Electrocoagulation removal of Cr(VI) from simulated wastewater using response surface methodology

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ABSTRACT

The present study envisages the performance of a laboratory scale electrocoagulation system for the removal of Cr(VI) from $100\,mg\,l^{-1}$ solution using Al–Al electrodes with an effective surface area of $100\,cm^2$, and placed 15 mm apart. The interaction between voltage × time, and amperage × time best explained the Cr(VI) reduction efficiency with the coefficient of determination (R^2) being 0.8873 and 0.9270 respectively. Similarly, the square root of energy consumption in Cr(VI) reduction had a linear correlation with voltage × time ($R^2 = 0.8949$), whereas, amperage × time better explained energy consumption ($R^2 = 0.9400$). Response surface methodology was used for the optimization of process variables (pH, voltage and treatment time), response modeling and predictions. Maximum Cr(VI) reduction efficiency of 90.4% was achieved at pH 5, 24 V and 24 min treatment time, and the treatment consumed $137.2\,KWh\,m^{-3}$ of electrical energy. Multiple response optimization for maximizing Cr(VI) reduction efficiency and minimizing energy consumption showed 49.6% Cr(VI) removal at pH 5, 12.8 V and 24 min treatment time. The response models developed explained 95.2% variability for Cr(VI) reduction efficiency and 99.4% variability for energy consumption. Results of the prediction models were validated through laboratory scale batch experiments.

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1. Introduction

Chromium is widely used in metallurgical, refractory and chemical industries for the production of chrome alloys, chrome plating, pigment production, tanning, and for the synthesis of oxidizing agents and corrosion inhibitors [1]. Wastewaters from these industries have chromium in hexavalent or trivalent, or both the forms, depending upon the redox potential, pH, presence of oxidizing or reducing agents, and the kinetics of redox reactions [2]. Cr(VI) is more toxic than the Cr(III), and at a dose of $10\,mg\,kg^{-1}$ of body weight, it can induce liver necrosis, nephritis, or even death in man [1]. Wastewaters containing chromium, designated as a priority pollutant by USEPA, have to be treated before being discharged into the environment. Various techniques like precipitation, adsorption, ion exchange, and reverse osmosis have been employed for the treatment of Cr(VI) containing wastewaters [3]. The technique most commonly used for the removal of Cr(VI) is precipitation, wherein Cr(VI) is first reduced to Cr(III), and then removed through precipitation. This technique has cer-

tain drawbacks, such as negligible process control, high chemical costs and generation of huge amount of hazardous heavy metal sludge.

Electrocoagulation has been successfully used for the removal of metals like arsenic [4–7], boron [8–10], copper, lead and cadmium [11], iron [12,13], chromium [14–21], and for the treatment of cutting oil emulsions and metal plating effluents [22,23]. In this technique, passing of electrical energy into the wastewater through sacrificial metal electrodes generates electrons at the anode, which causes the reduction of the Cr(VI) into Cr(III) [24]. The metal ions thus formed at the anode bring about coagulation and flocculation of the colloidal particles in the wastewater through neutralization of the surface charges, and the metal hydroxide precipitates thus formed are subsequently removed. According to Heidmann and Calmano [16], at higher currents, Cr(VI) is reduced directly at the cathode and precipitated as $Cr(OH)_3$. Electrocoagulation produces lesser amounts of hazardous sludge, and can be used under compact treatment facilities [24–26].

Optimization of the process variables during wastewater treatment can be achieved using response surface methodology (RSM) [18,27–34]. RSM makes treatment process modeling simple and efficient in terms of time and resource utilization. Zaroual et al. [21] studied the effect of operating conditions on the removal of Cr(III). Treatment optimization studies have been undertaken for dye wastewater [27–29], deproteinated whey wastewater [30],

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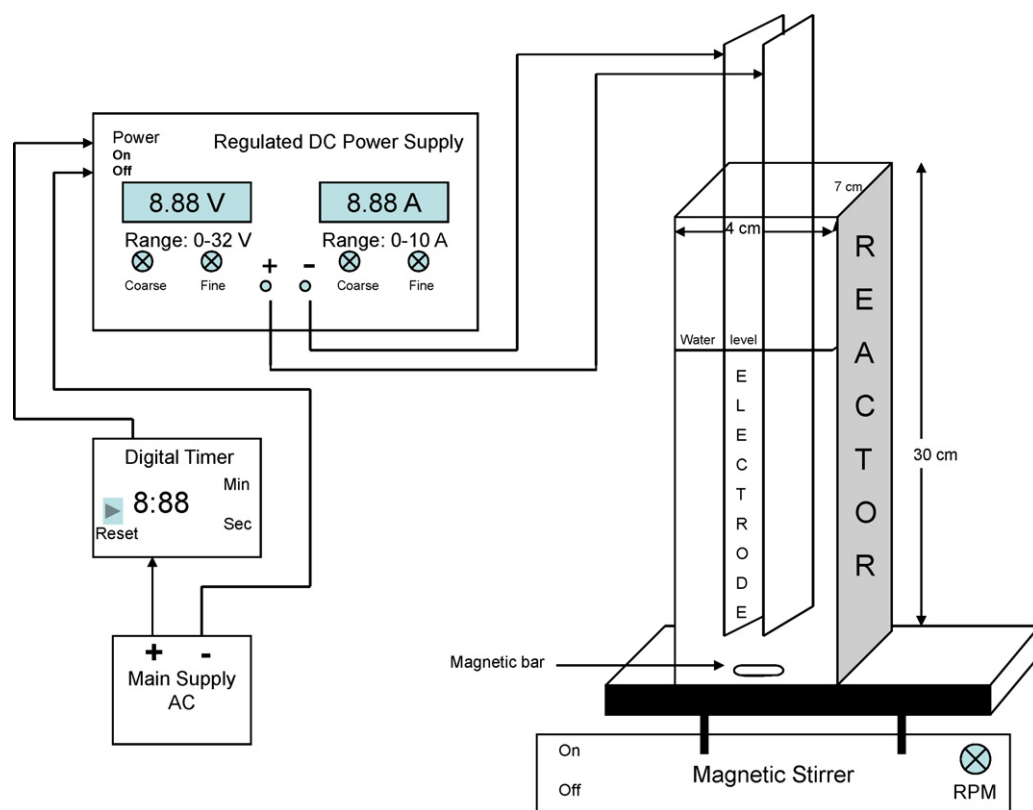
Fig. 1. Electrocoagulation experimental setup.

paint industry [31] and distillery [33]. RSM has also been documented in the removal of oil [34], adsorption of nickel [35], and biosorption of cadmium [36]. RSM was applied by Olmez to optimize Cr(VI) removal by electrocoagulation using stainless steel electrodes [18]. The optimum process variables were found to be 7.4 A applied current, 33.6 mM NaCl electrolyte and 70 min treatment time for complete reduction of Cr(VI). Heidmann and Calmano [16] studied the removal of Cr(VI) using Fe electrodes by varying applied current and treatment time. The best Cr(VI) removal rate was found below 0.1 A, and 10 mg l^{-1} Cr(VI) solution was reduced completely after 45 min. However, there is a dearth of literature regarding the improvement of design and performance of electrocoagulation *vis à vis* power consumption [24].

The present work was undertaken to test the hypothesis that electrocoagulation of wastewater can be optimized for pH, voltage and treatment time, and the variables chosen explaining maximum variability with minimum deviation, could be subjected to multiple response optimization through maximizing Cr(VI) reduction efficiency while minimizing energy consumption, to propose an economical and efficient technology for the removal of Cr(VI) from wastewater.

2. Materials and methods

2.1. Simulated wastewater

The reagents and chemicals used in the present study were of analytical grade, and procured from Central Drug House and Spectrochem, India. 100 mg l^{-1} Cr(VI) solution was prepared from $K_2Cr_2O_7$ in deionized water, and the pH was adjusted using 0.01 M H_2SO_4 or 0.01 M NaOH. KCl was used for maintaining a conductivity of 2 m mho cm^{-1}.

2.2. Experimental setup and procedure

Reactor was fabricated using 6 mm acrylic sheet having an area of 4 cm × 7 cm and a height of 30 cm. Electrodes were rested on a support, 3 cm above the base, and engraved with grooves for keeping a fixed distance of 15 mm between the electrodes. The solution was continuously stirred during the experiment at 100 rpm using a 21 mm magnetic bar. Aluminum electrodes, 5 mm thick and having an area of 5 cm × 40 cm were used as Al–Al pair for wastewater treatment.

Regulated DC power supply working in the range of 0–32 V and 0–10 A was procured from Aplab, India (Model L-3210). The instrument could be operated on either constant voltage or constant current mode with the help of coarse and fine tuning of voltage and amperage. Voltage was adjusted with regulated DC power supply in the range of 10–24 V using constant voltage mode. Current in amperage was recorded from the digital panel meter, and the average energy consumed was based on the amperage recorded at the start and at the end of the experiment. The ripple and noise of the instrument was less than 0.04%.

pH and conductivity (m mho cm^{-1}) were measured with digital pH meter (Equiptronics, India, Model EQ-610) and digital conductivity meter (Systronics, India, Model 304) respectively. Cr(VI)

Table 1
Experimental range and level of independent process variables.

Independent variables	Coded levels				
	−1.68	−1	0	+1	+1.68
	Actual values				
pH	3.64	5	7	9	10.36
Voltage (V)	5.23	10	17	24	28.77
Treatment time (min)	2.55	8	16	24	29.45

Table 2
Experimental design as per CCD.

Experimental run	Coded values (actual values)		
	pH	Voltage	Time
Star points ($\alpha = \pm 1$)			
1	−1 (5)	−1 (10)	−1 (8)
2	+1 (9)	−1 (10)	−1 (8)
3	−1 (5)	+1 (24)	−1 (8)
4	+1 (9)	+1 (24)	−1 (8)
5	−1 (5)	−1 (10)	+1 (24)
6	+1 (9)	−1 (10)	+1 (24)
7	−1 (5)	+1 (24)	+1 (24)
8	+1 (9)	+1 (24)	+1 (24)
Axial points ($\alpha = \pm 1.68$)			
9	−1.68 (3.64)	0 (17)	0 (16)
10	1.68 (10.36)	0 (17)	0 (16)
11	0 (7)	−1.68 (5.23)	0 (16)
12	0 (7)	1.68 (28.77)	0 (16)
13	0 (7)	0 (17)	−1.68 (2.55)
14	0 (7)	0 (17)	1.68 (29.45)
Center points ($\alpha = 0$)			
15	0 (7)	0 (17)	0 (16)
16	0 (7)	0 (17)	0 (16)
17	0 (7)	0 (17)	0 (16)
18	0 (7)	0 (17)	0 (16)
19	0 (7)	0 (17)	0 (16)
20	0 (7)	0 (17)	0 (16)

was determined colorimetrically (Standard Methods, method no. 3500-Cr D) [37]. 1,5-Diphenylcarbazide MW 242.28 was used as complexometric reagent for Cr(VI) estimation at 540 nm using double beam UV–visible spectrophotometer (Systronics, Model 2202). Process variables were chosen on the basis of trial experiments and available literature. pH (5, 7, 9) was chosen in a range so as to minimize the acid or alkali consumption, and make the technique more ecofriendly. Adoum and Reddithota [3,19] reported optimum pH for electrocoagulation in the range of 4–8. In the industrial effluents of the area, the pH of the untreated effluent is about 5. Voltage was set at 3 levels, 10, 17 and 24 V. It was observed that a higher voltage causes excessive heating of the system, and passivization of electrodes. Similarly, treatment time was defined at 8, 16 and 24 min for the reason that the most practicable time for hydraulic retention is 30 min, which reduces the reactor size.

Experimental setup for electrocoagulation assembly used is given in Fig. 1. 540 ml of Cr(VI) solution was taken in the electrocoagulation reactor after adjusting pH and conductivity. This submerged the electrodes up to a depth of 20 cm in the solution, to give an effective electrode area of 100 cm^2. Voltage was set at the desired level, and the power supply switched on. A digital timer regulated the treatment time. Treated wastewater was allowed to settle for 2 h, and the supernatant analysed for chromium. Cr(VI) reduction efficiency and energy consumption were determined using Eqs. (1) and (2) respectively.

$$\text{Cr(VI) reduction efficiency (\%)} = \frac{C_i - C_f}{C_i \times 100} \tag{1}$$

$$\text{Energy consumption (Wh)} = V \times A \times h, \tag{2}$$

where C_i and C_f represent the initial and final concentrations of Cr(VI) (mg l^{-1}) respectively.

2.3. Experimental design and model development

Experimental points for pH, voltage and treatment time were set using Rotatable Central Composite Design (CCD) (Table 1). Eight star points ($\alpha = \pm 1$), six axial points ($\alpha = \pm 1.68$) and six replicates at the centre point ($\alpha = 0$) were chosen as experimental points [38]. A total of 20 experiments were performed as per Table 2. The first 14 experimental runs were performed in triplicates, and the coefficient of variation (CV) was calculated to check uncertainty. Results of the last 6 experimental runs (representing central points) were used to check the reproducibility of results as per CCD.

First order models were developed using multiple linear regression analysis to simulate the main effects models. The main effects models are helpful in explaining the relative effects of the independent variables if the response surface is small and the curvature is negligible. β-Regression coefficients were computed for different independent variables. Presuming that the chemical reactions during electrocoagulation might result in interaction, the main effects model was modified to include two factor interactions. The model development was further extended to create response surface design using Response Surface Methodology. The data was fit into second order quadratic model using multiple regression. β-Regression coefficients were computed and data were subjected to ANOVA to eliminate non-significant model terms in the equation, and to generate a reduced second order model.

Table 3
Actual and predictive responses of Cr(VI) reduction efficiency and energy consumption.

Exp. no.	pH	Volt	Time	Response 1 Cr(VI) reduction efficiency (%)		Response 2 Energy consumption (Wh)		
				Actual	Predicted	Actual	Sqrt. actual	Sqrt. predicted
1	5	10	8	34.68	32.20	2.67	1.63	1.60
2	9	10	8	20.36	25.65	2.67	1.63	1.60
3	5	24	8	40.03	38.56	21.44	4.63	4.45
4	9	24	8	28.27	32.02	18.88	4.35	4.45
5	5	10	24	44.52	43.59	8.20	2.86	2.84
6	9	10	24	37.89	37.04	8.20	2.86	2.84
7	5	24	24	92.62	90.36	76.80	8.76	8.61
8	9	24	24	83.86	83.81	72.48	8.51	8.61
9	3.64	17	16	44.09	48.11	16.77	4.10	4.30
10	10.36	17	16	42.17	37.10	18.36	4.28	4.30
11	7	5.23	16	35.75	35.26	1.33	1.15	1.19
12	7	28.77	16	79.80	79.94	70.20	8.38	8.43
13	7	17	2.55	18.43	16.03	2.85	1.69	1.74
14	7	17	29.45	66.11	69.17	38.80	6.23	6.27
15	7	17	16	47.72	42.60	19.04	4.36	4.30
16	7	17	16	40.88	42.60	17.23	4.15	4.30
17	7	17	16	42.90	42.60	18.36	4.28	4.30
18	7	17	16	38.32	42.60	21.08	4.59	4.30
19	7	17	16	41.10	42.60	18.36	4.28	4.30
20	7	17	16	44.95	42.60	18.59	4.31	4.30

Table 4
First order and interaction models for Cr(VI) reduction efficiency and energy consumption.

	Model equation	R^2	β-Regression coefficients					
			pH	Voltage	Time	pH × voltage	pH × time	Voltage × time
Models for Cr(VI) reduction efficiency								
Main effects	$-6.17 - 1.63 \times \text{pH} + 1.89 \times \text{volt} + 1.97 \times \text{min}$	0.8101*	−0.140	0.572	0.680			
Main effects with two factor interaction	$52.69 - 3.03 \times \text{pH} - 1.01 \times \text{volt} - 1.67 \times \text{min} + 0.00383 \times \text{pH} \times \text{volt} + 0.083516 \times \text{pH} \times \text{min} + 0.18 \times \text{volt} \times \text{min}$	0.9229*	−0.262	−0.306	−0.578	0.010	0.236	1.409
Two factor interaction	$19.52 - 0.047 \times \text{pH} \times \text{volt} - 0.053 \times \text{pH} \times \text{min} + 0.141 \times \text{volt} \times \text{min}$	0.9110*				−0.125	−0.150	1.101
Volt × time interaction	$13.39 + 0.12 \times \text{volt} \times \text{min}$	0.8873*						
Amperage × time interaction	$20.21 + 0.36 \times \text{ampere} \times \text{min}$	0.9270*						
Models for energy consumption								
Main effect	$-52.18 - 0.15 \times \text{pH} + 2.96 \times \text{volt} + 1.65 \times \text{min}$	0.8159*	−0.014	0.762	0.483			
Main effect with two factor interaction	$-1.60 + 1.11 \times \text{pH} - 0.098 \times \text{volt} - 1.96 \times \text{min} - 0.06 \times \text{pH} \times \text{volt} - 0.013 \times \text{pH} \times \text{min} + 0.22 \times \text{volt} \times \text{min}$	0.9346*	0.091	−0.035	−0.573	−0.139	−0.057	1.472
Two factor interaction	$-13.90 + 0.08 \times \text{pH} \times \text{volt} - 0.12 \times \text{pH} \times \text{min} - 0.15 \times \text{volt} \times \text{min}$	0.9170*				0.180	−0.289	1.011
Volt × time interaction	$-13.82 + 0.13 \times \text{volt} \times \text{min}$	0.8380*						
Sqrt. (energy) vs. volt × time interaction	$0.64 + 0.013 \times \text{volt} \times \text{min}$	0.8949*						
Amperage × time interaction	$-7.16 + 0.42 \times \text{ampere} \times \text{min}$	0.9400*						

* Significant at $p \leq 0.001$.

Response data of Cr(VI) reduction efficiency and energy consumption were checked for the maximum to minimum ratios. A ratio greater than 10 indicates a higher likelihood that a transformation may improve the model [39]. Box–Cox plot was used for the requisite data transformation [40]. Model fitting and graphical analyses were carried using Design-Expert 7.1.5 (Stat-Ease Inc., Minneapolis, MN, USA) and self-coded software using Microsoft Excel. Selected response was fitted to linear, two factor interaction, quadratic and cubic polynomials using multiple regression analysis. The effects for all the model terms were calculated, and F-values, *Lack of fit*, and coefficient of determination (R^2) were compared to propose the statistically most significant model [41].

The Sequential Model Sum of Squares table showed accumulating improvement in the model fit, as model terms are added. ANOVA was performed for the model selected, and *Lack of fit* test was conducted to compare the residual error with the pure error obtained from the replicated design points. Insignificant *Lack of fit* was assessed on the basis of F-values. From the ANOVA table, significant model terms were identified at 95% significance level and model reduction was done by blocking non-significant effects, thus improving model fitting. *Goodness of fit* was evaluated from R^2 and CV in order to check the reliability and precision of the model.

The selected model was generated both in terms of coded factors (standardized equation) and actual factors (unstandardized equation). The variables in the quadratic equation were coded to generate the response surface by limiting the responses into a domain of -1 to $+1$. Unstandardized equations can be used for predicting the responses. Predictive models were developed in two phases from the data generated with the help of Design-Expert. In Phase-I, treatment efficiency was used as the response, and the model developed was validated through electrocoagulation experiments. Similarly, a model was also developed for energy consumption. From the models developed, optimal parameter values were determined for maximum Cr(VI) reduction efficiency and minimum energy consumption. In Phase-II, both the treatment efficiency and the energy consumption, were used as the responses, and the predictive models were subjected to maximizing Cr(VI) reduction efficiency, while minimizing energy consumption [39]. The optimal parameter values were again validated through electrocoagulation experiments at the new optimal parameters. The treatment efficiency and energy consumption for the two phases were compared. Using the model equation, one variable and two variable response plots were plotted [42].

3. Results and discussion

3.1. Optimization for Cr(VI) reduction efficiency

Cr(VI) reduction efficiencies (response 1) obtained for the 20 experiments conducted (Table 2) are given in Table 3. From the main effects model (Table 4), it is observed that the most important factors contributing to Cr(VI) reduction are time followed by voltage. The two factor interaction model revealed that maximum contribution to Cr(VI) reduction is made by voltage × time. The plot between volt × time *vs.* Cr(VI) reduction is linear ($R = 0.9419$), and explains 88.7% variability in the observed data. Cr(VI) reduction when regressed on amperage × time gave still a higher linear correlation coefficient of 0.9628 explaining 92.7% variability in the data.

Subjecting the data to RSM, response obtained for the six replicates at the centre point gave CV of 7.53%, within the acceptable range of 10%. Since, the ratio between the maximum and the minimum response was 5.02, response transformation was not carried out. Model fitting with the help of Design-Expert software sug-

Table 5
ANOVA table for Cr(VI) reduction efficiency and energy consumption.

Sources	Cr(VI) reduction efficiency (%)				Energy consumption (Wh)			
	Quadratic model		Reduced quadratic model		Quadratic model		Reduced quadratic model	
	F-value	Prob. >F	F-value	Prob. >F	F-value	Prob. >F	F-value	Prob. >F
Model	51.8	<0.0001*	118.7	<0.0001*	543.4	<0.0001*	1080.3	<0.0001*
pH	9.5	0.0117*	12.1	0.0037*	0.1807	0.6798 (NS)		
Volt	155.9	<0.0001*	198.9	<0.0001*	3326.9	<0.0001*	3676.3	<0.0001*
Time	220.5	<0.0001*	281.3	<0.0001*	1301.5	<0.0001*	1438.2	<0.0001*
pH × volt	0.0015	0.9699 (NS)			1.8807	0.2002 (NS)		
pH × Time	0.9243	0.3590 (NS)			0.0081	0.9300 (NS)		
Volt × Time	52.8	<0.0001*	67.4	<0.0001*	223.9	<0.0001*	247.5	<0.0001*
pH^2	0.0129	0.9117 (NS)			0.6	0.4566 (NS)		
Volt^2	26.1	0.0005*	34.0	<0.0001*	23.18	0.0007*	26.7	0.0001*
Time^2	0.0324	0.8608 (NS)			9.13	0.0129*	9.7	0.0077*
Lack of fit	1.79	0.2687 (NS)	1.2	0.4640 (NS)	0.8	0.5958 (NS)	0.7	0.6926 (NS)

NS = not significant $p \le 0.05$.
* Significant at $p \le 0.05$.

Table 6
Validation of optimum process variables.

|	Variables			Response 1	Response 2			Remarks
	pH	Volt	Time	Cr(VI) reduction efficiency (%)	Sqrt. energy (Wh)	Energy (Wh)	Energy (KWh/m^3)	
Phase 1								
Maximum Cr(VI) reduction efficiency	5	24	24	90.36	8.61	74.10	137.2	Maximizing response in Eq. (3)
Validation experiment	5	24	24	91.50	8.67	75.10	139.1	Average of three experiments
Minimum energy consumption	5	10	8	32.20	1.60	2.56	4.7	Minimizing response in Eq. (5)
Validation experiment	5	10	8	31.90	1.60	2.56	4.7	Average of three experiments
Phase 2. Maximizing chromium removal while minimizing energy consumption								
Parameters given by model	5	12.83	24	49.62	3.89	15.1	28.0	Multiple response optimization by solving both Eqs. (4) and (6)
Validation experiment	5	12.8	24	49.90	3.87	15.0	27.8	Average of three experiments
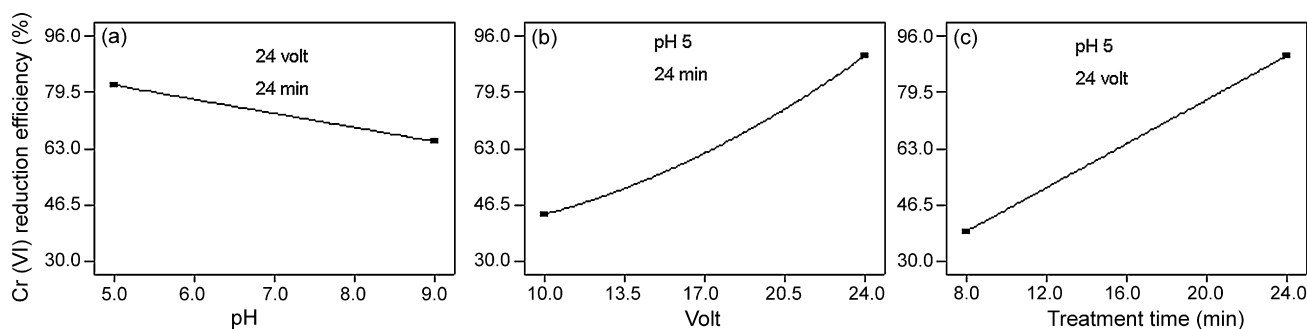
Fig. 2. One variable response plots (a) Cr(VI) reduction efficiency *vs.* pH, (b) Cr(VI) reduction efficiency *vs.* voltage and (c) Cr(VI) reduction efficiency *vs.* treatment time.

gested that a quadratic model provides the best fit, and the model was found to have insignificant *Lack of fit.* Subjecting the model to ANOVA indicated that only 5 of the 9 model terms are significant (Table 5). Reduced quadratic model in terms of unitless regression coefficients is given in Eq. (3).

Cr(VI) reduction efficiency (%)

$$= 42.60 - (3.27 \times pH) + (13.28 \times voltage) + (15.80 \times time)$$
$$+ (10.10 \times voltage \times time) + (5.30 \times voltage^2), \tag{3}$$

where pH, voltage and time are in coded units.

The multiple regression equation for actual factors is given in Eq. (4).

Cr(VI) reduction efficiency (%)

$$= 70.53617 - (1.63651 \times pH) - (4.66718 \times volt)$$
$$- (1.09182 \times min) + (0.18038 \times volt \times min)$$
$$+ (0.1082 \times volt^2). \tag{4}$$

The ANOVA table for reduced quadratic model for Cr(VI) reduction efficiency (Table 5) indicated that the model is significant at $p \leq 0.0001$, and its *Lack of fit* ($p \leq 0.4640$) is not significant. Responses predicted by the reduced quadratic model (Eq. (4)) are given in Table 3. The reduced quadratic model explained 95.2% variability indicating that the model is highly efficient in making the predictions. Running the reduced quadratic model for parameter optimization gave a pH of 5, 24 V and 24 min treatment time as optimal parameters, with Cr(VI) reduction efficiency coming out to be 90.36%. Validation experiments conducted under the optimal parameters gave 91.5% Cr(VI) reduction efficiency, in agreement with the predicted value (Table 6). One variable response plots between Cr(VI) reduction efficiency and the response variables (Fig. 2) indicated linear inverse relation with pH, exponential increase with voltage, and linear relation with time. The relation of Cr(VI) reduction efficiency with voltage and treatment time indicated synergistic interaction due to positive model term for volt × time in Eq. (3). Cr(VI) reduction efficiency is depicted in the contour plot (Fig. 3).

3.2. Optimization for energy consumption

Results obtained for energy consumption are given in Table 3. The main effects model revealed that the most important factors contributing to energy consumption are voltage and time (Table 4). Among the interactions, the most important interaction is between voltage and time ($R^2 = 0.8380$). Square root of energy as a function of voltage × time gave a better fit ($R = 0.9459$) explaining 89.4% variability. The linear correlation between energy consumption and amperage × time was 0.9695.

Response obtained for the six replicates at the centre point gave a CV of 3.02% indicating high precision in the results. Ratio between the maximum and the minimum response was 57.9, thus the square root transformation as suggested by Box–Cox plot of the energy consumption was performed. Quadratic model was found to be the best with insignificant *Lack of fit.* Subjecting the model to ANOVA indicated that only 5 of the 9 model terms are significant (Table 5). Standardized equation for energy consumption is represented by Eq. (5).

Square root of energy consumption (Wh)

$$= 4.30 + (2.15 \times voltage) + (1.35 \times time)$$
$$+ (0.73 \times voltage \times time) + (0.18 \times voltage^2)$$
$$- (0.11 \times time^2), \tag{5}$$

where pH, voltage and time are in coded units.

Eq. (6) is the unstandardized form for actual factors.

Square root of energy consumption (Wh)

$$= 0.54649 - (0.024281 \times volt) + (0.000268 \times min)$$
$$+ (0.013037 \times volt \times min) + (0.003628 \times volt^2)$$
$$- (0.001672 \times min^2). \tag{6}$$

The ANOVA table for reduced quadratic model for energy consumption (Table 5) indicated that the model is significant at $p \leq 0.0001$, and its *Lack of fit* ($p \leq 0.6926$) is not significant. Responses predicted by the reduced quadratic model (Eq. (6)) are given in Table 3. The reduced quadratic model gave R^2 equal to 0.994, indicating that the model is highly efficient in response
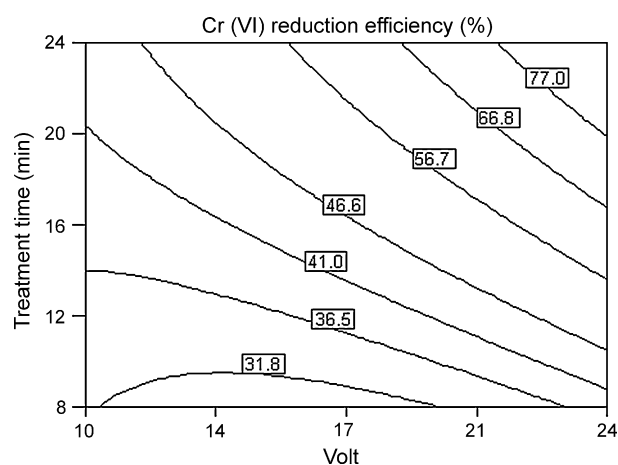

Fig. 3. Contour plot showing effect of voltage and treatment time on Cr(VI) reduction efficiency at pH 5.
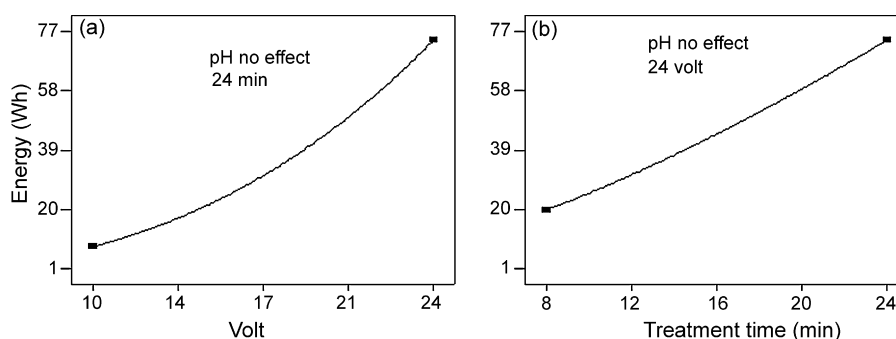
Fig. 4. One variable response plots (a) energy consumption *vs.* voltage and (b) energy consumption *vs.* treatment time.

predictions. Running the reduced quadratic model for minimizing energy consumption gave optimal points as pH 5, 10 V, and 8 min treatment time. These parameters predicted energy consumption of 4.7 KWh m^{-3} and Cr(VI) reduction efficiency of 32.20%. The suggested model was again validated, and the parameters were re-examined through electrocoagulation experiments (Table 6). One variable response plot (Fig. 4) for energy consumption indicated exponential increase with voltage, and linear increase with treatment time. Voltage and treatment time had a synergistic effect on energy consumption. The maximum energy consumption was 137.2 KWh m^{-3} (74.1 Wh) at 24 V and 24 min treatment time. The minimum energy consumption (4.7 KWh m^{-3}) was observed at 10 V and 8 min treatment time (Fig. 5).

3.3. Multiple response optimization

In Phase-II, model equations for Cr(VI) reduction efficiency and energy consumption were simultaneously solved to find the optimal process variables. Design-Expert software was used for maximizing Cr(VI) reduction efficiency while minimizing energy consumption, and the optimal variables obtained were pH 5, 12.83 V and 24 min treatment time, providing 49.62% Cr(VI) reduction efficiency and 28 KWh m^{-3} energy consumption. Voltage was a limiting factor due to passivization of cathode beyond 12.83 V, thereby increasing energy consumption leading to rise in wastewater temperature during the experiment. Validation experiments conducted at optimal parameters gave 49.90% Cr(VI) reduction efficiency and 27.8 KWh m^{-3} energy consumption, in agreement with the predicted responses (Table 6).

The study has shown that under the treatment conditions used for study, maximum Cr(VI) reduction efficiency can be achieved up to 90.4%. However, minimizing energy consumption, electrocoagulation gives the Cr(VI) reduction efficiency of 49.6%. The results indicated that voltage and treatment time had synergistic effect on the removal of Cr(VI) in terms of energy consumption. Further enhancement in Cr(VI) removal would require experiments using different pairs of sacrificial electrodes, the distance between them, effect of temperature on Cr(VI) reduction, specifications of the reactor, concentration of Cr(VI) in the wastewater, effect of interfering radicals, etc. The Cr(VI) remaining in the wastewater after the electrocoagulation, if sufficiently high, can be subjected to further electrocoagulation treatment in series, or can be removed using other technologies such as phytoremediation or chemical precipitation, etc. Besides, the removal of Cr(OH)$_3$ precipitates thus formed will require an appropriate facility, such as filtration or sedimentation, downstream the electrocoagulation process.

4. Conclusions

It is concluded from this study, that the most important factor explaining Cr(VI) reduction efficiency (R^2 = 0.8873) and square root of energy consumption (R^2 = 0.8949) in the process is voltage × time. The response variables are better correlated with amperage × time, R^2 being 0.9270 and 0.9400 for Cr(VI) reduction efficiency and energy consumption respectively. Response surface methodology has proved quite effective in optimizing the process of Cr(VI) reduction by electrocoagulation, both from efficiency and cost points of view. The methodology helped in accurate predictions of the Cr(VI) reduction efficiency under different process conditions. Phase-I, optimized process variables were pH 5, 24 V and 24 min treatment time for maximum Cr(VI) reduction efficiency (90.4%) consuming 137.2 KWh m^{-3} energy. In Phase-II, the optimized parameters (pH 5, 12.83 V and 24 min) gave 49.6% Cr(VI) removal consuming 28 KWh m^{-3}. Thus, significant reduction in energy consumption was achieved in Phase-II, which makes the process cost effective. Predicted models explained 95.2% and 99.4% variability for Cr(VI) reduction efficiency and energy consumption respectively.

Fig. 5. Contour plot showing effect of voltage and treatment time on energy consumption.

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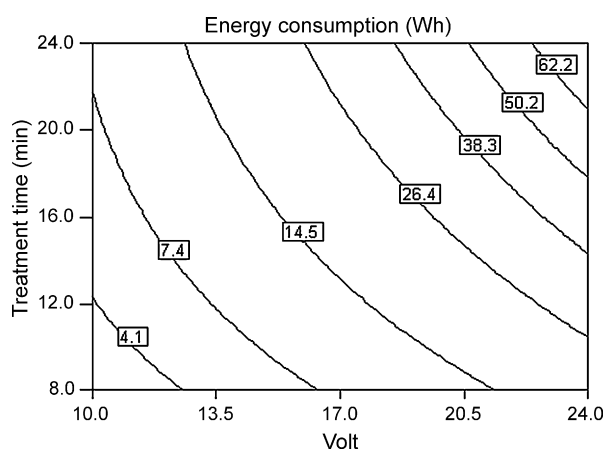
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