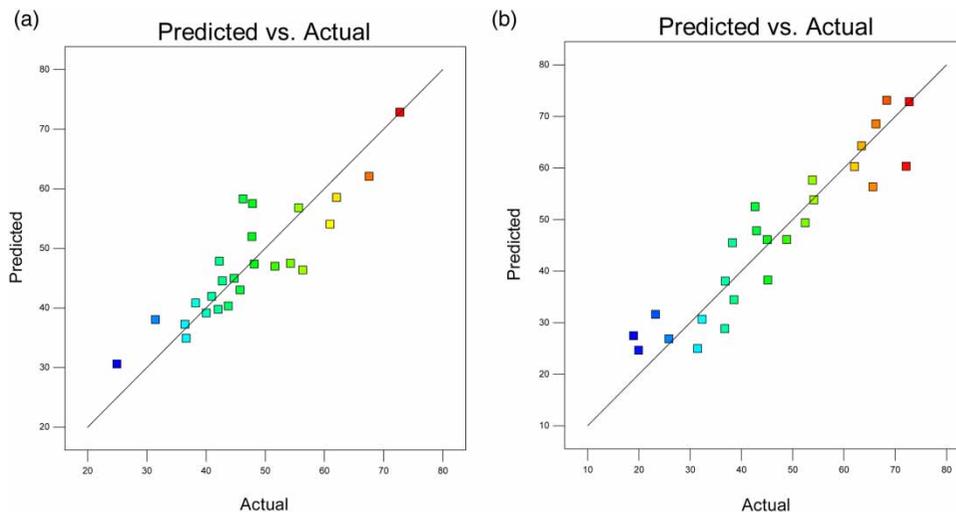
Source	Std. Dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Linear	17.34	0.1878	0.0525	-0.1281	10,018.51	
2FI	19.33	0.2423	-0.1787	-0.8586	16,504.93	
Quadratic	7.57	0.9096	0.8192	0.4793	4,624.34	Suggested
Cubic	8.49	0.9513	0.7728	-6.0113	62,263.56	Aliased

Df = degree of freedom; 2FI = two-factor interaction; Al/C = aluminum anode and graphite cathode.

than the aluminum arrangement of electrodes, as shown in Figure 2. The experimental values and predicted values were found close to the linear plot and scattered uniformly when graphite was introduced as a cathode, which indicates close agreement of real and predicted values.

Sometimes, mathematical models are found not to be satisfactory after fitting the function to the data described

by the experimental range studied. The more reliable way to test the significance and the adequacy of the fitted model is through the application of ANOVA. The fundamental concept of ANOVA is to provide a statistical test of whether or not the means of several treatments are equal or there is variation due to random errors inherent in the measurements of the generated responses (Bezerra

**Figure 2** | Regression plots of the actual data against the predicted values from the response surface models describing hexavalent chromium removal efficiency using a combination of electrodes: (a) aluminum cathode and (b) graphite cathode.

*et al.* 2008). The Fisher variance ratio, the F-value, is a statistically valid measure to determine how well the factors describe the variation in the mean of the data. The F-value indicates that the factors explain adequately the variation in the data about its mean, which provides a valid measure to ascertain how well the factors describe the variation in the mean of the data. The quadratic regression model is highly significant for graphite cathode arrangement, which is evident from the Fisher's F-test with a very low probability value ( $\text{Prob} > F = 0.0001$ ). The

significance of each coefficient of Equations (6) and (7) was determined by applying  $p$ -values of each as listed in Table 5. The regression model ( $Y_1$ ) is a significant model as its  $\text{Prob} > F$  value is less than 0.05, i.e., 0.005. In this particular arrangement of electrodes, the second-order effect of AC, AD, BD,  $A^2$ ,  $B^2$ ,  $C^2$ , and  $D^2$  are the significant model terms. The regression model ( $Y_2$ ) is also a significant model with a  $\text{Prob} > F$  value of  $<0.0001$ . The main effect of the second-order of AC,  $A^2$ ,  $C^2$ , and  $D^2$  is only found significant in order of model terms.

**Table 5** | ANOVA for response surface quadratic model for reduction of chromium

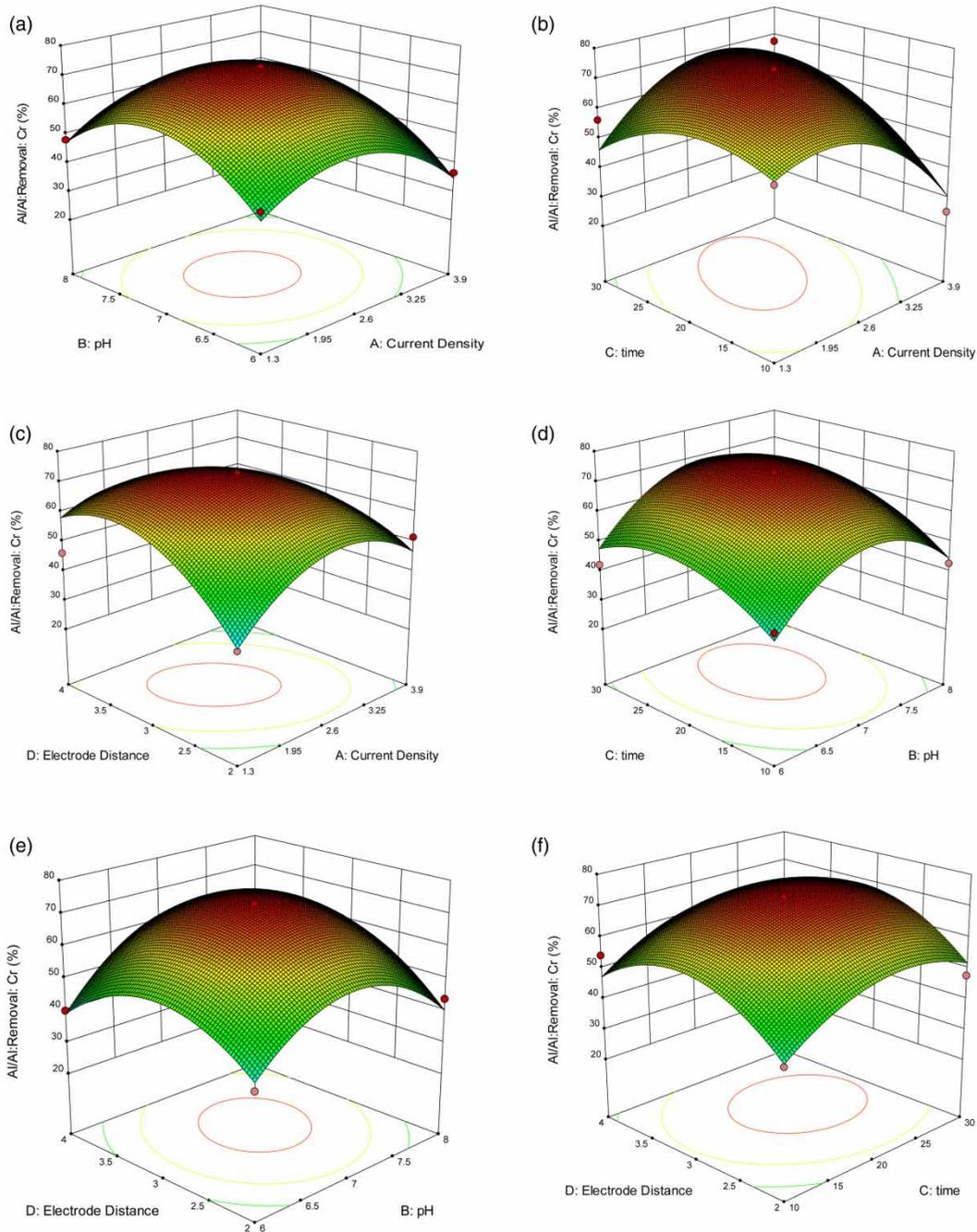
Response	Source	Sum of squares	Df	Mean square	F-value	p-value	Prob > F
Al(+)/Al(-)	Model	4,516.34	14	322.60	6.84	0.0005	Significant (mean = 50.82; Std. dev. = 6.87; CV % = 13.52)
	A – current density	83.21	1	83.21	1.76	0.2054	
	B – pH	155.52	1	155.52	3.30	0.0909	
	C – time	332.85	1	332.85	7.05	0.0188	
	D – electrode distance	109.20	1	109.20	2.31	0.1505	
	AB	8.12	1	8.12	0.17	0.6845	
	AC	438.90	1	438.90	9.30	0.0087	
	AD	225.00	1	225.00	4.77	0.0465	
	BC	6.00	1	6.00	0.13	0.7267	
	BD	59.29	1	59.29	1.26	0.0013	
	CD	0.25	1	0.25	5.298E-003	0.2812	
	$A^2$	1,338.04	1	1,338.04	28.36	0.0001	
	$B^2$	1,642.43	1	1,642.43	34.81	$<0.0001$	
	$C^2$	586.95	1	586.95	12.44	0.0034	
	$D^2$	1,153.87	1	1,153.87	24.45	0.0002	
	Residual	660.63	14	47.19			
	Lack of fit	660.63	10	66.06			
Pure error	0.000	4	0.000				
Cor. total	517,696	28					
Al(+)/C(-)	Model	8,077.66	14	576.98	10.06	$<0.0001$	Significant (mean = 50.01; Std. dev. = 7.57; CV % = 15.14)
	A – current density	354.25	1	354.25	6.18	0.0262	
	B –pH	445.30	1	445.30	7.77	0.0146	
	C – time	658.60	1	658.60	11.48	0.0044	
	D – electrode distance	210.00	1	210.00	3.66	0.0763	
	AB	14.82	1	14.82	0.26	0.6191	
	AC	353.44	1	353.44	6.16	0.0263	
	AD	105.06	1	105.06	1.83	0.1973	
	BC	0.42	1	0.42	7.368E-003	0.9328	
	BD	7.56	1	7.56	0.13	0.7219	
	CD	1.96	1	1.96	0.034	0.8560	
	$A^2$	944.46	1	944.46	16.47	0.0012	
	$B^2$	209.21	1	209.21	3.65	0.0768	
	$C^2$	402.69	1	402.69	7.02	0.0190	
	$D^2$	5,622.56	1	5,622.56	98.05	$<0.0001$	
	Residual	802.84	14	57.35			
	Lack of fit	802.84	10	80.28			
Pure error	0.000	4	0.000				
Cor. total	8,880.49	28					

AD, current density and electrode distance interaction effects; BC, pH and time interaction effects; BD, pH and electrode distance interaction effects; CD, time and electrode distance interaction effects; COD, chemical oxygen demand; CV, coefficient of variation.

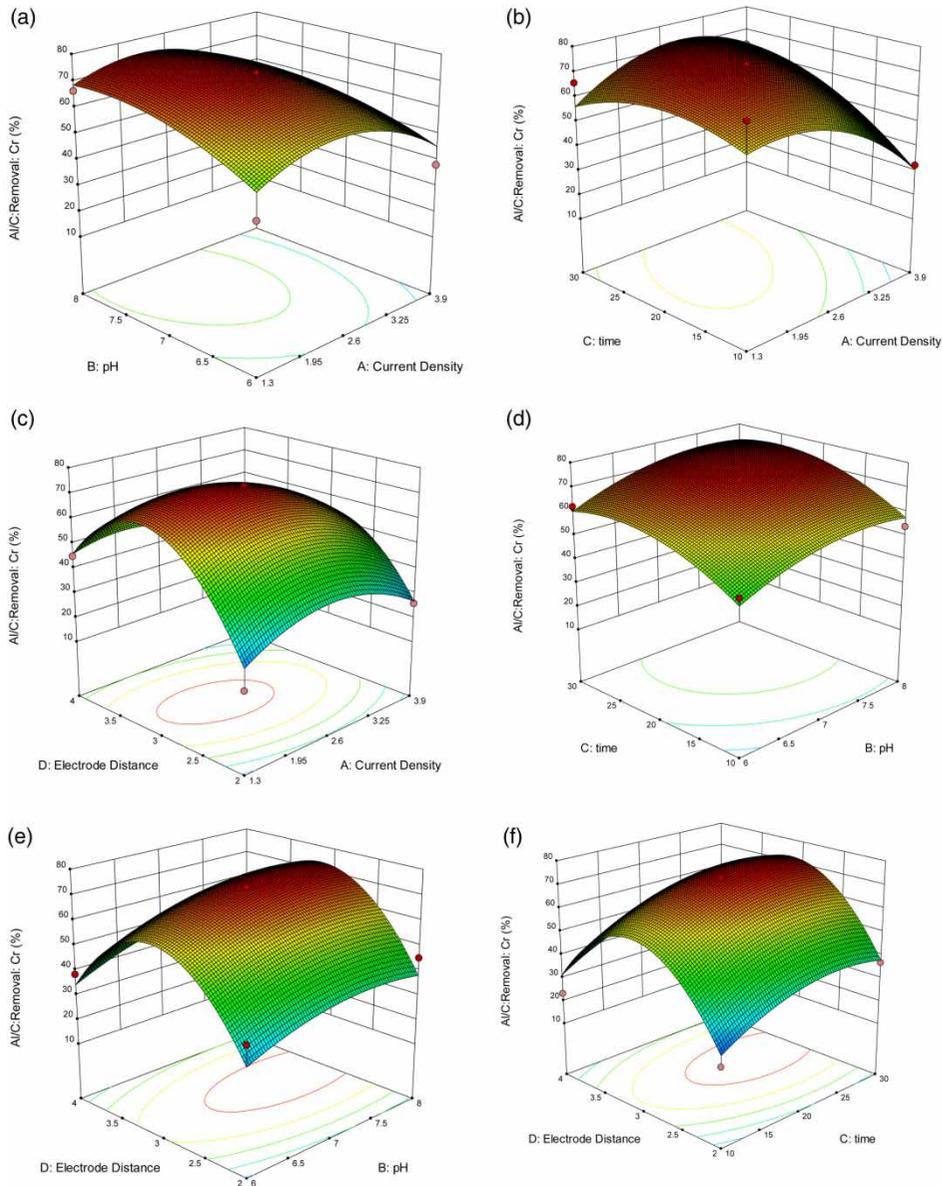
### Combined interaction effects of the parameters on chromium removal efficiency

The effect of the different operating variables such as current density, pH, time, and electrode distance with respect

to maximum hexavalent chromium removal is discussed below and given in Figures 3 and 4. Generally, the pH of the medium changes during the process, as also reported by other investigators, and this variation depends on the type of electrode and the initial value of pH which



**Figure 3** | 3D response surface plots showing the interaction effects of current density, pH, time, and electrode distance on reduction percentage of hexavalent chromium using aluminum as anode and cathode.



**Figure 4** | 3D response surface plots showing the interaction effects of current density, pH, time, and electrode distance on reduction percentage of hexavalent chromium using aluminum anode and graphite cathode.

can be explained by the occurrence of water electrolysis resulting in hydrogen evolution and production of  $\text{OH}^-$  ions (Aji *et al.* 2012). The relative stability of pH afterwards is probably due to the formation of the insoluble polyhydroxides species and the hydrolysis products which may form many monomeric ions  $\text{Al}(\text{OH})_3$  and/or polymeric hydroxy complexes depending on the pH of the aqueous medium and co-precipitate as  $\text{Al}(\text{OH})_3$  (Johnson & Amirtharajah 1983).

### Current density with pH

The current density and pH play an important role for chromium removal in EC processes. The removal efficiency increases as the current density increases until optimum current density, i.e.,  $2.38 \text{ mA/cm}^2$ . The results revealed that pH and current density have more significant roles in chromium removal from chromium-rich water and both the variables have interaction effects, as indicated in

Figures 3(a) and 4(a), which describe that removal of chromium increases first and reaches an optimum value of pH and current density, and after that starts decreasing when aluminum was used as a cathode. However, pH does not affect the higher removal in the case of graphite cathode for which removal was almost constant after neutral pH value. At high current densities, a large number of metal ions was produced via anodic metal dissociation, causing coagulation and more bubble formation at the cathode, causing floatation of generated floc (Sengil & Mahmut 2009). The increasing current density after an optimized value increased the cell potential due to which power consumption increased. The optimum removal percentage of chromium was 72.04% for the aluminum cathode and 70.83% for the graphite cathode arrangement for which current density and pH were 2.38 mA/cm<sup>2</sup> and 7.29, respectively. The size of hydrogen gas bubbles generated from the graphite cathode is small in comparison to aluminum. The gas bubbles with small size move quickly far away from the electrode surface which helps to agglomerate the colloidal pollutants and accumulation on the top layer of the water, while in the case of aluminum, gas bubbles accumulate on the cathode surface which directly adds to the electrical resistance by reducing the contact between the electrolyte solution and the electrode, blocking the electron transfer, and increasing the ohmic loss of the whole system.

### Current density with time

The EC process time is an important process variable for economic feasibility as well as removal efficiency and also responsible for controlling the rate of reaction. According to Faraday's law, the amount of aluminum dissociated in the EC system using Al electrodes may affect the retention time, which increased the Al ions in the cell. The effects of current density and time on removal of hexavalent chromium efficiency are shown in Figures 3(b) and 4(b) for aluminum and graphite cathode arrangement, respectively. The experiments were performed by varying the process time from 0 to 30 min with varied current density. The 3D response surface (Figures 3(b) and 4(b)) shows that the removal efficiency increased with increasing processing time at a particular time with current density. No further

removal was observed after the optimum value of time and current density, i.e., 23 min and 2.38 mA/cm<sup>2</sup>, which means low current density and such time was sufficient for removal. The main reason behind the process was that metal polymeric species formed by increasing the process time, due to which more hydroxyl radicals formed which increase the removal efficiency (Secula *et al.* 2011; Asaithambi *et al.* 2016).

### Current density with electrode distance

The effects of pH, current density, time at electrode distance are shown in Figures 3 and 4. The results revealed that at all values of the pH, percentage removal increased to an electrode distance of 3.5 cm, after which, percentage removal decreased because of less distance between the electrodes. The rate of metal dissolution was high and agglomeration of the chromium particles became fast while at a large electrode distance hydrogen gas bubbles are reduced proportionally. The hydrogen gas bubble is incorporated in the transport mechanism of the pollutants from the water since the graphite cathode has more capacity for hydrogen evolution reaction which is responsible for higher removal of the chromium under similar operating conditions, i.e., current density.

### Electrode distance with solution pH

The effects of inter-electrode distance between the anode and cathode and the solution pH for high removal were evaluated under different inter-electrode distances (2 to 4 cm) and pH (6 to 8), as plotted in Figures 3(e) and 4(e). It was observed that the chromium removal percentage increases by increasing inter-electrode distance to 3.5 cm for both the anode/cathode combinations. The reason for this was the electrical conductivity of the solution which was directly proportional to the distance between the anode and cathode because the resistance offered by the EC cell increased due to which overpotential of the cell increased that increases the cost of the treatment. Similar behavior has also been investigated by authors who treated water containing chemical oxygen demand (COD) (Asaithambi *et al.* 2016) and nitrophenol (Modirshahla *et al.* 2007) by the EC process. The pH of the synthetic water was

varied in the range of 6–8. The results revealed that the chromium removal efficiency increased at solution pH from 6 to the optimized value of 7.29, but decreased after the optimized value of pH in the case of aluminum cathode whereas removal efficiency was found to be constant after the optimized value of pH when graphite was used as a cathode. It was reported earlier that more hydroxyl radicals were formed in neutral condition than in acidic and alkaline mediums in the EC process due to monomeric hydroxometallic cation in acidic conditions and monomeric hydroxometallic anion primary species in alkaline conditions (David *et al.* 2015).

### Optimum power consumption

Power consumption in the EC process was accessed by optimized variables, i.e., current density, pH, time, and electrode distance, as listed in Table 6. The optimization of process variables for power consumption was optimized by BBD under desirability level function. Desirable criteria were set to obtain the optimum EC process condition through RSM. The criteria were the maximum removal of hexavalent chromium and process variables setting was within the ranges. Thus, the optimum power consumption corresponding to the optimum process variables has been calculated as per Equation (2). The results revealed that the power consumption was 0.425 kWh/m<sup>3</sup> when aluminum was used for the cathode material, whereas 0.194 kWh/m<sup>3</sup> power was consumed for the graphite cathode arrangement in the optimized EC process under the desirability level of 0.896, which was approximately two times less than the aluminum cathode arrangement. The possible reason behind this may be a potential difference between the electrodes of the EC reactor, as overpotential of the cathode offers more resistance due to hydrogen adsorption at the graphite cathode surface (Allouche

*et al.* 2005), which enhance the electromotive force and reduces the corresponding potential between the cell terminal and also hydrogen evolution reaction at the graphite cathode (Chen *et al.* 2012). The production capacity of hydrogen gas of a graphite material is higher than an aluminum material, which is more responsible for the higher removal efficiency of chromium. Plausible reasons may be the structure and the porous nature of graphite which support the diffusion of water molecules without any interference (Yuvaraj & Santhanaraj 2014). Thus, the treatment cost of chromium-rich water can be reduced significantly by using a graphite cathode with an aluminum anode.

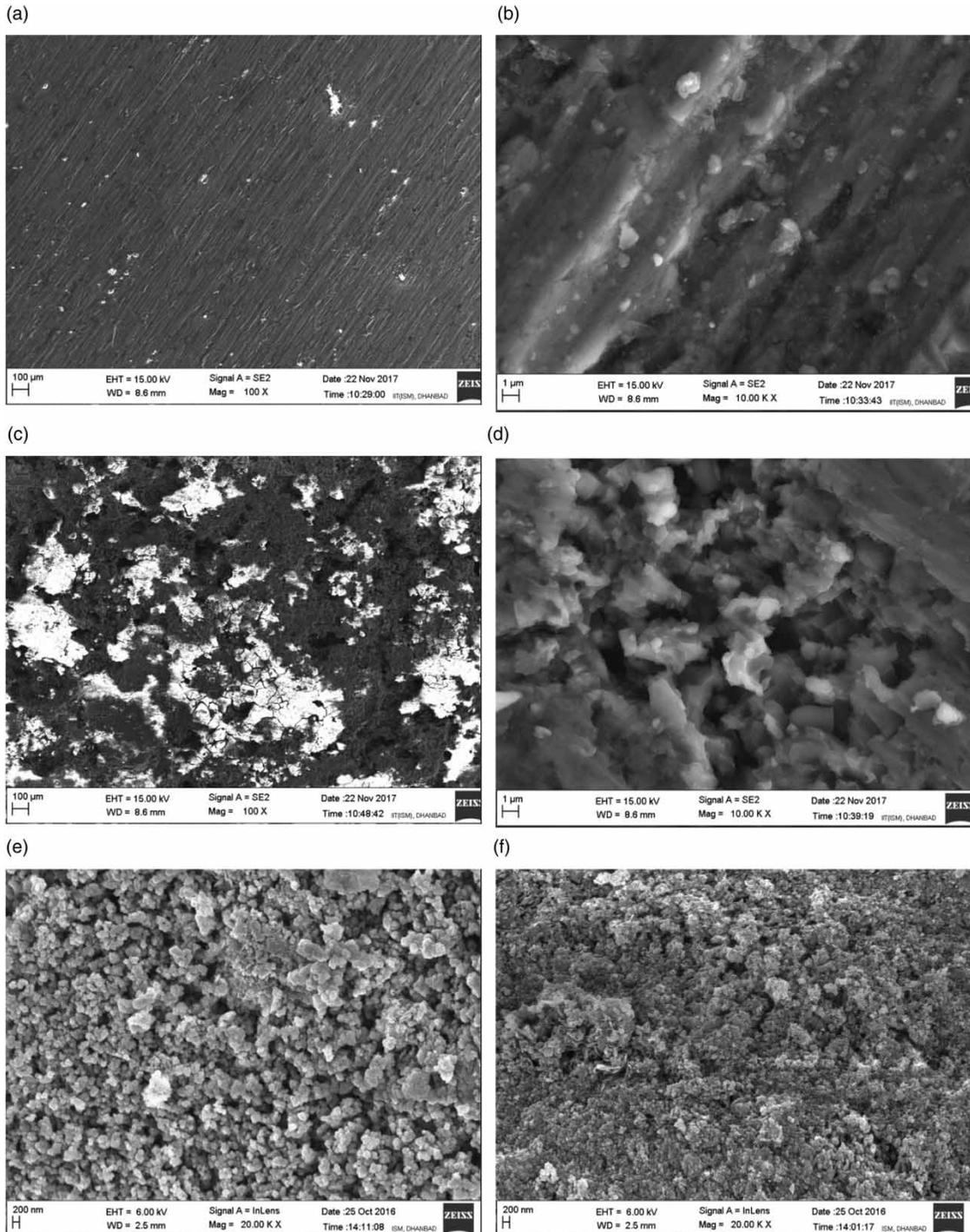
### Morphological characteristics (FE-SEM analysis)

The morphological characteristics of the electrode surface and flocs agglomerates was examined by using scanning electron micrographs as depicted in Figure 5. The electrode surface morphological characteristics were studied at 100 X and 10.0 KX magnification for close and detailed analysis of the aluminum electrode before (Figure 5(a) and 5(b)) and after (Figure 5(c) and 5(d)) uses. Before the experimental runs, surface morphology showed a compact, fine, and linear structure with smaller pore size. After completing the experimental runs, morphographs shown in Figure 5(c) and 5(d) at low and high magnification, respectively, depict coarse grain distribution and increased pore size with surface cracking as metal dissociates during the electrochemical reaction occurring at the anode surface.

The morphological characteristics of flocs generated during experiments have been examined at 20.0 KX magnification, which is depicted in Figure 5(e) and 5(f) with reference to cathode material, i.e., aluminum and graphite, respectively. The experiment with graphite cathode

**Table 6** | Optimum solution of the process under desirability condition

Parameters	Unit	Optimum value	Solution
Current density	mA/cm <sup>2</sup>	2.385	Al(+)/Al(-): 72.04% removal and corresponding power consumption at optimum condition is 0.425 kWh/m <sup>3</sup> . Al(+)/C(-): 70.83% removal and corresponding power consumption at optimum condition is 0.194 kWh/m <sup>3</sup>
pH	–	7.29	
Time	min	23	
Electrode distance	cm	3.518	



**Figure 5** | Surface morphology of electrodes (a)–(d) and flocs (e) and (f).

generated small size and highly dense flocs and porous in structure while the aluminum cathode arrangement generated less porous and larger size flocs in granular form. The

flocs generated were dense in the case of the graphite cathode electrochemical arrangement because of small size gas bubble formation with a faster rate.

## CONCLUSIONS

This study has evaluated the monopolar graphite cathode effect on electrical power consumption to treat chromium-rich water and compare the water electrolysis mechanism of aluminum as well as optimization through the RSM application. The results revealed that the graphite cathode was more significant in terms of power consumption for the approximate same removal efficiency in the process. The calculated power consumption was more than two times when aluminum was selected as cathode electrode arrangements due to the overpotential difference of electrode vicinity and resistance reaction in the cell. The pH of the aqueous solution was alkaline due to the excess of hydroxide ions present in the cell and adoption of hydrogen on a graphite cathode surface in comparison to the aluminum cathode. Thus, the EC process with graphite cathode and aluminum anode materials was found economically significant in comparison to the arrangement with the aluminum cathode to provide alkaline water. The pragmatic application of electrochemical process and water electrolysis development by a graphite cathode have led to the determination that water electrolysis is an effective means of hydrogen gas bubble managing mechanism and output of alkaline water.

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