



## Optimizing the removal of trivalent chromium by electrocoagulation using experimental design

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### ABSTRACT

The ability of electrocoagulation to remove Cr(III) from aqueous solutions is studied using aluminium anode and taking into account many factors such as pH, potential, time and temperature.

In order to check these factors and their effects on the electrocoagulation of Cr(III), we have established a model of this technique following a methodological strategy using experiments design. The mathematical model is established, using a central composite design rotatable and uniform. The model describes the change of the measured responses of chromium removal efficiency, energy consumption and aluminium dissolved according to the pH, potential, time and temperature.

The graphical representation of this model in the space of the variables enabled us to define the optimum conditions for these parameters. The optimum value of pH, potential, time and temperature are respectively 4.23, 9.14 V, 10 min, and 27.5 °C. An efficiency of 91% of the removal chromium is observed with an energy consumption of 3.536 kWh/m<sup>3</sup>.

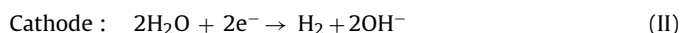
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### 1. Introduction

The industries of textile, tannery and other industries generate a lot of pollutants. Chromium is one of the major sources of environmental pollution. It is discharged into the environment through the disposal of waste from industries like leather tanning, metallurgical and metal finishing, textiles and ceramics, pigment and wood preservatives, photographic sensitizer manufacturing, etc. In the environment, chromium occurs mainly in trivalent and hexavalent forms. The hexavalent chromium Cr(VI) is toxic and carcinogenic while the element in its trivalent state Cr(III) is an essential nutrient for plant and animal metabolism in trace amounts [1]. However, Cr(III) has also been shown to be a potential hazard, especially in the aquatic environment. Mammalian *in vitro* tests have shown that trivalent chromium is a potential toxic, because it is a competitive inhibitor of a many cellular process [2]. The techniques for recovering or removing Cr from wastewater are chemical reduction and precipitation, adsorption by several types of adsorbents such as activated carbon [3], Pinus sylvestris bark [4], sphagnum moss peat [5] and bone charcoal [6,7], ions exchange [8] and membrane technologies [9,10]. Most of these methods suf-

fer from some drawbacks such as high capital and operational costs.

In recent years, electrocoagulation has been successfully used to treat a variety of industrial wastewater [11–19]. The goal of this method is to form flocs of metal hydroxides within the effluent to be cleaned by electrodisolution of soluble anodes. Three main processes occur during electrocoagulation: electrolytic reactions at the surface of electrodes, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or flotation. The main reactions at the electrodes of aluminium are



$\text{Al}_{\text{aq}}^{3+}$  and  $\text{OH}^-$  ions generated by electrode reactions (I) and (II) react to form various monomeric and polymeric species which transform finally into  $\text{Al}(\text{OH})_3$  according to complex precipitation kinetics [20].

Electrocoagulation has the potential to be the distinct economical and environmental choice for treatment of wastewater and other related water management issues. Electrocoagulation is an efficient technique since adsorption of hydroxide on mineral surfaces are a 100 times greater on *in situ* rather than on precipitated hydroxides when metal hydroxides are used as coagulant. Electrocoagulation needs simple equipments, designable for virtually any

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size. It is cost-effective, and easily operable. The start-up and operating costs are relatively low. It requires low maintenance cost with no moving parts. Since practically no chemical addition is required in this process, it brings minimum chance of secondary pollution. It needs low current, and it can be run even by green processes, such as, solar, wind-mills and fuel cells. Electrocoagulation process can effectively destabilize small colloidal particles. It produces minimal sludge. Gas bubbles produced during electrolysis can enhance flotation. It removes the smallest colloidal particles efficiently compared to conventional chemical and biological techniques, because the smallest charged particles have greater probability of being coagulated by the electric field that sets them in motion.

Although electrocoagulation has numerous advantages, it has some drawbacks as discussed below. The sacrificial anodes need to be replaced periodically. It requires a high conductivity of the wastewater suspensions. In case of the removal of organic compounds, some toxic chlorinated organic compound may be formed in situ if chlorides are also present. An impermeable oxide film may be formed on the electrodes that may interfere with the performance of the electrocoagulation cell. However, changing polarity may help reduce this interference.

This work focuses on removal of chromium from effluent by electrocoagulation using aluminium as electrode material and in continuous system. Some studies [21,22] show the effectiveness of this method in batch system with mild steel electrode using bipolar or monopolar configurations.

In the electrocoagulation process, many factors such as pH, applied potential and the application time influence the process efficiency. The process efficiency may be increased by the optimization of these factors. In conventional multifactor experiments, optimization is usually carried out by varying a single factor while keeping all the other factors fixed at a specific set of conditions. This method is time consuming, requires large number of experiments.

These limitations of a classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM) [23]. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing the process and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a domain that satisfies the operating specifications. The application of statistical experimental design techniques in electrocoagulation process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs.

The purpose of this paper is to optimize and model the removal of Cr(III) from polluted waters using the electrocoagulation process by searching a possible optimum in the response surface representing the relationship between, on the one hand, the chromium removal efficiency, in the other part, the energy consumption and the variables governing the treatment.

In this work the relationship between the chromium removal, the energy consumption and four quantitative variables, i.e. pH, electrolysis potential, electrolysis times and temperature, are determined by a parabolic model for a set of experiments according to a fractional central composite design. The Statistical calculations are done by using JMP (John's Macintosh Project) software [24].

## 2. Experimental

The electrocoagulation (EC) is carried out in a mechanically stirred reactor (STR) (Fig. 1). The chromium solution is introduced

continuously in the electrochemical reactor, having a capacity of 5 l. The STR consisted of a dished-bottom cylindrical tank of internal diameter  $D = 20.6$  cm and ratio  $H/D = 0.73$  equipped with a Rushton propeller of 6 cm diameter placed, 6 cm from the bottom in order to avoid settling and favour EC. The anode and cathode were both flat aluminium electrodes of rectangular shape. The effective area of the anode is  $S = 109$  cm<sup>2</sup> and the distance between both electrodes is  $e = 10$  mm.

These electrodes are connected to a digital DC power supply (Didalab, France); this later is used to apply the desired potential. An ammeter is optional for monitoring the electrolysis current during experiment. Conductivity and pH are measured using a CD810 conductimeter (Radiometer Analytical, France) and a ProfilLine pH197i pHmeter (WTW, Germany), respectively.

The mixing rate used is 300 rpm to ensure a good mixing.

A stock chromium solution (200 mg/l) is prepared, with distilled water, using chromium basic sulphate (Cr(OH)SO<sub>4</sub>, 26% as Cr<sub>2</sub>O<sub>3</sub>) used in tanning process. The pH is adjusted to desirable value using NaOH or H<sub>2</sub>SO<sub>4</sub> with high purity.

During this experiment, the pH of solution is adjusted to required value and the reactor is maintained at a fixed temperature. The desired potential and flow are applied. The effluent from the electrocoagulation unit is sampled. After 30 min, the steady state operation is achieved.

Samples are filtered, with commercial paper filtration, and the remaining Cr(III) is determined in the solution by atomic absorption spectrophotometry (AAS, Varian model AA-20).

The removal chromium efficiency is calculated as

$$\% \text{ Removal efficiency} = \frac{C_i - C_f}{C_i} \times 100$$

where  $C_i$  is the initial chromium concentration (mg/l) and  $C_f$  is the final chromium concentration (mg/l).

The percentage of aluminium remaining in solution is calculated by the following relation:

$$\% = \frac{\text{mass}_{\text{dissolved}}}{\text{mass}_{\text{remained}}} \times 100$$

The weight of dissolved aluminium is calculated by the Faraday's law:

$$m = \frac{M \times I}{z \times F} \times \frac{3600}{Q}$$

where  $Z = 3$  is the number of electrons corresponding to aluminium oxidation,  $M$  is the molecular weight (g/mol),  $F$  is Faraday's constant (96,500 C),  $I$  is the electrolysis current (A) and  $Q$  is the volume flow rate (m<sup>3</sup>/h).

The energy consumption  $W$  (kWh/m<sup>3</sup>) in the electrocoagulation process results mainly in ohmic losses rather than electrolysis reactions, and calculated from:

$$W = \frac{U \times I}{Q \times 1000}$$

where  $U$  is the voltage (V),  $I$  is the electrolysis current (A) and  $Q$  is the volume flow (m<sup>3</sup>/h).

### 2.1. Statistical analysis

Optimization of the removal of chromium by electrocoagulation is achieved by using the RSM. A rotatable central composite design uniform is used to study the empirical relationships between three responses (chromium removal efficiency, energy consumption and dissolved aluminium) and four factors: pH, potential, time and temperature. Table 1 shows the levels attributed to each variable.

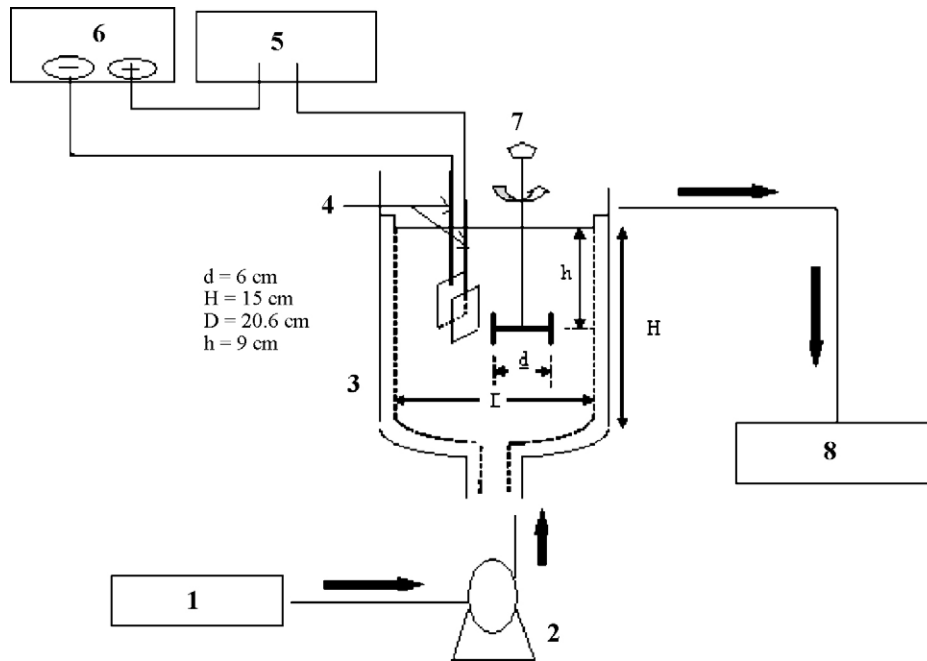


Fig. 1. Schematic diagram of experimental set-up. (1) Inlet reservoir; (2) pump; (3) thermostated electrochemical reactor; (4) cathode and anode; (5) ammeter; (6) DC power supply; (7) agitator; (8) outlet reservoir.

2.1.1. Mathematical model

The behaviour of the system is explained by the following quadratic equation:

$$\eta = \beta_0 + \sum_{j=1}^4 \beta_j X_j + \sum_{j=1}^4 \sum_{j'=1, j \neq j'}^4 \beta_{jj'} X_j X_{j'} + \sum_{j=1}^4 \beta_{jj} X_j^2$$

Table 1  
The central composite design presented according to the standard order.

Order		Coded variables values			
Logical run	Random run	$X_1$	$X_2$	$X_3$	$X_4$
1	30	-1	-1	-1	-1
2	22	1	-1	-1	-1
3	21	-1	1	-1	-1
4	26	1	1	-1	-1
5	1	-1	-1	1	-1
6	5	1	-1	1	-1
7	29	-1	1	1	-1
8	4	1	1	1	-1
9	27	-1	-1	-1	1
10	25	1	-1	-1	1
11	20	-1	1	-1	1
12	13	1	1	-1	1
13	10	-1	-1	1	1
14	8	1	-1	1	1
15	18	-1	1	1	1
16	23	1	1	1	1
17	24	-2	0	0	0
18	31	2	0	0	0
19	12	0	-2	0	0
20	3	0	2	0	0
21	6	0	0	-2	0
22	8	0	0	2	0
23	5	0	0	0	-2
24	19	0	0	0	2
25	7	0	0	0	0
26	1	0	0	0	0
27	6	0	0	0	0
28	7	0	0	0	0
29	9	0	0	0	0
30	4	0	0	0	0
31	2	0	0	0	0

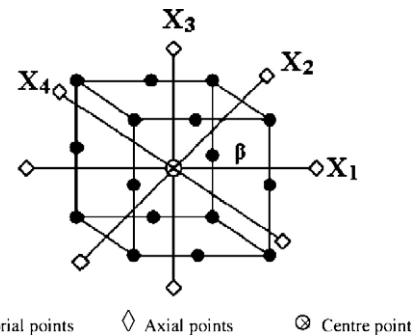


Fig. 2. A central composite rotatable design for four factors  $X_1, X_2, X_3$  and  $X_4$ .

where  $\eta$ : theoretical response function;  $X_j$ : coded variables of the system;  $\beta_0, \beta_j, \beta_{jj'}$  and  $\beta_{jj}$ : true model coefficients.

The observed response  $y_i$  for the  $i$ th experiment is

$$y_i = \eta_i + e_i \quad (e_i : \text{error}).$$

2.1.2. The central composite design

Thirty-one experiments are used to estimate the model coefficients. The graphical representation of the distribution of these experimental points is given in Fig. 2. The corresponding four variable central composite design is shown in Table 2. The variables are

Table 2  
Natural and coded variables.

Natural variable ( $x_j$ )	Coded variables $X_1, X_2, X_3, X_4$				
	-2	-1	0	1	2
$x_1 = \text{pH}$	2	3	4	5	6
$x_2 = \text{potential (V)}$	2.5	4.5	6.5	8.5	10.5
$x_3 = \text{time (min)}$	10	15	20	25	30
$x_4 = \text{temperature (}^\circ\text{C)}$	15	20	25	30	35

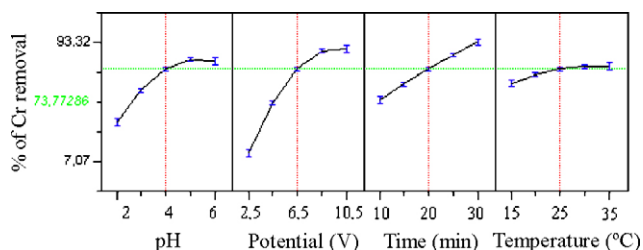


Fig. 3. Main effects plot of parameters for chromium removal efficiency.

coded according to the following equation:

$$X_i = \frac{x_i - x_0}{\Delta x}$$

where  $X_i$  is the dimensionless value of an independent variable,  $x_i$  is the real value of an independent variable,  $x_0$  is the value of  $x_i$  at the center point and  $\Delta x$  is the step range.

The 31 experiments can be divided into three groups as follows:

$N_F = 2^4$  factorial experiments carried out at the corners of the cube;  $N_a = 2 \times 4$  axial experiments carried out on the axes at a distance of  $\pm\alpha$  from the center. The distance  $\alpha$  is calculated so as to obtain rotatability. A four central composite design is rotatable if:

$$\alpha = \pm(N_F)^{1/4} = \pm 2$$

$N_0$  experiments are carried out at the center of the experimental domain. In our case, the  $N_0$  value was fixed at 7 so as to obtain orthogonality and isovariance by rotation properties. The experiments repeated at the center of the domain (25–31 in Table 1) leads to calculate an independent estimation of the 'pure' experimental error variance.

### 2.1.3. Validation of the model

In the case of a composite design, the validation of the model is 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.

'Statistica' software is performed for regression and graphical analysis of data obtained. The optimum of studied parameters (pH, potential, time and temperature) is obtained by analysing the response surface contour plots.

## 3. Result and discussion

The most important parameters, which affect the efficiency of electrocoagulation, are pH, potential, time and temperature of the solution. In order to study the combined effect of these factors, experiments are performed for different combinations of the physical parameters using statistically designed experiments. The pH range studied is between 2 and 6. The potential is between 2.5 and 10.5 V. The time is varied between 10 and 30 min and temperature between 15 and 35 °C.

The main effects of each of the parameter on chromium removal efficiency, energy consumption and dissolved aluminium are given in Figs. 3–5, respectively. Fig. 3 shows that the removal efficiency increases with increasing pH, potential, time or temperature. Indeed, the removal efficiency of chromium depends on the quantity of aluminium generated in the medium. The later depends on electrolysis potential, electrolysis time, pH solution and temperature. Indeed, when the potential (or time) increases, the quantity of dissolved aluminium in solution increases, therefore the amount of aluminium hydroxide  $\text{Al}(\text{OH})_3$  formed is important. Consequently,

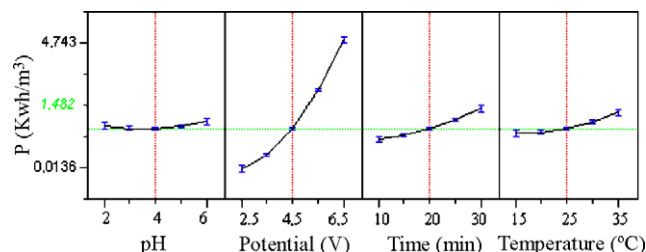


Fig. 4. Main effects plot of parameters for energy consumption.

we note high chromium removal efficiencies at high potential. Furthermore, the electrocoagulation is most effective when the pH of the medium is  $\geq 4$ . The mechanism of chromium removal is probably the precipitation as chromium hydroxide  $\text{Cr}(\text{OH})_3$  and adsorption on formed hydroxide precipitate  $\text{Al}(\text{OH})_3$ . However,  $K_s(\text{Al}(\text{OH})_3) \ll K_s(\text{Cr}(\text{OH})_3)$ , in fact, it is the aluminium hydroxide which is formed initially in the medium. Furthermore, during all the experiences, we note only the formation of white aluminium hydroxide that becomes green with time. Then the probable mechanism of chromium removal is adsorption. Fig. 4 shows that the energy consumption increases with each parameter. The energy consumption is high at higher electrolysis potential. The same trend was found by Chen et al [16]. Moreover, it is shown from Fig. 5 that the amount of aluminium remaining in the solution decreases with the increase of one of parameters: pH, potential or time. On one hand, when the pH of the medium increases, the precipitation of hydroxide of aluminium is favoured, on the other hand the quantity of aluminium in solution increases with time and electrolysis potential. In the same time, the amount of  $\text{OH}^-$  generated raises with potential or time. Consequently, the aluminium hydroxide is formed. Fig. 5 shows that the amount of aluminium remaining in the solution decreases and becomes stable when the temperature increases. The total precipitation of aluminium hydroxide is gotten at 25 °C. At weak temperature, the conductivity of solution is lower, then the amount of  $\text{OH}^-$  generated is insufficient to total precipitation of aluminium. The increase of temperature improves the formation of aluminium hydroxide.

Table 3 shows the experimental results of removal efficiency of chromium, energy consumption and the amount of aluminium remaining in the solution for the 31 experiments. Using the experimental results, the regression model equations (second-order polynomial) relating the three responses are developed and are given in Eqs. (1), (2) and (3), respectively. Apart from the linear effect of the parameter for the three responses, the RSM also gives an insight into the quadratic and interaction effect of the parameters. These analyses are done by means of Fisher's 'F' test and Student 't' test. The Fisher's 'F' test is used to determine the significance of each of the interaction among the variables, which in turns may indicate the patterns of the interactions among the variables. In general, the larger the magnitude of  $F$ , the smaller the value

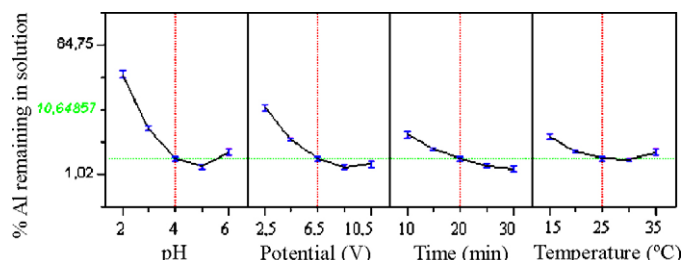


Fig. 5. Main effects plot of parameters for aluminium remaining in solution.

**Table 3**  
The experimental data for chromium removal efficiency, energy consumption and the dissolved aluminium remaining in solution according to central composite design.

Logical run	Response %E		Response P (kWh/m <sup>3</sup> )		Response %Al	
	%E experimental	%E predicted	P experimental	P predicted	%Al experimental	%Al predicted
1	7.07	6.17	0.486	0.505	71.62	70.50
2	36.66	38.43	0.362	0.347	18.37	17.46
3	58.70	59.74	2.206	2.178	24.82	24.49
4	84.56	85.55	2.103	2.109	23.21	22.83
5	50.1	49.71	0.975	1.031	35.04	35.88
6	70.44	70.55	0.934	0.990	6.05	6.10
7	75.61	75.36	3.069	3.014	12.17	11.75
8	90.35	89.73	3.023	3.061	33.27	33.35
9	13.61	14.95	0.386	0.342	84.75	83.01
10	45.32	44.62	0.45	0.462	10	10.90
11	72.28	71.22	3.254	3.156	18.83	19.25
12	93.32	94.42	3.426	3.364	1.02	-1.47
13	54.6	52.66	0.617	0.568	49.15	50.01
14	71.23	70.90	0.782	0.805	2.5	1.17
15	82.05	81.00	3.683	3.692	8.89	8.14
16	92.83	92.78	4.079	4.017	9.59	10.68
17	33.63	35.19	1.508	1.578	65.13	65.40
18	80.42	79.16	1.768	1.745	14	14.90
19	12.26	12.66	0.014	-0.040	43.49	43.87
20	88.28	88.11	4.743	4.845	6.56	7.36
21	53.34	51.43	0.983	1.063	24.5	26.48
22	91.2	93.34	2.275	2.242	4.81	4.00
23	64.62	63.62	1.361	1.298	24.84	25.09
24	74.22	75.45	1.979	2.090	14	14.92
25	75.45	73.77	1.484	1.482	11.05	10.65
26	73.48	73.77	1.473	1.482	10.45	10.65
27	72.32	73.77	1.48	1.482	10.94	10.65
28	73.27	73.77	1.482	1.482	10.82	10.65
29	73.14	73.77	1.474	1.482	10.3	10.65
30	75.82	73.77	1.496	1.482	10.9	10.65
31	72.93	73.77	1.485	1.482	10.08	10.65

of  $P$ , the more significant is the corresponding coefficient term. The regression coefficient,  $F$  and  $P$  values for all the linear, quadratic and interaction effects of the parameter are given in Tables 4–6 for three responses, respectively. It is observed that the coefficients for the linear effect of all the factors pH, potential, time and temperature ( $P < 0.0001$  for all) for three responses are highly significant except pH ( $P = 0.0096$ ) for energy consumption is slightly less significant. However, for the removal efficiency of chromium, all of the interaction effect of the variables is found highly significant except the interaction between pH and temperature ( $P = 0.1269$ ) and the interaction between potential and temperature ( $P = 0.1139$ ). For the energy consumption, the whole interactions of variables, except the interaction pH–potential ( $P = 0.2204$ ) and the interaction pH–time

( $P = 0.1143$ ), are considered as very significant factors. Whereas, all interaction of variables is highly significant except the interaction time–temperature, for the responses aluminium remaining in solution. The significance of these interaction effects between the variables will have been lost if experiments are carried out by conventional methods.

The coefficient of the quadratic effect of all the variables pH, potential, time and temperature is highly significant for three responses, except the quadratic effect of time for the response removal efficiency of chromium that are found not significant. Consequently, the best fitting response functions, for the three models are then conveniently written as follows:

**Table 4**  
Estimated regression coefficients and corresponding  $F$  and  $P$  values for chromium removal efficiency.

Term	Coefficient	Sum of squares	$F$	$P$
Constant	73.772857	–	–	<0.0001
$X_1$	11.01125	2909.9430	1122.72	<0.0001
$X_2$	18.862917	8539.4310	3294.702	<0.0001
$X_3$	10.475417	2633.6245	1016.111	<0.0001
$X_4$	2.95625	209.7459	80.9246	<0.0001
$X_1X_2$	-1.615625	41.7639	16.1134	0.0010
$X_1X_3$	-2.856875	130.5878	50.3836	<0.0001
$X_1X_4$	-0.648125	6.7211	2.5931	0.1269
$X_2X_3$	-6.983125	780.2246	301.0279	<0.0001
$X_2X_4$	0.673125	7.2496	2.7970	0.1139
$X_3X_4$	-1.458125	34.0181	13.1249	0.0023
$X_1X_1$	-4.157902	494.3674	190.7379	<0.0001
$X_2X_2$	-5.846652	977.4980	377.1404	<0.0001
$X_3X_3$	-0.346652	3.4363	1.3258	0.2665
$X_4X_4$	-1.059152	32.0788	12.3767	0.0029

**Table 5**  
Estimated regression coefficients and corresponding  $F$  and  $P$  values for energy consumption.

Term	Coefficient	Sum of squares	$F$	$P$
Constant	1.482	–	–	<0.0001
$X_1$	0.0417917	0.041917	8.6555	0.0096
$X_2$	1.2212417	35.794349	7391.224	<0.0001
$X_3$	0.2947083	2.084472	430.4255	<0.0001
$X_4$	0.198125	0.942084	194.5323	<0.0001
$X_1X_2$	0.0221875	0.007877	1.6264	0.2204
$X_1X_3$	0.0290625	0.013514	2.7905	0.1143
$X_1X_4$	0.0694375	0.077145	15.9298	0.0011
$X_2X_3$	0.0775625	0.096255	19.8758	0.0004
$X_2X_4$	0.2851875	1.301311	268.7094	<0.0001
$X_3X_4$	-0.074938	0.089850	18.5533	0.0005
$X_1X_1$	0.0449771	0.057847	11.9450	0.0033
$X_2X_2$	0.2300521	1.513400	312.5040	<0.0001
$X_3X_3$	0.0427271	0.052204	10.7798	0.0047
$X_4X_4$	0.0529771	0.080256	16.5722	0.0009



**Table 6**

Estimated regression coefficients and corresponding F and P values for aluminium remaining in solution.

Term	Coefficient	Sum of squares	F	P
Constant	10.648571	–	–	<0.0001
X <sub>1</sub>	–12.62583	3825.8800	2466.681	<0.0001
X <sub>2</sub>	–9.126667	1999.1051	1288.894	<0.0001
X <sub>3</sub>	–5.618333	757.5761	488.4362	<0.0001
X <sub>4</sub>	–2.541667	155.0417	99.9609	<0.0001
X <sub>1</sub> X <sub>2</sub>	12.845	2639.9044	1702.04	<0.0001
X <sub>1</sub> X <sub>3</sub>	5.8175	541.4929	349.1197	<0.0001
X <sub>1</sub> X <sub>4</sub>	–4.76625	363.4742	234.3447	<0.0001
X <sub>2</sub> X <sub>3</sub>	5.47125	478.9532	308.7982	<0.0001
X <sub>2</sub> X <sub>4</sub>	–4.435	314.7076	202.9032	<0.0001
X <sub>3</sub> X <sub>4</sub>	0.4075	2.6569	1.7130	0.2091
X <sub>1</sub> X <sub>1</sub>	7.3761905	1555.8426	1003.107	<0.0001
X <sub>2</sub> X <sub>2</sub>	3.7411905	400.2405	258.0493	<0.0001
X <sub>3</sub> X <sub>3</sub>	1.1486905	37.7318	24.3270	0.0002
X <sub>4</sub> X <sub>4</sub>	2.3399405	156.5709	100.9468	<0.0001

**Table 7**

Regression variance analysis for chromium removal efficiency.

Source	Degree of freedom	Sum of squares	Mean square	F <sub>statistics</sub>	P
Model	14	16644.150	1188.87	458.6915	<0.0001
Residual	16	41.470	2.59	–	–
Total	30	16685.619			

Chromium removal efficiency models:

$$\eta = 73.772 + 11.01X_1 + 18.862X_2 + 10.475X_3 + 2.956X_4 - 1.615X_1X_2 - 2.856X_1X_3 - 6.983X_2X_3 - 1.458X_3X_4 - 4.157X_1^2 - 5.846X_2^2 - 1.059X_4^2 \quad (1)$$

Energy consumption:

$$\eta = 1.482 + 0.0417X_1 + 1.2217X_2 + 0.294X_3 + 0.198X_4 + 0.069X_1X_4 + 0.077X_2X_3 + 0.285X_2X_4 - 0.074X_3X_4 + 0.044X_1^2 + 0.230X_2^2 + 0.0427X_3^2 + 0.052X_4^2 \quad (2)$$

Aluminium remaining in solution:

$$\eta = 10.648 - 12.626X_1 - 9.127X_2 - 5.618X_3 - 2.542X_4 + 12.845X_1X_2 + 5.817X_1X_3 - 4.766X_1X_4 + 5.471X_2X_3 - 4.435X_2X_4 + 7.376X_1^2 + 3.741X_2^2 + 1.149X_3^2 + 2.340X_4^2 \quad (3)$$

The statistical significance of the ratio of mean square variation due to regression and mean square residual error is tested using ANOVA. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the model. According to the ANOVA (Tables 7–9), the  $F_{statistics}$  values for all regression are higher. The large value of  $F$  indicates that most of the variation in the response can be explained by the regression equation. The associated  $P$  value is used to estimate whether  $F_{statistics}$  is large enough to indicate sta-

**Table 8**

Regression variance analysis for energy consumption.

Source	Degree of freedom	Sum of squares	Mean square	F <sub>statistics</sub>	P
Model	14	42.000612	3.00004	619.4831	<0.0001
Residual	16	0.077485	0.00484	–	–
Total	30	42.078097			

**Table 9**

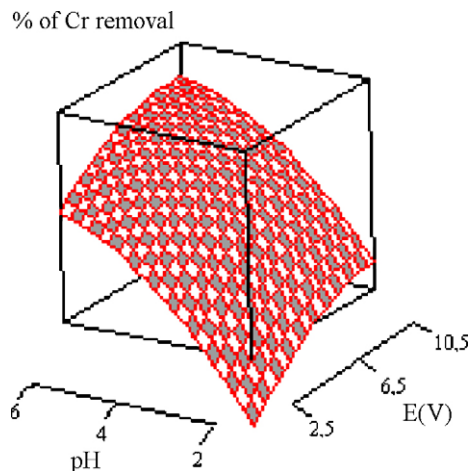
Regression variance analysis for aluminium remaining in solution.

Source	Degree of freedom	Sum of squares	Mean square	F <sub>statistics</sub>	P
Model	14	12934.633	923.902	595.6727	<0.0001
Residual	16	24.816	1.551	–	–
Total	30	12959.449			

tistical significance. A  $P$  value lower than 0.01 indicates that the model is considered to be statistically significant. The  $P$  values for all of the regressions are lower than 0.01. This means that at least one of the terms in the regression equation have a significant correlation with the response variable. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct.

Further, the ANOVA for chromium removal efficiency, energy consumption and aluminium remaining in solution indicates that the second-order polynomial model (Eqs. (1), (2) and (3)) is highly significant and adequate to represent the actual relationship between the response and variables, with very small  $P$  values and a high value of coefficient of determination ( $R^2 = 0.9994$ ,  $R^2 = 1$ ,  $R^2 = 0.9996$  for chromium removal efficiency, energy consumption and aluminium remaining in solution, respectively). This implies that 99.94%, 100% and 99.96% of sample variation for chromium removal efficiency, energy consumption and aluminium remaining in solution, respectively, are explained by the model.

The 3D response surface and 2D contour plot are generally the graphical representation of the regression equation. This representation shows the relative effects of any two variables when the remaining variables are kept constant. We will use it to search the optimal values of the process parameters: maximum chromium removal efficiency with low energy consumption and less aluminium remaining in solution. Then, the response surface plots and contour plots to estimate the removal efficiency (Figs. 6 and 7), energy consumption (Figs. 8 and 9) and aluminium remaining in solution (Figs. 10 and 11), are given. Thus, the surface and contour plots for chromium removal efficiency in Fig. 7 shows the interaction effect of pH and potential at fixed values of the time ( $t = 10$  min,  $X_3 = -2$ ) and of the temperature ( $T = 27.5$  °C,  $X_4 = 0.5$ ). The response surface of mutual interactions between the variables is found to

**Fig. 6.** Response surface plot of chromium removal efficiency (time = 10 min and temperature = 27.5 °C).

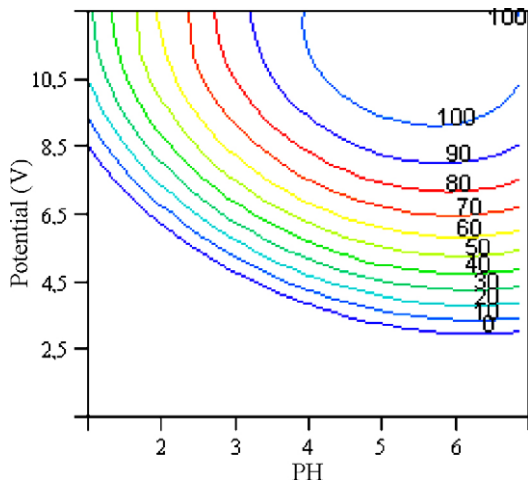


Fig. 7. Contour plot of estimated response surface of chromium removal efficiency (time = 10 min and temperature = 27.5 °C).

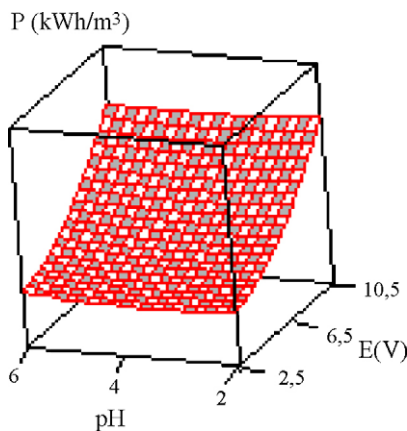


Fig. 8. Response surface plot of energy consumption (time = 10 min and temperature = 27.5 °C).

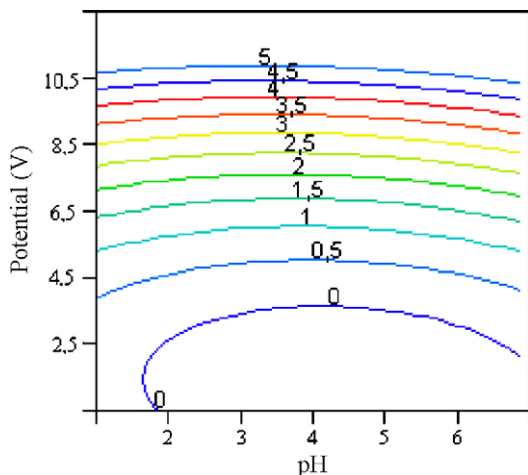


Fig. 9. Isoresponse contour plot for energy consumption (time = 10 min and temperature = 27.5 °C).

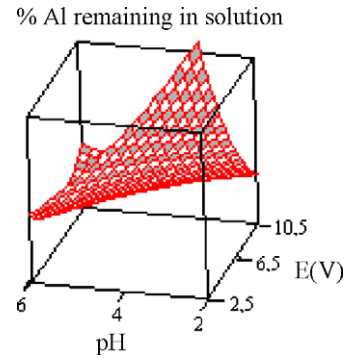


Fig. 10. Response surface plot of aluminium remaining in solution (time = 10 min and temperature = 27.5 °C).

be elliptical and the maximum chromium removal efficiency is obtained in the following cases:

- The pH and the electrolysis potential increase simultaneously.
- The pH increases and the potential is between 9.14 and 10.5 V and remains unchanged.
- The potential increases and pH is between 4.14 and 6 and remains stable.

The geometrical representation of the response energy consumption shows at fixed pH, when the potential increases the energy consumption increases. We also note that, the influence of pH is not significant. Then, to have a weak energy it is beneficial to work with low potential. The lowest value of the potential which gives maximum of chromium removal is 9.14V. However, the contour plots of percentage of aluminium remaining in solution (Fig. 11 Fig. 11) shows that at fixed potential, when the pH increases the quantity of dissolved aluminium decreases. We must, then, choose a value of pH corresponding to a lower aluminium content in solution and which approaches the pH of a effluent of tanning. Thus, this pH is 4.23. From where, the optimum condition for treatment of discharge charged out of trivalent chromium is given in Table 10. Under these conditions, the estimated values of chromium removal efficiency, energy consumption and aluminium remaining in solution for the treatment by electrocoagulation of the trivalent chromium are respectively, 91%, 3.536 kWh/m<sup>3</sup> and 0.57%. This result is experimentally confirmed.

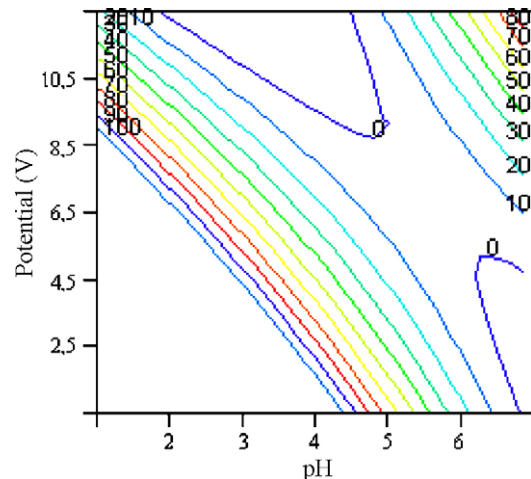


Fig. 11. Isoresponse contour plot for aluminium remaining in solution (time = 10 min and temperature = 27.5 °C).

**Table 10**

Optimum values of the process parameter.

Parameter	Optimum values
pH	4.23
Potential (V)	9.14
Time (min)	10
Temperature (°C)	27.5

#### 4. Conclusion

The present study clearly demonstrated the applicability of electrocoagulation process using the aluminium anode for chromium removal. This study clearly showed that RSM is one of the suitable methods to optimize the best operating conditions to maximize the chromium removal. An orthogonal central composite uniform rotational design is successfully employed for experimental design and analysis of results. Satisfactory empirical model equations are developed for three parameters, the chromium removal efficiency, energy consumption and aluminium remaining in solution using RSM to optimize the parameters. Graphical response surface and contour plot is used to locate the optimum point.

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