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Electrocoagulation treatment of the food dye waste industry: Theoretical and experimental study

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Abstract

The performance of the electrocoagulation treatment of synthetic food dye waste industry was studied using iron anode. The influence of several parameters as electrolysis current, chloride concentration, electrolysis time and pH was investigated.
In order to verify these factors and their impact on the discoloration efficiency, an experimental design model was established. The mathematical model was created using a rotatable, uniform and central composite design. This model described the color removal efficiency and the energy consumption according to the studied parameters. The graphical representation of the model according to the parameters allowed us to define optimal treatment conditions. The optimal values of electrolysis current, chloride concentration, electrolysis time and pH were respectively 14.4 mA/cm^2, 5.76 g/L, 39 mn and 7. 94.52% of color removal efficiency is achieved with an energy consumption of 3.90 KWh/m^3.

1. Introduction

Various food industries are using azo dyes in the food (like confectionery, pastry, cheese rind…) for red coloration of foods for example [1]. The food dye industry generates liquid waste containing a high concentration of azo dyes as red Ponceau 4R, red Carmoisine….

The persistence of azo dyes in the environment causes pollution of water and soil. Therefore, an adequate treatment of these dyes remains necessary before discharging them into the natural environment [2]. There biodegradation is generally difficult. Thus, serious ecological and environmental problems are created [3].

Various elimination techniquesof monoazo dyes have been used, like advanced oxidation process "electro Fenton" [2,4], Fenton [5] , photocatalysis [6,7] and adsorption [8,9]. Oxidation by ozone, super-iron (VI) and hypochlorite were the most efficient treatment methods, but they are less preferable due to the operating cost and the generation of a second pollution resulting from the presence of residual chlorine [10,11].

In recent years, electrocoagulation has shown its efficiency to treat the several dye waste [12–17]. The electrocoagulation (EC) technique using iron or aluminum anode is an electrochemical process that was developed to overcome the drawbacks of conventional treatment techniques [18–21].

The anode oxidation generated a metallic cation. This later, under suitable conditions (pH, concentration…) lead to metal hydroxide formation which was able to remove a wide variety of pollutants [22].

The objective of this work is to develop and optimize the treatment parameters by electrocoagulation of food dyes waste industry using iron electrode in a batch reactor. In the electrocoagulation process, many factors such as pH, electrolysis current and electrolysis time have a big influence on treatment efficiency. However, using conventional multifactor experiments, optimization is usually carried out by varying a single parameter and keeping all the others fixed at a constant value. This method requires a lot of experiments and time. The limitation of a classical method can be avoided by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology [23].

Several research studies have used the methodology of response surface [24–28] to optimize different parameters which could influence the quality of waste treatment efficiency.

In this paper, the influence of four parameters using electrocoagulation technique (electrolysis current, electrolysis times, chloride concentration and pH) on color removal efficiency of Ponceau 4R dye and energy consumption was determined by a parabolic model for a set of experiments. The optimization was obtained by using a Response Surface Methodology (RSM), rotatable uniform and central composite design [29]. The Statistical calculations were done by using JMP software [30].

2. Experimental procedure

The objective of this work is to achieve the treatment of liquid waste from a food dye industry. The physicochemical characteristics of the liquid waste were reported on Table I. The results showed that the later were charged with Ponceau 4R red dye and chlorides. But to achieve this, electrocoagulation treatment were carried out on synthetic waste containing Ponceau 4R red dye at concentration of 1g/l.
pH measurement was performed using HANNA pH meter instrument types HI8519N.
Spectrometric measurement was performed at the wavelength λ = 508 nm (figure 1) using spectrophotometer type Helios gamma.

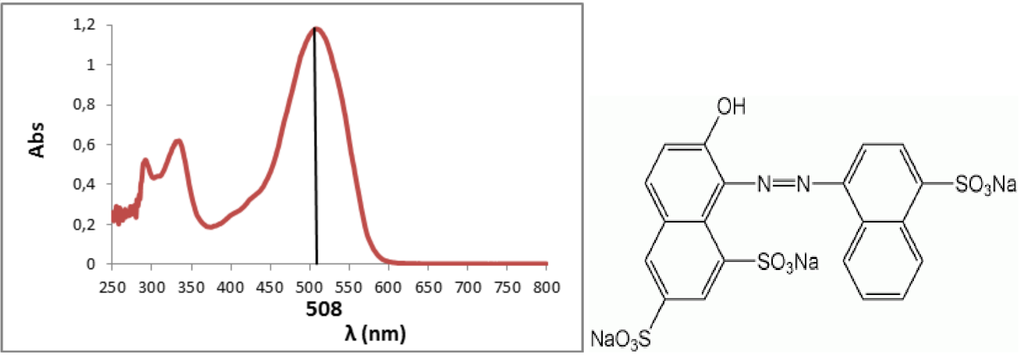


Fig. 1 : *UV-visible spectrum and Chemical formula of red Ponceau 4R (40 mg/l).*

Table I : Physicochemical characteristics of the industrial liquid waste

Parameter	**Value**
pH	7.45
σ (mS/cm)	94.5
Cl^- (g/l)	117
DCO (g/l)	18
Dye (g/l)	16

2.1. Experimental setup:

Electrocoagulation experiments were performed in a closed batch reactor 100 cm^3 of capacity and using iron electrodes. Electrolysis current is applied by a DC power supply (0-30V, 5A). The distance between iron electrodes (2 x 2) cm^2(figure 2).

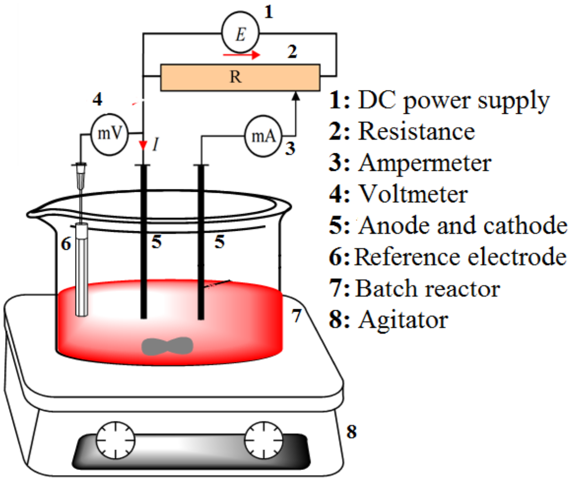


Fig. 2 : *Experimental device used for electrocoagulation treatment*

The initial pH of each sample was adjusted with NaOH or H_2SO_4. After each experiment, pH value was measured and the solution was filtered. After filtration, spectrometric measurement was performed in order to evaluate the color removal efficiency. The treatment efficiency (% Y) was calculated using the following equation (1):

$$Y\% = \frac{Abs_0 - Abs_t}{Abs_0} * 100 \qquad (1)$$

Where: Abs_0: absorbance without treatment

Abs_t: absorbance after treatment

Energy consumption (Ce) was performed following the equation (2):

$$Ce(Wh/l) = \frac{U * I * t}{V} * 100 \qquad (2)$$

Where: U: Potential (V); I: Current (A); t: Time (h) and V: volume of solution (l).

2.2. Statistical analysis:

Statistical analysis was used in agriculture, biology and chemistry to study the empirical relationships between one or more measured responses and a number of variables [31]. The optimization of color removal efficiency by electrocoagulation was obtained by using a response surface methodology (RSM).

2.3. Choice of factors:

The preliminary experiments and previous work [24,26,27,32] as well as the knowledge already acquired have led us to choose the four factors: electrolysis current, electrolysis time, chloride concentration and pH of the solution. Chloride concentration was chosen because the industrial dye waste contained a lot of chloride ions.

2.4. Choice of the experimental field:

To carry out this study, a choice of the field of variation of each factor is very important. In this area, two elements must be taken into consideration [33]:

- The range of factors variation must be sufficiently wide to show significant response variations.
- It must be sufficiently restricted to be able to simulate the variations which may occur in an uncontrolled way during the implementation of the method.

The four main variables levels were selected based on preliminary tests. The corresponding four variable central composite designs, the independent parameters, the experimental field and the levels of each variable are given in Table II.

Table II : Experimental range and levels of the independent test variable.

Natural variables (x_i)	**Unit**	**Coded variables X_1, X_2, X_3, X_4***				
		-2	-1	0	1	2
x_1= i	mA/cm^2	5	15	25	35	45
x_2= [NaCl]	g/l	1	2.75	4.5	6.25	8
x_3= Time	mn	5	15	25	35	45
x_4= pH	-	5	6	7	8	9

* $X_1 = (x_1 - 25)/10$; $X_2 = (x_2 - 4.5)/1.75$; $X_3 = (x_3 - 25)/10$ and $X_4 = (x_4 - 7)/1$

2.5. Choice of the type of design:

Among the designs which allow the use of a second degree polynomial model, we have chosen a central composite design [34], which presented optimal qualities in the prediction of the calculated response at any point of the field, a high resolution and a limited number of trials.

The central composite design is a factorial design of type 2^k to which, we have added axial and central points. The number of central points as well as the distance from the axial points to the center are determined according to the rotational isovariance criterion (the error on the prediction model must only be a function of the distance at the center of the design) using the JMP Software [30].

For four factors, realization of a complete factorial design had five levels requiring $5^4=625$ experiments, this number was very large, in order to achieve a reasonable number of experiments, we realized a rotatable central composite design with uniform precision with only 31 experiments [23].

2.6. The central composite design:

The effect of the four parameters : electrolysis current (X_1: i in mA/cm^2), NaCl concentration (X_2: [NaCl] in g/l), electrolysis time (X_3: t in mn) and pH of the solution (X_4: initial pH), on the color removal efficiency was studied using a rotatable, uniform and central composite designs 2^4 with seven repetitions of the central point (N_0), which will allow to estimate the repeatability of the method and therefore to test the significance of the model coefficients. The graphical representation of the distribution of these experimental points was given in figure 3.

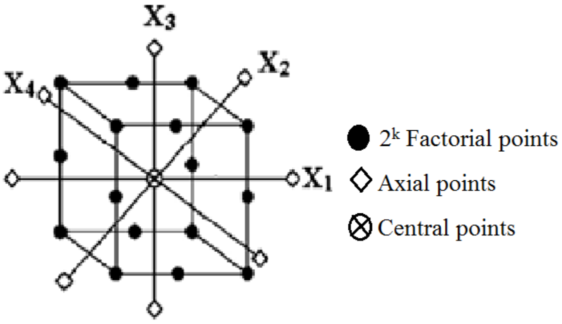


Fig. 3 : *A central composite rotatable design for four factors X_1, X_2, X_3 and X_4*

In this work, a total of 31 experiments (table III) were performed and can be divided into three groups as follows:

$$N = 2^k + 2 * k + N_0; \tag{3}$$

k is the number of factors (k=4);
$N_f = 2^k = 2^4$: the 16 experiments of the factorial design carried out at the corners of the cube;
The variables $X_i = \pm1$(table II) were coded as X_i to the following equation (4):

$$X_i = (x_i - x_0) / \Delta x_i \tag{4}$$

Where X_i was the coded values of an independent variable, x_i was the value of the natural variable, x_0 was the value of x_i at the center point and Δx_i was the step range.
$N_\alpha = 2 * k = 2 * 4$: 8 axial experiments carried out on the axes at a distance of ± α from the center. The distance α was calculated as to obtain rotatability.
A four central composite design was rotatable if:

$$\alpha = \pm (N_f)^{1/4} = \pm2 \text{ [35]}; \tag{5}$$

$N_0 = 7$ experiments are carried out at the center of the experimental domain. In our case, the N_0 value was fixed at 7 as to obtain orthogonality and isovariance by rotation properties and leads to calculate an independent estimation of the pure experimental error variance.

2.7. Mathematical model:

The system behavior was explained by the following quadratic equation (6):

$$\hat{y} = b_0 + \sum_{j=1}^{4} b_j X_j + \sum_{j=1}^{4} \sum_{j'=1; j\neq j'}^{4} b_{jj'} X_j X_{j'} + \sum_{j=1}^{4} b_{jj} X_j^2 \tag{6}$$

Where: $\hat{y}$: theoretical response function; X_j: coded variables of the system; b_0, b_j, $b_{jj'}$ and b_{jj}: true model coefficients.
The observed response y_i for the i^{th} experiment was: $y_i = \hat{y} + e_i$; (e_i: error)
Let $b_u X_u$ be the general term of the 15 terms (1 constant + 4 variables j + 6 interactions jj' + 4 squared variables jj = 15) generally used for the construction of the model, they must be mutually orthogonal 2 by 2, and the normal equation gave the b_u coefficients with the least-squares method.

$$b_u = \frac{Y_u}{\sum_{i=1}^{n} X_{iu}^2} \quad \text{Where } Y_u = \sum_{i=1}^{n} X_{iu} y_i \tag{7}$$

X_{iu} and y_i being the X_u and y values for the i^{th} experiment; Y_u was named contrast.

Table III : Matrix of the central composite design and the analysis results

Order		**Coded variables values**				**Response % Y**			**Response Ce (Wh/l)**			
Logicalrun	Randomrun	X_1	X_2	X_3	X_4	$\%Y_{experimental}$	$\%Y_{predicted}$	Residues (e_i)	$Ce_{experimental}$	$Ce_{predicted}$	Residues (e_i)	
1	30	-1	-1	-1	-1	53.82	45.22	8.6	2.31	1.905	0.405	N_f
2	22	1	-1	-1	-1	86.86	91.43	-4.57	10.22	9.842	0.378	
3	21	-1	1	-1	-1	15.54	17.71	-2.17	1.65	2.591	-0.941	
4	26	1	1	-1	-1	82.3	73.13	9.17	5.81	5.908	-0.098	
5	01	-1	-1	1	-1	94.67	89.98	4.69	5.67	5.126	0.544	
6	05	1	-1	1	-1	94.05	90.60	3.45	23.19	22.143	1.047	
7	29	-1	1	1	-1	95.6	95.62	-0.02	3.57	3.712	-0.142	
8	04	1	1	1	-1	94.91	105.45	-10.54	15.35	16.109	-0.759	
9	27	-1	-1	-1	1	56.48	45.36	11.12	2.16	0.814	1.346	
10	25	1	-1	-1	1	94.71	93.13	1.58	9.8	9.337	0.463	
11	20	-1	1	-1	1	12.41	14.30	-1.89	1.56	2.285	-0.725	
12	13	1	1	-1	1	67.17	71.28	-4.11	6.23	6.187	0.043	
13	10	-1	-1	1	1	80.03	87.65	-7.62	4.48	4.060	0.42	
14	08	1	-1	1	1	92.58	89.83	2.75	23.19	21.667	1.523	
15	18	-1	1	1	1	94.89	89.74	5.15	3.64	3.431	0.209	
16	23	1	1	1	1	94.1	101.14	-7.04	16.33	16.413	-0.083	
17	24	-2	0	0	0	22.02	29.88	-7.86	0.48	0.583	-0.103	N_α
18	31	2	0	0	0	93.21	87.48	5.73	20.7	21.503	-0.803	
19	12	0	-2	0	0	94.76	103.69	-8.93	5.17	7.78	-2.61	
20	03	0	2	0	0	94.29	87.49	6.8	4.92	3.216	1.704	
21	06	0	0	-2	0	5.66	13.45	-7.79	1.6	1.58	0.02	
22	28	0	0	2	0	93.73	88.07	5.66	14.1	15.026	-0.926	
23	15	0	0	0	-2	94.22	97.46	-3.24	8.67	8.431	0.239	
24	19	0	0	0	2	94.39	93.28	1.11	6.5	7.645	-1.145	
25	07	0	0	0	0	94.26	93.88	0.38	6.17	7.035	-0.865	N_0
26	11	0	0	0	0	93.04	93.88	-0.84	7.75	7.035	0.715	
27	16	0	0	0	0	93.04	93.88	-0.84	6.5	7.035	-0.535	
28	17	0	0	0	0	93.82	93.88	-0.06	7	7.035	-0.035	
29	09	0	0	0	0	94.26	93.88	0.38	7.33	7.035	0.295	
30	14	0	0	0	0	94.34	93.88	0.46	6.83	7.035	-0.205	
31	02	0	0	0	0	94.43	93.88	0.55	7.67	7.035	0.635	

3. Results and discussion

Table III showed the experimental data for each color removal efficiency (%Y) and energy consumption (Ce). The 14 terms are easily calculated by substituting data values in the expressions for the least squares estimates of the coefficients (tables IV and V). The fitted response surface was:

Color removal efficiency (%Y):

$$\begin{aligned} \hat{y} = 93.884 + 14.401\,X_1 + \ldots\ldots - 1.043\,X_4 \\ + 2.302X_1{*}X_2 + \ldots\ldots - 0.617X_3{*}X_4 \\ - 8.801X_1^2 + \ldots\ldots + 0.374X_4^2 \end{aligned} \qquad (1)$$

Energy consumption (Ce):

$$\begin{aligned} \hat{y} = 7.035 + 5.23\,X_1 + \ldots\ldots - 0.196\,X_4 \\ - 1.155X_1{*}X_2 + \ldots\ldots + 0.006X_3{*}X_4 \\ + 1.002X_1^2 + \ldots\ldots + 0.250X_4^2 \end{aligned} \qquad (2)$$

From this equation it was possible to compute estimated values ($\hat{y}_i$) and the corresponding residuals: ($e_i = y_i - \hat{y}_i$) (table III). An estimate of the variance of the experimental error (s_r^2) was obtained by dividing the residual sum of squares $\sum_i e_i^2$ (table III) by ν (number of degrees of freedom = number of experiments minus number in the model (i.e. 31 - 15 = 16) [tables VI. VII]:

$$s_r^2(\%Y) = (944.332)/16 = 59.02 \text{; (table VI)} \quad (3)$$

$$s_r^2(Ce) = (22.9757)/16 = 1.436 \text{; (table VII)} \quad (4)$$

Analyses were performed using the Snedecor factor 'F' [36]. The latter was used to determine the significance of each of the interaction among the variables.

In general, the more the amplitude of 'F' was large and the value of 'P' was small.The corresponding coefficient was significantly more important.

The experimental Snedecor factor was obtained by dividing the mean square of the coefficient b_u (CM_u) by the variance of the experimental error (s_r^2):

$$F_{exp} = CM_u / s_r^2 \quad (5)$$

The estimate of the individual mean square (CM_u) was obtained by dividing the sum of squares of each coefficient (SS_u) by its degree of freedom (ν_u=1):

$$CM_u = SS_u / \nu_u \quad (6)$$

Table IV : The estimated regression coefficients. F and P values corresponding to color removal efficiency

Term	**Coefficient *(b_u)***	**Degree of freedom *(ν_u)***	**Sum of squares *(SC_{bu})***	**$F_{exp}(b^2_u/S^2_{bu})$**	**P**	**Signifiance**
constant	93.884286	-	-	-	<0.0001	-
X_1	14.400833	1	4977.2160	84.3299	<0.0001	***
X_2	-4.050833	1	393.8220	6.6726	0.0200	*
X_3	18.653333	1	8350.7243	141.4880	<0.0001	***
X_4	-1.043333	1	26.1251	0.4426	0.5153	NS
X_1 X_2	2.3025	1	84.8241	1.4372	0.2480	NS
X_1 X_3	-11.39625	1	2077.9922	35.2078	<0.0001	***
X_2 X_3	8.28875	1	1099.2540	18.6249	0.0005	***
X_1 X_4	0.39125	1	2.4492	0.0415	0.8411	NS
X_2 X_4	-0.88625	1	12.5670	0.2129	0.6507	NS
X_3 X_4	-0.6175	1	6.1009	0.1034	0.7520	NS
X_1^2	-8.801071	1	2214.9937	37.5291	<0.0001	***
X_2^2	0.4264286	1	5.1999	0.0881	0.7704	NS
X_3^2	-10.78107	1	3323.7263	56.3145	<0.0001	***
X_4^2	0.3714286	1	3.9450	0.0668	0.7993	NS

***: significant at a level of 0.1% ($F_{0.001}$ (1. 16) = 16.12); **: significant at a level of 1% ($F_{0.01}$ (1. 16) = 8.53);
*: significant at a level of 5% ($F_{0.05}$ (1. 16) = 4.49) and NS: non-significant.

Where $F_\alpha(\nu_1.\nu_2)$ is the Snedecor function at ν_1 and ν_2 degree of freedom for a probability α.

The estimate of the sum of squares of the coefficients (SS_u) was obtained by multiplying the square of the coefficient (b_u) by the sum of squares of the values of X_u:

$$SS_u = b_u^2 \sum X_{iu}^2 \quad (7)$$

The investigation of the equations of two models showed that, for a significance level of 95% only the factors for:

- Color removal efficiency (table IV): current density, electrolysis time, chloride concentration and the interactions (electrolysis current - electrolysis time; electrolysis current - electrolysis current; electrolysis time - electrolysis time and chloride concentration - electrolysis time) were significant for the model.
  According to Amani-Ghadim et al. [27].the electrolysis current and the electrolysis time were the most important factors in the electrocoagulation process with an iron anode.
- Energy consumption (table V): electrolysis current, electrolysis time, chloride concentration and the interaction (electrolysis current-electrolysis time; current density-current density and electrolysis current-chloride concentration) were significant for the model.

Table V : The estimated regression coefficients. F and P values corresponding to energy consumption

Term	**Coefficient** ***(b$_u$)***	**Degree of freedom** ***(v$_u$)***	**Sum of squares** ***(SC$_{bu}$)***	**F$_{exp}$*(b^2_u/S$^2_{bu}$)***	**P**	**Signifiance**
Constant	7.0357143	-	-	-	<0.0001	-
X_1	5.23	1	656.46960	457.1579	<0.0001	***
X_2	-1.140833	1	31.23602	21.7524	0.0003	***
X_3	3.3616667	1	271.21927	188.8740	<0.0001	***
X_4	-0.196667	1	0.92827	0.6464	0.4332	NS
$X_1 X_2$	-1.155	1	21.34440	14.8640	0.0014	**
$X_1 X_3$	2.27	1	82.44640	57.4147	<0.0001	***
$X_2 X_3$	-0.525	1	4.41000	3.0711	0.0988	NS
$X_1 X_4$	0.14625	1	0.34222	0.2383	0.6320	NS
$X_2 X_4$	0.19625	1	0.61622	0.4291	0.5217	NS
$X_3 X_4$	0.00625	1	0.00062	0.0004	0.9836	NS
X_1^2	1.0019048	1	28.70478	19.9897	0.0004	***
X_2^2	-0.384345	1	4.22420	2.9417	0.1056	NS
X_3^2	0.3169048	1	2.87183	1.9999	0.1765	NS
X_4^2	0.2506548	1	1.79661	1.2511	0.2798	NS

***: significant at a level of 0.1% ($F_{0.001}$ (1. 16) = 16.12); **: significant at a level of 1% ($F_{0.01}$ (1. 16) = 8.53);
*: significant at a level of 5% ($F_{0.05}$ (1. 16) = 4.49) and NS: non-significant.

For a significance level of 95%, the models were:
Color removal efficiency (%Y):

$$\begin{aligned}
&\qquad\quad (\pm2) \qquad\quad (\pm2) \qquad\qquad (\pm2)\\
&\hat{y} = 93.884 + 14.401\,X_1 - 4.051\,X_2 + 18.653\,X_3\\
&\qquad - 11.396 X_1{*}X_3 + 8.288 X_2{*}X_3 \qquad\qquad (8)\\
&\qquad\quad (\pm2) \qquad\qquad (\pm2)\\
&\qquad - 8.801\,X_1^2 - 10.781\,X_3^2\\
&\qquad\quad (\pm1) \qquad\quad (\pm1)
\end{aligned}$$

Consumption of energy (Ce):

$$\begin{aligned}
&\hat{y}.10^{-1} = 70.35 + 52.3\,X_1 - 11.41\,X_2 + 33.62\,X_3\\
&\qquad\qquad (\pm2) \qquad\quad (\pm2) \qquad\quad (\pm2)\\
&\qquad - 11.55\,X_1{*}X_2 + 22.7\,X_1{*}X_3 \qquad\qquad (9)\\
&\qquad\quad (\pm3) \qquad\qquad (\pm3)\\
&\qquad + 10.02\,X_1^2\\
&\qquad\quad (\pm2)
\end{aligned}$$

The quantities between brackets below the coefficients represent standard deviations (tables IV and V); for example:

- %Y:

$$S_{bj} = \sqrt{2.46} = 1.57 \approx 2$$

$$S_{bjj'} = \sqrt{3.69} = 1.92 \approx 2$$

$$S_{bjj} = \sqrt{1.23} = 1.11 \approx 1$$

- Ce:

$$S_{bj} = \sqrt{5.98.10^{-2}} = 0.245 \approx 2.10^{-1}$$

$$S_{bjj'} = \sqrt{8.97.10^{-2}} = 0.299 \approx 3.10^{-1}$$

$$S_{bjj} = \sqrt{2.99.10^{-2}} = 0.173 \approx 2.10^{-1}$$

The analysis of variance (ANOVA) was presented in the tables VI and VII for two models (8 and 9). A ‘P’ value lower than 0.0001 indicates that the model was considered to be statistically significant. The P values for all of the regressions were lower than 0.0001. This means that at least one of the terms in the regression equation had a significant correlation with the response variable.

The estimated variances of coefficients s_{bu}^2 given in tables (IV and V) were therefore calculated by the following equation:

$$s_{bu}^2 = \frac{S_r^2}{\sum_i X_{iu}^2} \qquad (9)$$

The significance of the effects can be estimated by comparing the values of the ratio b_u^2/s_{bu}^2 (Snedecor factor) to a critical value. $F_{0.95}$ (1. 16) = 4.49 [36], of the F distribution, at a 95% level of confidence with ν_1 =1 and ν_2 =16 degrees of freedom. The experimental Snedecor factor and the level of significance for all the linear, quadratic and interaction effects of the parameters were given in Tables IV and V for two responses, respectively.

Table VI : Regression variance analysis for color removal efficiency (%Y)

Source	Degree of freedom	Sum of squares	Mean square	F_{exp}^a	P	S^b
Model	14	22328.821	1594.92	27.0230	<0.0001*	c
Residual	16	944.332	59.02			-
Total	30	23273.153				-

a. F_{exp}: Snedecor factor; b. Significance test;
c. Significant at a level of 0.1% ($F_{0.001}$(14.16) =5.41) [36].

Table VII : *Regression variance analysis for energyconsumption (Ce)*

Source	Degree of freedom	Sum of squares	Mean square	F_{exp}^a	P	S^b
Model	14	1107.4618	79.1044	55.0874	<0.0001*	c
Residual	16	22.9757	1.4360			-
Total	30	1130.4375				-

a. F_{exp}: Snedecor factor; b. Significance test;
c. Significant at a level of 0.1% ($F_{0.001}$(14.16) =5.41) [36].

The pareto diagram presented the classification of the orthogonal estimation of the coefficients, from the highly significant coefficient to the insignificant coefficient (figures 4 and 5). Figure 4 made up that the electrolysis time (t) and electrolysis current (i) were larger significant on the color removal efficiency than the quadratic effect of electrolysis time, the interaction (i - t), the quadratic effect of electrolysis current and finally and the interaction ([NaCl]–t).

Figure 5 made up that the electrolysis current and electrolysis time were larger significant on the energy consumption than the interaction (i-t), the chloride concentration, the quadratic effect of electrolysis current and the interaction ([NaCl]–i).

The main effects plot of each parameter on the color removal efficiency and energy consumption (prediction profilers) were given in figure 6.

Term	Orthogonal estimation
t	16.41275
i	12.67104
t*t	-10.45183
i*t	-8.18731
i*i	-7.72066
NaCl*t	5.95481
NaCl	-3.56426
i*NaCl	1.65416
NaCl*NaCl	1.38513
pH	-0.91801
NaCl*pH	-0.63670
t*pH	-0.44363
pH*pH	0.35673
i*pH	0.28108

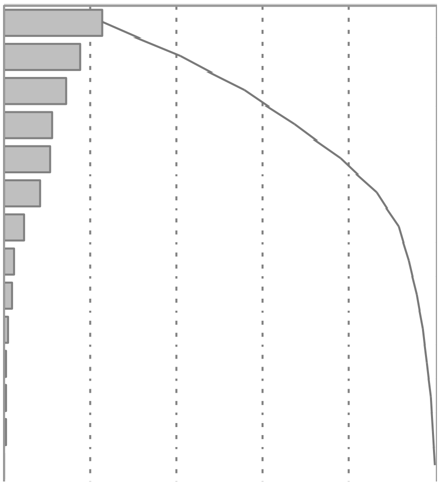


Fig. 4 : *The Pareto diagram of color removal efficiency %Y*

Term	Orthogonal estimation
i	4.601786
t	2.957872
i*t	1.630816
NaCl	-1.003800
i*i	0.960371
i*NaCl	-0.829776
NaCl*NaCl	-0.425934
NaCl*t	-0.377171
t*t	0.280348
pH*pH	0.240739
pH	-0.173044
NaCl*pH	0.140990
i*pH	0.105069
t*pH	0.004490

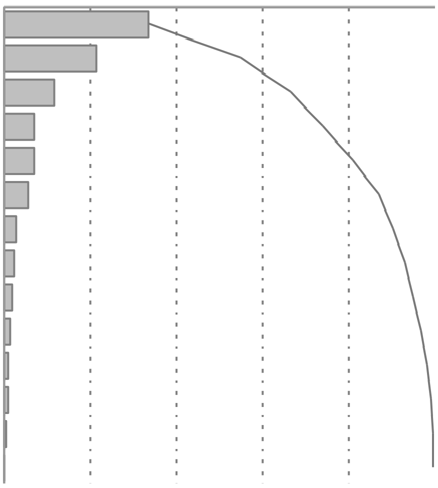


Fig. 5 : *The Pareto diagram of energy consumption Ce*

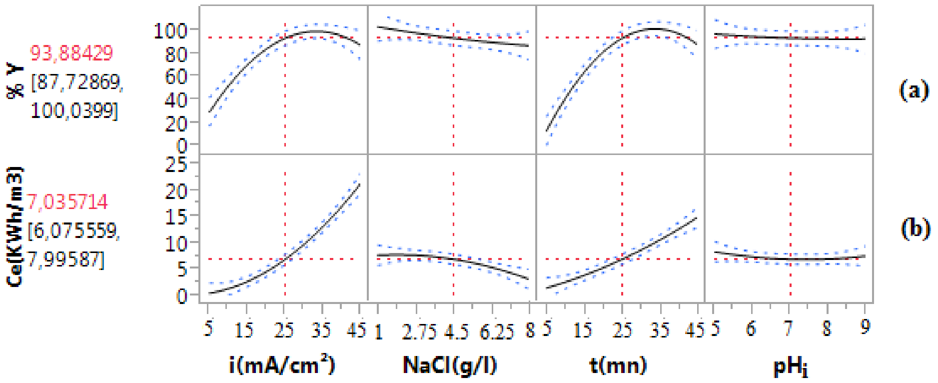


Fig. 6 : *Main effects plot of parameters on*
(a): The color removal efficiency;(b): Energy consumption.

Figure 6a illustrated that the high color removal efficiency was reached at high electrolysis current (i =30 mA/cm^2) and at long electrolysis time (t = 30mn). However, the initial pH of the solution did not have significant effect on the color removal efficiency. The same result was obtained by Alboyeh and Amani-Ghadim[24.27]using an iron anode. The color removal mechanism was probably explained by the formation of solid iron hydroxides which will react by adsorption with organic matter present in solution.

Presence of Cl$^-$ ions caused an increase of solution conductivity. But Cl$^-$ ions can react by complexation with iron ions instate of iron hydroxide leading to a slight decrease in the color removal efficiency.

Figure 6b showed that the energy consumption increased with the electrolysis current and the electrolysis time and decreased when the chloride concentration increased. The latter contributed to enhance solution conductivity.

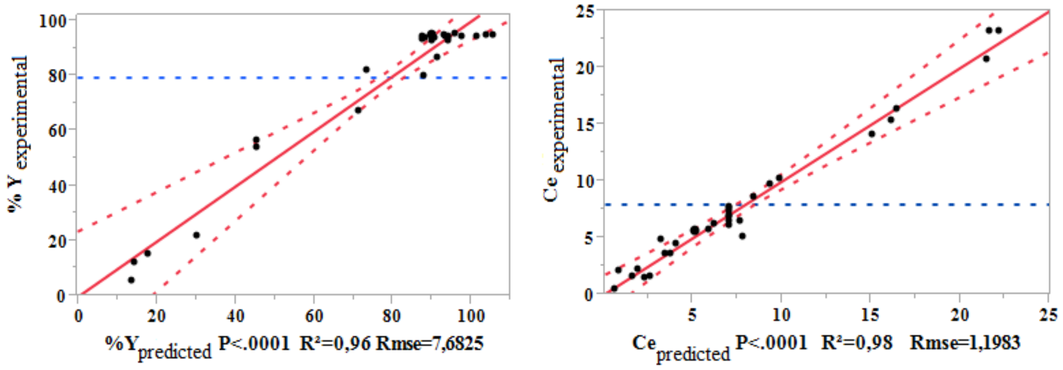
3.1. Validation of the model

For the central composite design, validation of the model was tested by an appropriate analysis of variance (ANOVA). The model was considered adequate if the variance due to regression was significantly different from the total variance. The regression models have high values of correlation coefficient for color removal efficiency and the energy consumption, respectively R^2 = 0.959 and 0.979 (figure 7). These results showed a good correlation between experimental and predicted values for each response. These R^2 values were desirable,because it had been suggested that for a good fit of the model. R^2 should be at least 80% [32]. Therefore, 96% of the variations of the color removal efficiency were explained by the independent variables.

3.2. Optimization

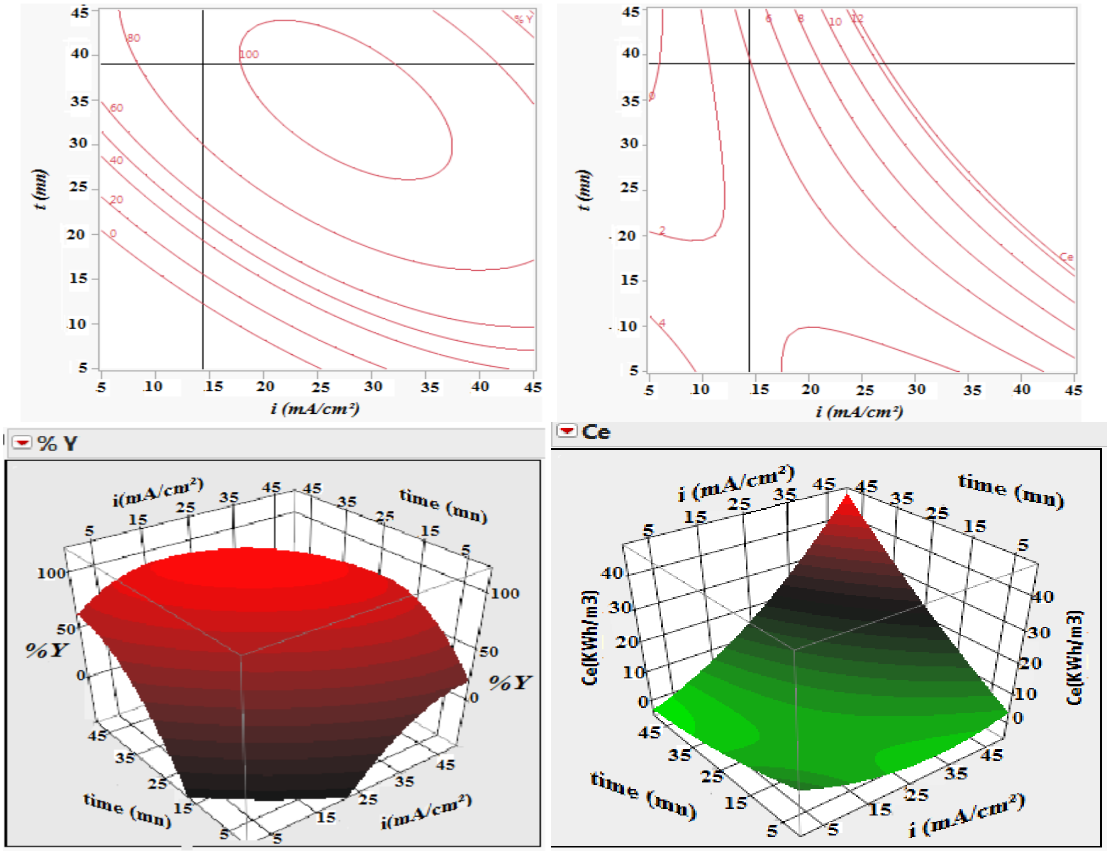
To determine the optimum conditions for the color removal efficiency and energy consumption, the models of %Y_{pred} and Ce_{pred} in the variation space (electrolysis time; electrolysis current) at pH = 7 and [NaCl] = 5.76 g/l were presented on figure 8 (a and b). According to figure 8a, it was observed that the color removal efficiency

% Y increased with electrolysis time (at fixed electrolysis current) and with electrolysis current (at fixed electrolysis time) or when the both parameters were increased at the same time. The 100% color removal efficiency was obtained at electrolysis current range of (20-37.5) mA/cm² and at electrolysis time range of (25-43) mn.



(a) $R^2 = 0.959$; $R^2_{adjusted} = 0.923$ **(b)** $R^2 = 0.979$; $R^2_{adjusted} = 0.961$

Fig. 7 : *Correlation between experimental and predicted values for (**a**) Color removal efficiency and (**b**)energy consumption.*



(a) **(b)**

Fig. 8 : *Response surface and contour plot of (**a**) color removal efficiency; (**b**)energy consumption (pH = 7 and [NaCl] = 5.76 g/l)*

For the energy consumption response (Ce), figure 8b underlined the lines of optimization of this response. The optimum range of energy consumption was (2-4) KWh/m^3 for electrolysis current range of (10-15) mA/cm² and electrolysis time range of (10-40) mn.

The optimum of high removal efficiency and low energy consumption was obtained by superposition of figures 8a and 8b. Result was illustrated on figure 9. The results were predictable because the released iron ions from the anode increased with increasing the electrolysis current and the electrolysis time. according to Faraday's law [37]. From figure 9, the optimal values of the process variables for maximum color removal efficiency and minimum energy consumption were shown in table VIII.

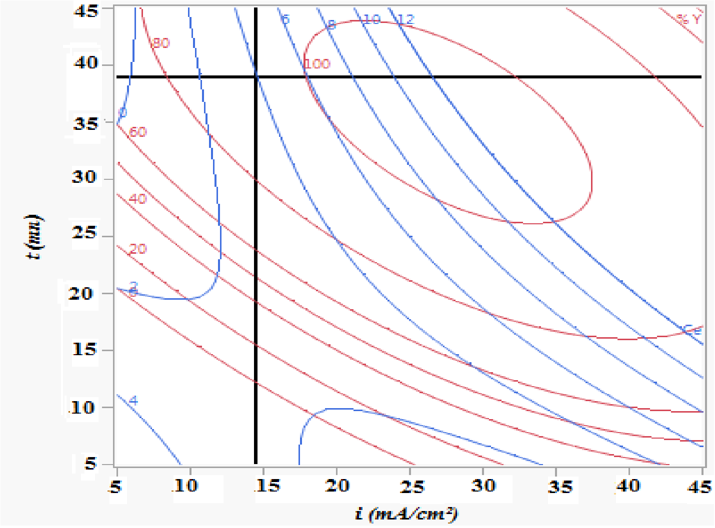


Fig. 9 : *Response surface and contour Plot of color removal efficiency (%Y) and energy consumption (Ce) according to the optimized parameters; pH = 7. [NaCl] = 5.76 g/l.*

Table VIII : Optimal parameters determined by RSM model

Parameter	**Optimised value**
i (mA/cm^2)	14.4
[NaCl] (g/l)	5.76
t (mn)	39
pH	7

Under these conditions, the estimated values of color removal efficiency and energy consumption by electrocoagulation treatment of the synthetic dye waste were respectively 94.52% and 3.90 KWh/m^3.

The theoretical optimized parameters were experimentally tested. The color removal efficiency of 94% was obtained with an energy consumption of 3.44KWh/m^3 (Table IX).

Table IX : Predicted and experimental values of color removal efficiency and energy consumption for synthetic dye waste electrocoagulation treatment

	Predicted results	**Experimental results**
Color removal efficiency %	94.52	94.06
Energy consumption(KWh/m^3)	3.90	3.44

At least, it was proved that experimental and predicted parameter values, for synthetic dye waste treatment by electrocoagulation using iron anode, were similar.

Conclusion

The performance of the electrocoagulation using iron anode for the removal dye Ponceau 4R from an aqueous solution was modeled and optimized using the response surface methodology.

The effects of four main operating parameters, as electrolysis current, electrolysis time; pH and chloride concentration were evaluated by the response surface and plot contour.

Therefore; the correlation coefficient (R^2=0.959) is important between the experimental and predicted color removal efficiency. Optimal conditions proposed by the RSM, for maximum color removal efficiency of 94.52% with energy consumption of 3.9 KWh/m^3 are: i = 14.4 mA/cm^2, [NaCl] =5.76 g/l, pH = 7 and t = 39 mn.

The experimental and predicted parameter values, for synthetic dye waste treatment by electrocoagulation using iron anode, were similar.

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