Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21322

87 (2017) 326–337
August

Optimization of semi-continuous process treatment by electrocoagulation-flocculation-filtration for removal of Novacron Blue 4R (NB4R) dye using response surface methodology

Nizar Barrak[a,b*], Sami Achour[a], Rabeb Mannai[a], Manel Zaidi[a], Moez Kechida[c], Ahmed Noureddine Helal[a]

[a]*Laboratory "Bioressources: Integrative Biology & Valuation "BIOLIVAL", Higher Institute of Biotechnology of Monastir, University of Monastir, Monastir, Tunisia, email: barrak.nizar@gmail.com (N. Barrak), samnaw2001@yahoo.fr (S. Achour), mannai.rabeb@yahoo.fr (R. Mannai), zaidimanel2407@gmail.com (M. Zaidi), ahelal584@gmail.com (A.N. Helal)*
[b]*Faculty of Sciences of Bizerte, University of Carthage, Tunisia*
[c]*Textile Industrial Company (SITEX), 5070 Ksar Hellal, Tunisia, email: kechida.moez@sitex.com.tn (M. Kechida)*

Received 7 February 2017; Accepted 9 August 2017

ABSTRACT

Novacron Blue 4R (NB4R) dye was removed in a semi-continuous process treatment by electrocoagulation-flocculation-filtration. Our results showed that the quadratic second order equation provided the best correlation for the decolorization of NB4R dye (CR%). On the other hand, the regression equation proved the large interaction between the current intensity and the initial concentration of the dye. Experiments were conducted to find the desired conditions for removal of the dye and lower Operation Cost. The results showed that CR% = 90.84% (R^2 = 95.8%) of color removal for initial dye concentration of 30 mg/L, using a current intensity of 1 A and a flow rate of flocculent (FRF) injected of 9.14 mL/min. Under these conditions, electrical energy consumption (EEC: kWh/m^3), electrode consumption (EMC: kg/m^3), chemical consumption (CC: kg/m^3) and operation cost (OC: US$/$m^3$) were respectively 0.073851 KWh/m^3; 0.0184 kg/m^3; 0.015 kg/m^3 and 0.08474 US$/$m^3$.

Keywords: Dye Novacron Blue (NB4R); Electrocoagulation-flocculation-filtration; Operation cost; Optimization; Response surface methodology

1. Introduction

Anthraquinone is considered one of the major groups among reactive dyes. It has a carbonyl chromophore group (>C–O) on a quinone nucleus. The general formula derived from anthracene shows that the chromophore is a quinone ring on which hydroxyl or amino groups can be attached. The color of this group of dye is related to the anthraquinone nucleus and modified by the type, number and position of substituents [1].

A large amount (10–50%) [2] of reactive dyes are released into the environment because they are very soluble by design and therefore are not all used up by textile fibers during the dyeing process [3]. The presence of the aromatic ring in chemical structures of the reactive dyes, as Novacron Blue 4R (NB4R), favors a high stability against light, oxidants, and biological degradation [4]. Despite, the degradation of reactive dyes in anaerobic condition is applied successfully. It is not proper to use this biological method treatment of textile wastewater because the breakdown of reactive dyes leads to the formation of aromatic amines, which may be more toxic than the dye molecules as such [5]. So, their presence in the environment can cause several health problems. Effectively, the acute exposure to this color can cause respiratory diseases and allergic dermatoses [6–10], change in immunoglobulin levels [11], increased risks of colon and rectum cancers [12], high risk of contracting bladder cancer [13], genotoxicity [14], and bears teratogenic potential [15].

Various methods were applied for elimination a reactive textile dyes, such as biological methods [16,17] oxidation

*Corresponding author.

[18–20] flocculation [21], membrane filtration [22], adsorption [23], photo-catalysis [24] and sonolysis [25,26]. Nevertheless, the diversification and the usefulness of these methods were limited because of low efficiency and high operating cost. So, we need to develop more efficient and inexpensive methods which require minimum chemical and energy consumptions.

For the treatment of organic pollution in waste water, several electrochemical techniques have been developed, such as electro-oxidation, electrochemical reduction, electrocoagulation, electro-flotation [27]. These techniques show higher efficiency than any other biological, physical and chemical process [28,29]. Some authors proposed as an effective method for the treatment textile wastewater, by electrocoagulation [30,31]. This technique of treatment has significant advantages such as simple equipment and operation, easy automation, rapid sedimentation rates and reduction in the amount of sludge produced [32]; also, it requires less coagulant ions for the treatment of wastewater [33].

Because of their availability and relatively low cost, aluminum and iron are the most anode materials used in the electrocoagulation process [34,35]. When applying a direct electric current to these electrodes, metal ions can be generated. The hydrogen production in cathode and electrolytic oxidation of anode leads to the generation *in situ* of coagulants followed by hydroxyl ions (Fig. 1) [36,37].

The main reactions at the electrodes of aluminum are:

At anodes: $Al_{(s)} \rightarrow Al^{(+3)}\,(aq) + 3e^-$ (1)

At the cathode: $3H_2O + 3e^- \rightarrow 3/2\, H_{2(g)} + 3OH^-$ (2)

Ions generated by electrode reactions (1) and (2) react to form various monomeric species ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^+$, $Al(OH)_4$), and polymeric species ($Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$). Finally, they are transformed into $Al(OH)_3(s)$. Therefore, these complexes (polymeric hydroxide) which are a highly charged cations, destabilize the negatively charged of dyes allowing the formation of flocs. This amorphous metal hydroxide precipitates was developed when the amount of aluminum (or iron) in the solution exceeds the solubility of the metal hydroxide, hich causes *sweep-floc* coagulation [38].

The removed dye, by electrocoagulation, is accomplished in a three step processes as follows (Fig. 2) [40,41].

i. Electrolytic reactions at surface of electrodes.
ii. Formation of coagulants in aqueous phase.
iii. Adsorption of soluble dyes on coagulants.

The technique of treatment of dye by electrocoagulation has some disadvantages mainly: dissolved sacrificial electrodes and expense of electricity [32]. For this reason, it is necessary to develop a combined or hybrid system able to remove effectively the pollutants from textile wastewater and reduce the cost of energy consumption.

Some authors assumed that, when injected the flocculent during electrocoagulation, it enhances the formation of larger flocs of dyes. These larger flocs settle more rapidly and are easily removed, so it can reduce the time requisite for treatment. Therefore, it reduces the amount of energy consumption and the expended dissolved material of the electrodes [43–45].

For modeling complex systems, it is necessary to analyze problems in which a response of interest is influenced by a set of independent variables and their simultaneous

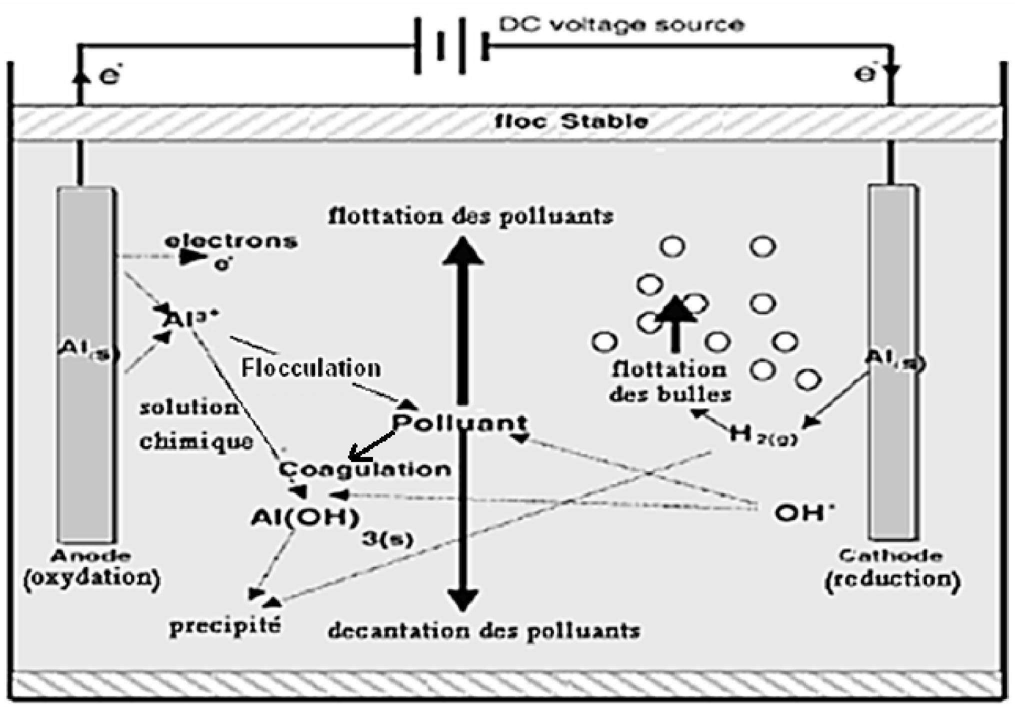


Fig. 1. Diagram of the electrocoagulation process with aluminum plates [39].

effects. Response surface methodology (RSM) is generally used to optimize conditions for desirable responses [46–49].

One of main advantages of RSM, compared with conventional methods,is the reduction of experimental trials by providing sufficient information for statistically validated results and the evaluation of the relative significance of parameters and their interactions [47,50]. Also, RSM gives a mathematical model that can be used to predict the response of the process for any new condition. The Adequacy of the proposed model is revealed using the diagnostic checking tests provided by analysis of variance (ANOVA) [51,52]. For these reasons, in several industrial processes, RSM is almost used to evaluate results and efficiency of the operations.

The aim of the present study is to optimize dye removal of Novacron Blue 4R (NB4R) from aqueous solution, at least cost, by electrocoagulation-flocculation-filtration process using RSM. For this purpose, Box Behnken design was used to develop a mathematical correlation between dye removal efficiency and three selected independent parameters including current intensity, initial dye concentration and flow rate of flocculent (FRF) injected. During this study the role of different influential operational parameters on dye removal was investigated at several levels.

Eventually, this research will assess the suitability of electrocoagulation for industrial applications on the treatment of textile wastewater.

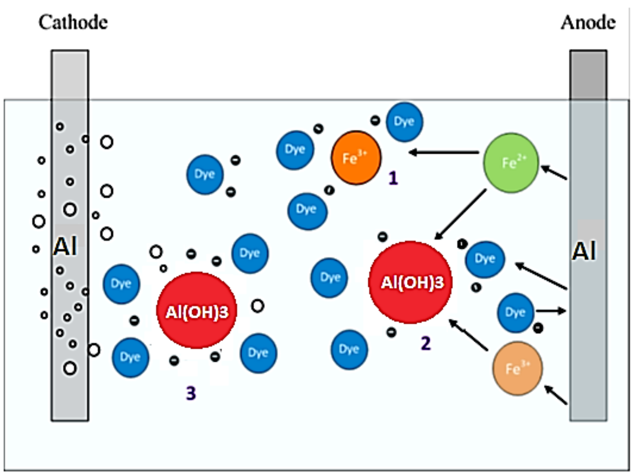


Fig. 2. Schematics of dye removal mechanism of electrocoagulation process with iron electrode (1. Precipitation; 2. Adsorption; 3. Flotation) [42].

2. Materials and methods

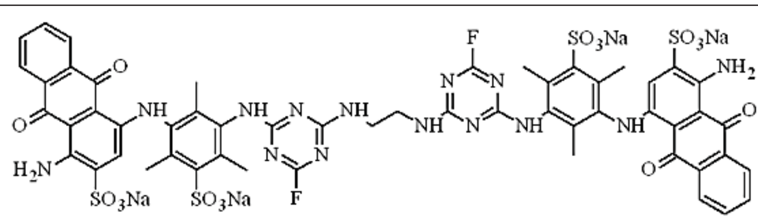
2.1. Chemical structure of color

The commercially available Reactive dye: Novacron Blue 4R (NB4R) was obtained from Textile Industrial Company (SITEX), 5070 Ksar Hellal, Tunisia, with a molecular structure and characteristic as summarized in Table 1.

2.2. Reactor design

The units used in the electrocoagulation treatment are composed of: (1) electrochemical reactor, consisting of acrylic column with a height of 60 cm and a diameter of 19.54 cm with a total volume of 16.71 L. This reactor is provided with two aluminum electrodes of rectangular shape (335 mm × 130 mm × 1 mm), used as anode and cathode, which corresponds to S = 435.5 cm^2 of each electrode surface. The distance between the two electrodes was e = 5 mm, which is a typical value in EC cells. The electrodes were placed at the bottom in the middle of the column; (2) DC power supply (Laboratory DC. Power supply Model M10-SP600 SL); (3) a peristaltic pump (Ismatec ISM404B MCP Peristaltic Pump Head Cole Parmer 78002-00- ISO 9001 certified) for injection the flocculent solution to electrochemical reactor; (4) receptacle, fill with anionic polyacrylamide (an industrial grade organic polymer prepared in the laboratory by dissolving 0.5 g per 1 liter of distilled water); (**5**) centrifugal pump to transfer the dye solution treatment by EC to colon filtration; (6) column filtration for phase separation (filled with a silica powder whose the average of particle size is

Table 1
Characteristics of reactive dye: Novacron Blue 4R (NB4R)

Chemical structure	 Tetrasodium 1,2-bis(4 fluoro-6-[5-(1- amino- 2- sulfonatoanthraquinone- 4- ylamino) -2, 4, 6- trimethyl - 3 - sulfonatophenylamino]-1, 3, 5- triazin -2- ylamino) ethane))
IUPAC name	
λ_{max}	595 nm
Purity (%)	70–80
MW (g/mol^1)	1401.202

equal to 23 μm); (7) Magnetic stirrer was used for preparing complete mixed solutions in the EC reactor (Fig. 3).

2.2. Experimental procedure

Dye solutions were prepared by dissolving proper amounts of NB4R (30–127.33 mg/L) in distilled water. The experiments were carried out in a semi-continuous mode with a liquid volume of 13.71 L. In each run, 30 ml of the water treatment was taken from the column of filtration. The filtrate obtained was collected for the analysis of water properties and the electrodes were well polished by sandpaper before each test. All experiments were repeated twice, and the experimental error was 3%.

The conductivity of solutions was adjusted by the addition of NaCl (3.5 g/L). The initial pH of the solution was adjusted before the experiment by Sulfuric Acid (H_2SO_4) and Sodium Hydroxide (NaOH) at 8, and pH values were measured using pH meter (370 pH meter Jenway). During each run, the reactor unit was stirred at 20 rpm by a magnetic stirrer for 45 min.

2.2.1. Absorbance characteristics

The dye concentrations were determined from their absorbance characteristics in the UV–VIS range (200–800 nm) with the calibration method. HACH Lange DR 3900 spectrophotometer was used. For these measurements, the maximum absorption (λ_{max} = 595 nm) wavelength of dye was determined by measuring their absorbance. The calculation of color removal efficiency (CR%) after Electrocoagulation-Flocculation-Filtration treatment was performed using this formula Eq. (3) [42].

$$CR\% = \frac{\mathrm{Abs}_{595}(t_0) - \mathrm{Abs}_{595}(t_{45})}{\mathrm{Abs}_{595}(t_0)} \tag{3}$$

where Abs_{595}: measuring the absorbance at 595 nm at initial instant = 0 min, Abs_{595}: measuring the absorbance at 595 nm after a 45 min = 45 min.

2.2.2. Current density

Current density is very important parameter in electrocoagulation as it determines the coagulant dosage rate, bubble production rate, size and growth of the flocks, which can affect the efficiency of the electrocoagulation [37]. The current density (CD) was calculated through the equation as follows Eq. (4).

$$CD = \frac{I}{2 \cdot S_{electrode}} \tag{4}$$

where CD is the current density (A/m^2), I is the current intensity (A) and S is surface area of each electrode (m^2) [53].

In this study, the effects of current density on the removal efficiencies were studied by varying the range from 11.38 to 34.40 A/m^2.

2.2.3. Energy consumption

Electrical energy consumption and current efficiency are very important economical parameters in electrocoagulation process and calculated using the commonly used Eq. (5) [54].

$$E = U \cdot I \cdot t_{EC} \tag{5}$$

where E is the electrical energy in kWh, U the cell voltage in (V), I the current in ampere (A) and t_{EC} is the time of electrocoagulation process h.

The electrical energy consumption (EEC: kWh/m^3) has been calculated with Eq. (6) [55,56].

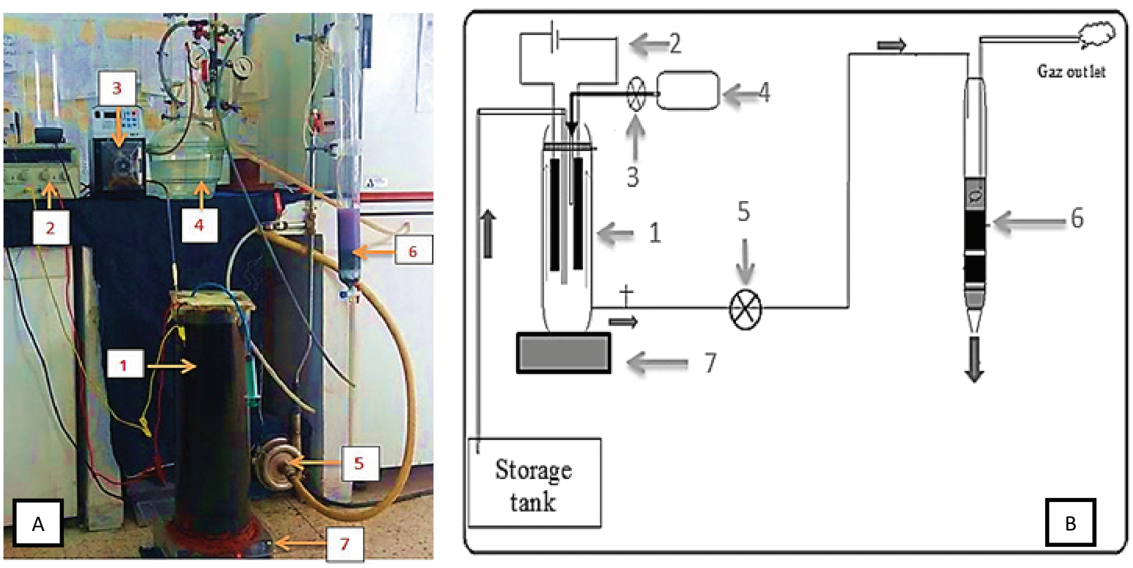


Fig. 3. (A): Experimental setup for the electrocoagulation; (B): Schematic diagram of electrocoagulation reactor process: [(1) Electrolytic cell. (2) DC power supply; (3) Peristaltic pump; (4) Tank of flocculents solution; (5) Centrifugal pump; (6) column for filtration; (7) Magnetic stirrer)].

$$EEC = \frac{(U \cdot I \cdot t)}{(V)} \quad (6)$$

The electrodes consumption (EMC: kg/m^3) have been calculated with Eq. (7) [42,57].

$$EMC = \frac{(t \cdot I \cdot M)}{n \cdot F \cdot V} \quad (7)$$

where V is the volume of the treated water (m^3), n is the number of electrons in oxidation/reduction reaction (n =3), F is the Faraday constant (F = 96.487°C/mol) and M is the molecular weight of the aluminum (g/mol).

2.2.4. Operation cost

The one of the most important parameters in EC processes is operating cost for the reason that the operating cost affects the application of any method of wastewater treatment. The operating cost includes material (mainly electrodes) cost, electrical energy cost, labor, maintenance and other costs [56]. In this study, the operating cost was calculated together with electrodes, electrical energy and chemical costs. So, energy, electrodes and chemical consumption costs were taken into account as major cost items [58–60].

Calculation of operating cost is expressed as.

$$\text{Operating cost} = a \cdot EEC + b \cdot EMC + c \cdot CC \quad (8)$$

where EEC is electrical energy consumption (kWh/m^3); EMC is the electrodes consumption (kg/m^3); CC: chemical consumption (kg/m^3).

EEC, EMC and CC are consumed quantities per m^3 of treated wastewater. *a*, *b* and *c* are successively the given values for the Tunisian market costs (2016) of electrical energy (0.03 $/kWh), aluminum electrode (1.6 $/kg) and chemical flocculent (3.58 $/kg).

2.3. Experimental design

The Box-Behnken design (BBD), used extensively in response surface methodology (RSM) experimental design, was employed to evaluate the individual and interactive effects of three main controllable variables on the dye removal efficiency (output response), such as initial concentration of dye. Furthermore, current intensity and flow rate of flocculent solution injected have been introduced as RSM input variables, which their experimental ranges in coded and actual values are presented in Table 2.

2.3.1. Statistical analysis

The statistical analyses were performed by the use of multiple regressions and ANOVA with the software Minitab v 14.0. The significance of each variable was determined by applying P-value. The P-value related to the F-value could be used to show whether the F-value is large enough or not. In other words, P-values lower than 0.05 (at the significance level of 95%) confirms that the regression model is statistically very significant [61].

Table 2
Experimental range and levels of independent process variables

Independent variables	Code levels		
	–1	0	+1
Initial concentration of dye (mg/L) or (absorbance (a.u) at 595 nm)	30 or 1	78.83 or 2.5	127.33 or 4
Flow rate of flocculent (mL/min)	3	6	9
Courant intensity (A) or Current density (A/m^2)	1 11.48	2 22.96	3 34.44

The general form of the regression equation including single terms, square terms and interaction terms is presented in Eq. (9).

$$Y = b_0 + \underbrace{\sum\nolimits_{(i=1)}^{k} b_i X_i}_{singleterms} + \underbrace{\sum\nolimits_{(i=1)}^{k} b_i i X_i^2}_{squareterms} + \sum\nolimits_{i}^{i<j} \underbrace{\sum\nolimits_{j} b_{ij} X_i X_j}_{interactionterms} \quad (9)$$

where Y is the response variable, b represents the coefficients of the model, and X represents the factor variables. The quality of regression equation can be evaluated using analysis of variance (ANOVA). R^2 is the amount of variance explained by the model. Detailed descriptions of model quality terms are given elsewhere [62].

3. Results and discussion

The factors considered in this study are dye concentration (mg/L), current intensity (A) (or CD: current density (A/m^2)) and flow rate of chemical flocculent solution injected (mL/min) whereas the experimental result or the response to treat is the removed dye (CR%).

To minimize the operation cost (OC), we used the response surface methodology (RSM) with the experimental design Box-Behnken, and determined the optimal experimental conditions for maximum color removal, minimum energy, electrode consumption and volume of chemical flocculent added.

3.1. Response regression equation

The factors considered in this study are current intensity (I(A)) [1–3], initial dye concentration (mg/L) [30, 78.83, 127.33] and FRF (mL/min) [3,6,9], whereas the experimental result of the response is the percentage of color removal (CR%). Multiple regression coefficients of a second-order polynomial model describe the responses. The regression model equation was as follows:

$$\begin{aligned} CR\% &= 109.245 - 22.535(I) + 2.937(FRF) - 28.901(Abs) \\ &+4.262(I^2) - 0.115(FRF^2) + 3.433(Abs^2) + 0.582(I * FRF) \\ &+0.903(I * Abs) + 0.252(FRF * Abs) \end{aligned} \quad (10)$$

where $CR\%$: percentage of color removal (%); I: current intensity (A); Abs: absorbance (a.u) at 595 nm; FRF: flow rate of chemical flocculent (mL/min); *R*2: regression coefficient.

The variance analysis ANOVA and of the regression equation of the removed dye (*CR*%), gave us the squared multiple correlation coefficient R^2 equal to 95.8% with high accuracy >0.9. We can assume that the model may be predictable and can give a good correlation between parameters and response. Furthermore, we can deduce from the equation that the coefficients of current intensity (22.535) and absorbance value (28.901) are the most important terms affecting the response value of color removed (CR%).

Our results are similar to that of Barrak et al. [63]. For the optimization and modeling of the electrocoagulation process to remove of Indigo dye, they used response surface methodology with aluminum anode. The authors reported that the significance of the second-order regression model was determined by R^2 (88.3%).

3.2. Variance analysis (ANOVA)

The statistical significance of mean square variation ratio, due to regression, mean square residual error and the significance and adequacy of the model was tested using analysis of variance (ANOVA). The obtained results of the statistical analysis are given in Table 3.

The sum of squares (SS) related to residual error is very less as compared to the total sum of squares for the model incorporating CR% (106.02 < 2505.86). An analysis of variance shows high *F*-values (12.58) for the response color removed. According to the ANOVA analysis, the regression adjusted average squares and the linear regression adjusted average squares were 12.58 and 7.40, respectively for CR%. On the other side, *P*-value is less than 0.05 (α = 0.05 or 95% confidence) for regression and linear coefficients. These parameters show that the quadratic RSM models can navigate the design space well and the model accuracies are adequate to predict the performance of EC process.

3.3. Contour plot

The effects of initial dye concentration and current intensity, while keeping flow rate of flocculent (FRF) in the middle levels (6.1 mL/min), are shown in Fig. 4. According to this figure, when the initial dye concentration increased, a decrease in the removal efficiencies of color was observed (CR%). It was also observed that, when the absorbance decreased from 127.33 to 30 mg/L and the current intensity increased from 1 to 3 A, the color removal efficiencies increased from 55 to 85%. This is due to the fact that, when current intensity increases, the amount of oxidized aluminum increases and consequently hydroxide flocs, with high adsorption rate, increase and this leads to improve the efficiency of color removal [64,65]. On the other hand, when current intensity increases, the density of bubbles augments while their size decreases. Therefore, size and growth rate of produced flocs increase and this in turn, affects the efficiency of the decolorization of dye [66,67]. Therefore, with increasing of dye concentration, amount of produced flocs is insufficient to absorb all dye molecules, so the color removal decreased [68].

The response surface plots can be employed to study the surfaces and locate the optimum [51,52]. We obtained the maximum dye removal efficiency of 82% which was observed for current intensity of 3 A after 45 min of operation from the dye solutions of 30 mg/L.

Ghosh et al. investigated the electrocoagulation to remove crystal violet (CI42555) from its aqueous solution. The effects of various operational parameters on dye removal efficiency were studied. The results showed that the removal efficiency enhanced when the current density increased and CR% decreased when the initial dye concentrations were more than 100 mg/L and conductivity of dye solutions more than 16.13×10^{-1} S/m [69].

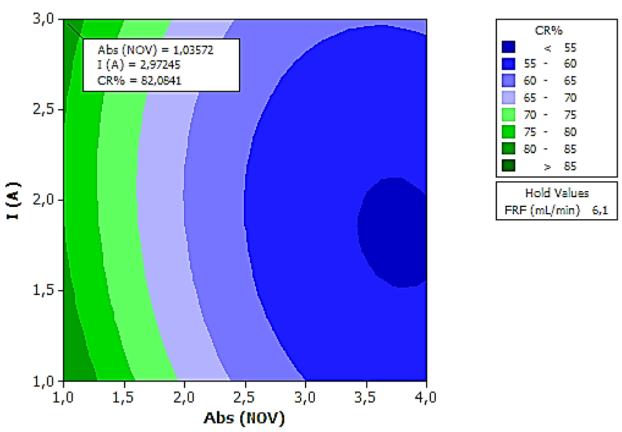


Fig. 4. Contour plots of predicted NB4R removal efficiency as a function of the initial dye concentration and current intensity (I:A) (keeping flow rate at central point levels at 6.1 mL/min).

Table 3
Analysis of variance (ANOVA) of the model of the color removed (CR%)

Source		Regression	Linear	Square	Interaction	Residual error	Total
CR%	DF	9	3	3	3	5	14
	SS	2399.84	2090.56	284.08	25.19	106.02	2505.86
	MS	266.649	156.859	94.695	8.398	21.205	
	F	12.58	7.40	4.47	0.40		
	P	0.006	0.028	0.070	0.762		

3.4. Analysis of the main effects plot

A main effect occurs when the levels of different factors affect the response differently. The main effect graph represents the responses of each factor level connected by a line. When the line is horizontal (parallel to the X-axis), therefore no main effect is present. In the other situation, when the line is not horizontal, it indicates the existence of a principal effect [70].

Diagrams in Fig. 5 show the behavior of the response of color removal (CR%) through the different variations of factors such as current intensity, dye concentration and flow rate of flocculent.

An increase in the levels of initial dye concentration (30–78.83 mg/L) results in a decrease in the dye removal (CR%) from 80 to 60%, then when the initial dye concentration increase from 78.83 to 127.33 mg/L, we obtained a slight variation of responses (CR%). One of the reasons which can explain this phenomenon is that, when the amount of dye in the solution is higher than 78.83 mg/L, the intermediate products formed in the solution increase the resistance by blocking the electrode active sites, and thus, decrease the metallic hydroxide flocs in the solution. On the other hand, at higher concentration of dye, the amount of metallic hydroxide $(Al(OH)_n$ is not enough to remove all the dye. Therefore, lower dye concentrations increase the response of color removal.

According to Fig. 5, the effect of current intensity on the response (CR%) proves that the increase in current from 2 to 3 A, increases the color removal from 63 to 68%. This is due to the fact that ionic species production on the anode increases, therefore, which enhances flocs production in the solution [64,65].

Similar results were reported by Singh et al. in their study of treatment brilliant green dye by electrocoagulation. They report that the important parameters, affecting the removal efficiency of Brilliant Green dye by electrocoagulation, include current intensity, time and initial dye concentration. Initial dye concentration is the most significant one [71]. As well, Alinsafi et al. Reported that current is a critical operational factor in electrocoagulation process due to its effect on coagulant rate, bubble production rate, size and growth of the flocs [72,73].

According to Fig. 5, the amount of flocculents injected during electrocoagulation treatment of dye, has a positive relationship with the percentage of dye removal. When the flow rat injected from 3.05 to 9.14 mL/min, the percentage of dye removal increased from 25% to 75%. This is due to an increase of the quantity of flocculent which enhances floc stability. Furthermore, the strength of floc is dependent on the attractive forces between particles. Thus stronger bridges between flocs may be created by a higher amount of flocculent present in the solution [44].

The study realized by Nourouzi et al. about the removal of Reactive Black 5 dye by sequential electrocoagulation–flocculation method,shows that, the addition of flocculent, during treatment with electrocoagulation, was able to increase the percentage of dye removal. They also affirm that, the amount of flocculent has a positive relationship with the decolorization of dye. Effectively, the percentage of dye removal increased to an average of 25%, when the concentration of flocculent injected was increased from 0 to 16 mg/L [45]. This improvement may be due to the creation of larger flocs, according to the effect of the ability of the flocculent to treat fine colloidal particles. This larger flocs well be easily eliminated by settling [43,44].

3.5. Interactions plot

To compare the relative strength of the effects across factors, we need the interaction plots. For two factors assimilated, a single interaction plot is created. Interactions plots are plots of means for each level of a factor with the level of a second factor held constant. When the response at a factor level depends upon the levels of other factors, this means that an interaction is present. The higher the degree of interaction, the greater the departure of the lines from the parallel state [74].

According to Fig. 6, the interaction plot between current intensity and initial dye concentration on color removal (CR%) shows that there are a considerable interaction between the above mentioned two factors on the response as confirmed with response Eq. (10).

This strong interaction between the initial dye concentration and the current intensity can be explained according to the adsorption of dye molecules by metallic hydroxide

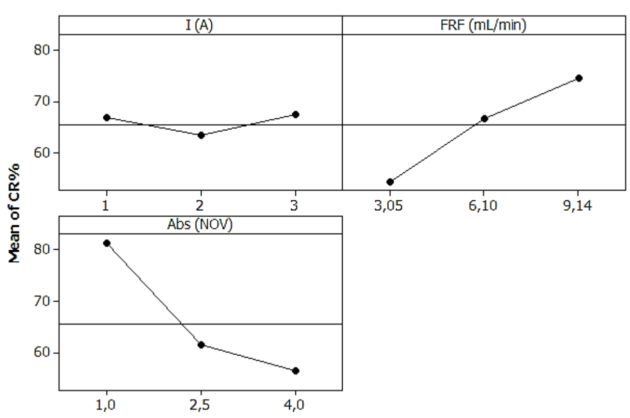


Fig. 5. Analysis of main effects plots of the response color removed (CR%).

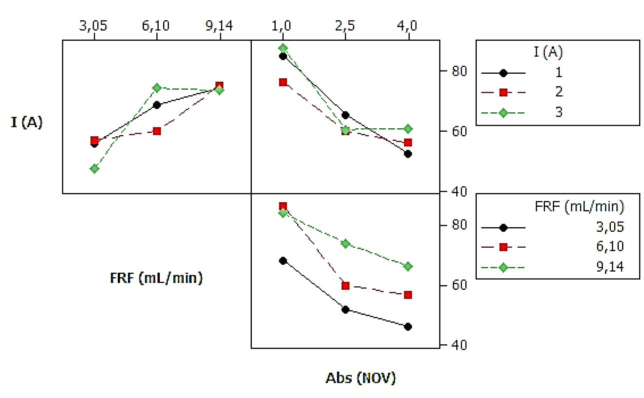


Fig. 6. Analysis of interaction plots of the color removed (CR%), [where dye values of absorbance (Abs (Nov) at 595 (a.u), flow rate of flocculent injected (mL/min) and current intensity (A)].

flocs. In fact, the production of polymeric cations by aluminum hydroxideis proportionally to the concentration of dyes present in the medium. Al^{3+} ions undergo water hydrolysis and the resulting aluminum hydroxides produce more sludge with a consequent removal of color [68,75–77].

Kuleyin and Balcioglu concluded that, after 10 min of treatment by EC of crystal violet, the color removed efficiency decreases from 90% to 55% when increases the initial dye concentration from 90 mg/L to 570 mg/L. On the other hand, when current density increases from 5.8 to 17.36 mA/cm², there was increase from 55 to 95% in color removal [78]. This relationship between factors of initial dye concentration and current intensity was consistent with our results.

3.6. Residual plots

Fig. 7 gives the residual plots for CR%. The four-in-one residual plot displays four different residual plots together in one graph window. This layout is useful for comparing the plots to determine whether the model meets the assumptions of the analysis.

In addition to the mentioned criteria for evaluating the adequacy of the developed models, the difference between experimental and predicted responses (residuals) could be utilized for investigating the adequacy of the model graphically. Residuals are considered as unexplained variations by model and they will occur based on a normal distribution if the model is a good predictor [79].

In Fig. 7.1, normal probability plots of residuals and residuals versus fit plots (Fig. 7.2) have been shown for the CR% processes describing models. If the residuals are normally distributed, (i) the points in normal plot of residuals (Fig. 7.1) should generally form a straight line and (ii) residuals versus fits plot should represent a random pattern of residuals on both sides of zero (0) (Fig. 7.2). According to these plots, the residuals for the model of CR% have been distributed randomly.

Besides, as illustrated in Fig. 7, the residual plots of the model CR% are distributed randomly without any specific patterns, indicating that the selected quadratic model is adequate and can be used to predict the response.

Amani-Ghadim et al. [80], reported that the residual plots for removal efficiency of C.I. Reactive Red 43 dye from aqueous solution by batch electrocoagulation using aluminum anodes, the normal probability plots of the residuals and residuals versus the fitted values were distributed randomly.

3.7. Optimized conditions

Many designed experiments involve determining optimal conditions that will produce the best value for the response [81]. Minitab.v.14.0. Software, for numerical optimization, has been used in order to find the specific point that maximizes the desirability function. The desired goal was selected by adjusting the weight or the importance parameters that might alter the characteristics of a goal [82,83].The goal fields for response have five options: none, maximum, minimum, target, and within range. In order to determine the optimum process parameters for the maximum color removal (CR%) and economic electrical energy consumption (EEC, kWh/m³), electrodes consumption (EMC, kg/m³) and chemical consumption (CC,

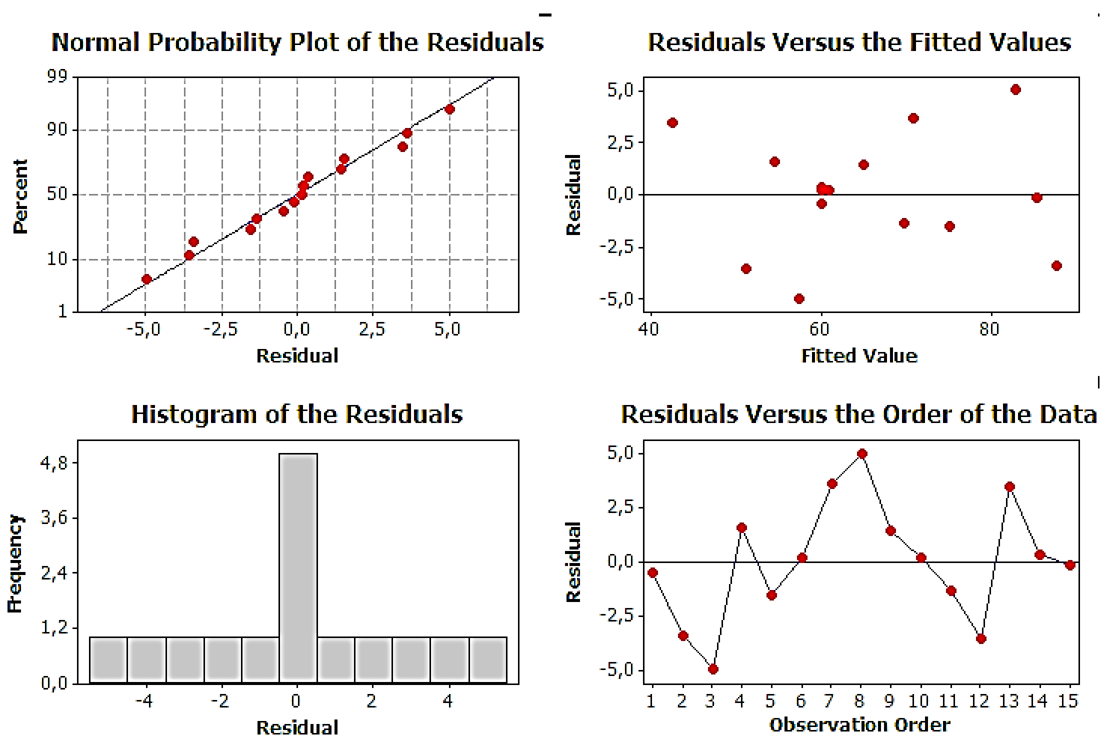


Fig. 7. Residual plots for response color removed CR%.

	Predicted response	Experimental values
Global solution	I = 1A	I = 1 A
	Abs (Nov) = 1 a.u; [Nov] = 30 mg/L	Abs (Nov) = 1 a.u; [Nov] = 30 mg/L
	Flow rat of chemical flocculent = 9.14 mL/min	Flow rat of chemical flocculent = 9.14 mL/min
Responses	CR% = 91%; desirability = 0.89335	CR% = 90.84 %
CR%	EEC = 0.0741 KWh/m^3; desirability = 1	EEC =0.07385 KWh/m^3
	EMC = 0.0183 Kg/m^3; desirability = 1	EMC = 0.0184 Kg/m^3
	Composite desirability = 0.941323	
Calculation of operation cost	*a* = 0.03 US$/Kwh	*a* = 0.03 US$/Kwh
OC = *a* EEC + *b* EMC + *c* CC	*b* = 1.6 US$/kg	*b* = 1.6 US$/kg
	c =3.54 $/kg	*c* = 3.54 $/kg
	EEC = 0.0741 KWh/m^3	EEC =0.073851.KWh/m^3
	EMC = 0.0183 Kg/m^3	EMC = 0.0184 Kg/m^3
	CC = 0.015 kg/m^3	CC = 0.015 kg/m^3
	OC = 0.08460 US$/m^3	OC = 0.08474 US$/m^3

kg/m^3), the desired function methodology optimization of Derringer and Suich was used in this present study [84].

A comparison for optimum conditions between predicted and experimental responses using Box-Behnken design is given below:

The optimization diagram (Fig. 8) illustrates the effect of each factor (columns) on responses or composite desirability (rows). The vertical red lines on the diagram represent the current factor parameters. The number at the top of a column indicates the current factor level parameters (red). The horizontal blue lines and numbers represent the responses to the current level factors [85].

The performance of all design and response variables are shown in Fig. 8, where the best optimization is approached by an overall desirability of 0.941325 at optimum operating conditions of reaction time at 45 min, current intensity at 1 A, initial color absorbance at 1 a.u (corresponding to 30 mg/L) and flow rate of chemical flocculent injected at 9.14 mL/min. In these conditions, the Minitab Software gives respectively, a decolorization value for Novacron (NB4R) dye of 91.27% and for operating cost OC = 0.08460 US$/m^3.

When these conditions were applied experimentally, we obtained respectively CR% = 90.84% and OC = 0.08474 US$/m^3. Thus, when the experimental conditions proposed by Minitab were applied to our experimentation, the values of the responses obtained are almost equal to the values obtained by calculating. Hence our model is globally validated but could be more improved.

Industrial conditions of SITEX (Textile Industrial Company) use in average 25 kg/d of Novacron Blue 4R (NB4R) dye. 10–50% of this quantity is rejected in water discharge, corresponding to a concentration of 3–15 mg/L. These concentrations compared to those used in this study (30–127.33 mg/L) are about 10 times lower. Therefore, we assumed that the cost treatment of SITEX wastewater, by this technique of electrocoagulation, would be reduced greatly.

Kobya et al. also studied Remazol Red 3B decolorization using iron electrodes and found that 99% decolorization was possible under optimum conditions. The authors found that energy consumption could achieve 3.3 kWh/kg dye at a cost of 0.642 US$/m^3 [86].

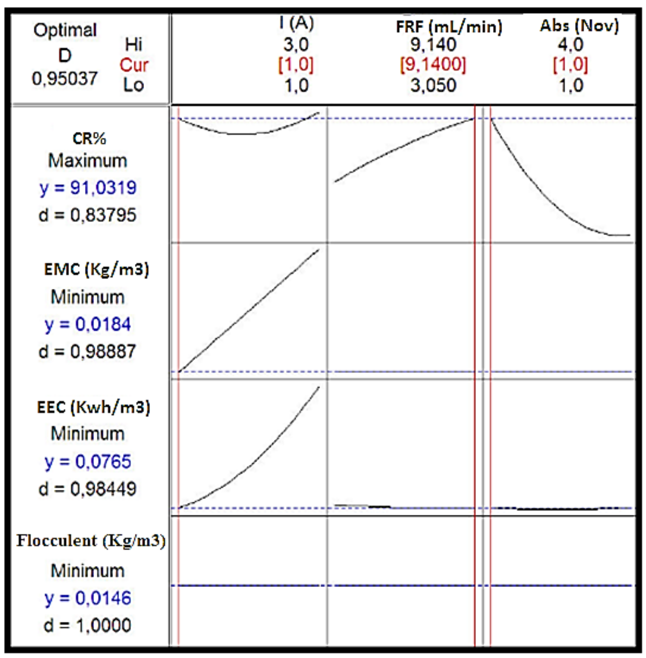


Fig. 8. Response of optimization of color removal (CR%), electrical energy consumption (EEC, kWh/m^3), electrodes consumption (EMC, kg/m^3) and chemical consumption (CC, kg/m^3).

Ghosh et al. were able to decolorize 99.75% of crystal violet by electrocoagulation when initial treatment concentration was 100 mg/L, current density 1.112 A/m^2, solution conductivity of 1.61 S/m, pH of 8.5, and for 60 min of electrolysis. The cost for optimum treatment, in these conditions, was 0.2141 US$/m^3 [75]. On the other hand, Phalakorkule et al. using electrocoagulation for treating Reactive Blue 140 reactive dye and disperse dye II and initial dye concentration of 100 mg/L, found that color removal was 95% with an energy consumption of 1 kWh/m^3 [87].

Sengil et al. [2] were able to decolorize 98% of Reactive Black 5 dye from synthetic wastewater by using electrocoagulation with injection of flocculent. The optimum operating cost was 1.74$. This result was obtained when, current density was 193.5 A/m^2, solution conductivity was 1,000.8 μScm^{-1}, dosage of flocculent injected was 14.4mg/L, and treatment time was 13.9 min [88].

4. Conclusion

In this work, we used a combined semi-continuous process of electrocoagulation-flocculation-filtration, for removal of Novacron Blue 4R (NB4R) dye. Response surface methodology (RSM) was applicated to optimized operation conditions and minimizes the cost of treatment.

The effects of various operational parameters on dye removal efficiency were investigated. Experimental conditions were optimized by observing the effects of interactions among the variables on color removal efficiencies (CR%). The RSM results demonstrated significant effects of two operating variables. Initial concentration of dye and current intensity were the most important factors in the process, as well as their interactive effects. Box-Behnken design (BBD) was used to determine the optimal removal efficiency and operation cost.

High R^2 value of % for color removal, through ANOVA, verified that the accuracy of the proposed second-order regression model was acceptable. The maximum predicted and experimental color removal were 91% and 90.84% respectively, using optimized conditions of the current intensity at 1 A, initial concentration of dye at 30 mg/L and flow rate of flocculent at the concentration of 0.5 g/L.

The optimized costs for removal of color, at pH 8, inter-electrodes distance of 5 mm, electrolysis time of 45 min and NaCl concentration of 3 g/L, were respectively OCp = 0.08460 US$/m^{3}and OCe = 0.08474 US$/m^{3}for predicted and experimental results.

Acknowledgments

N.B: This project is in the framework of a doctoral thesis MOBIDOC-PASRI the program financed by the EU and managed by the ANPR (National Agency for Promotion of Scientific Research as at Support Unit Support Program for Research and Innovation System (PASRI).

References

[1] H. Zollinger, Color Chemistry, 2nded., VCH Verlagsgesell-Schaft. (1991).
[2] J.R. Easton, Colourin Dye House Effluent, P Cooper (Society of Dyers and Colourists), UK., 9 (1995).
[3] N. Kirby, R. Marchant, G. McMullan, Decolourisation of synthetic textile dyes by Phlebiatremellosa, FEMS Microbiol. Lett., 188(1) (2000) 93–96.
[4] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour Technol., 77(3) (2001) 247–255.
[5] S. Meriç, D. Kaptan, T. Ölmez, Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, Chemosphere, 54(3) (2004) 435–441.
[6] T. Estlander, Allergic dermatoses and respiratory diseases from reactive dyes, Contact Dermatitis, 18(5) (1988) 290–297.
[7] R. Nilsson, R. Nordlinder, U. Wass, B. Meding, L. Belin, Asthma, rhinitis, and dermatitis in workers exposed to reactive dyes, Br. J. Ind. Med., 50(1) (1993) 65–70.
[8] K.L. Hatch, H.I. Maibach, Textile dye dermatitis, J. Am. Acad. Dermatol., 32(4) (1995) 631–639.
[9] B.M. Manzini, A. Motolese, A. Conti, G. Ferdani, S. Seidenari,Sensitization to reactive textile dyes in patients with contact dermatitis, Contact Dermatitis., 34(3) (1996) 172–175.
[10] S.M. Wilkinson, K. McGechaen, Occupational allergic contact dermatitis from reactive dyes, Contact Dermatitis., 35(6) (1996) 376–376.
[11] H.S. Park, M.K. Lee, B.O. Kim, K.J. Lee, J.H. Roh, Y.H. Moon C.S. Hong, Clinical and immunologic evaluations of reactive dye-exposed workers, J. Allergy Clin. Immunol. Pract., 87(3) (1991) 639–649.
[12] A.J. Roos, R.M. Ray, D.L. Gao, K.J. Wernli, E.D. Fitzgibbons, F. Ziding, H. Checkoway, Colorectal cancer incidence among female textile workers in Shanghai, China: a case-cohort analysis of occupational exposures, Cancer Causes Control., 16(10) (2005) 1177–1188.
[13] C.A. Gonzales, E. Riboli, G. Lopez-Abente, Bladder cancer among workers in the textile industry: Results of a Spanish case-control study, Am. J. Ind. Med., 14(6) (1988) 673–680.
[14] K.M. Wollin, B.D. Gorlitz, Comparison of genotoxicity of textile dyestuffs in Salmonella mutagenicity assay, in vitro micronucleus assay, and single cell gel/comet assay, J. Env. Pathology Toxicol Oncolgy, 23(4) (2004) 267–278.
[15] A. Birhanlı, M. Ozmen, Evaluation of the toxicity and teratogenity of six commercial textile dyes using the frog embryo teratogenesis assay–Xenopus, Drug Chem. Toxicol., 28(1) (2005) 51–65.
[16] S. Koparal, Y. Yavuz, C. Gurel, U.B. Ogutveren, Electrochemical degradation and toxicity reduction of C.I. Basic Red 29 solution and textile wastewater by using diamond anode, J. Hazard Mater., 145(1) (2007) 100–108.
[17] H. Wang, Q. Li, N. He, Y. Wang, D. Sun, W. Shao, Y. Lu, Removal of anthraquinone reactive dye from wastewater by batch hydrolytic–aerobic recycling process, SEP PURIF TECHNOL., 67(2) (2009) 180–186.
[18] S. Song, J. Yao, Z. He, J. Qiu J. Chen, Effect of operational parameters on the decolorization of CI Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation, J. Hazard Mater., 152(1) (2008) 204–210.
[19] E. Petrucci, D. Montanaro, Anodic oxidation of a simulated effluent containing Reactive Blue 19 on a boron-doped diamond electrode, Chem. Eng J. 174(2) (2011) 612–618.
[20] J.R. Guimaraes, M.G. Maniero, R.N. de Araujo,A comparative study on the degradation of RB-19 dye in an aqueous medium by advanced oxidation processes, J. Environ. Manage, 110 (2012) 33–39.
[21] X. Jiang, K. Cai, J. Zhang, Y. Shen, S. Wang, X. Tian, Synthesis of a novel water-soluble chitosan derivative for flocculated decolorization, J. Hazard Mater., 185(2) (2011) 1482–1488.
[22] I. Koyuncu, Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity, Desalination, 143(3) (2002) 243–253.
[23] G. Moussavi, M. Mahmoudi, Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles, J. Hazard Mater., 168(2) (2009) 806–812.
[24] R. Pelegrini, P. Peralta-Zamora, A.R. de Andrade, J. Reyes, N. Duran, Electrochemically assisted photocatalytic degradation of reactive dyes, Appl. Catal B., 22(2) (1999) 83–90.
[25] E. Şayan, M.E. Edecan, An optimization study using response surface methods on the decolorization of Reactive Blue 19 from aqueous solution by ultrasound, Ultrason. Sonochem., 15(4) (2008) 530–538.
[26] M. Siddique, R. Farooq, Z.M. Khan, Z. Khan, S.F. Shaukat, Enhanced decomposition of reactive blue 19 dye in ultrasound assisted electrochemical reactor, Ultrason. Sonochem., 18(1) (2011) 190–196.

[27] Z. Wang, X. Xu, Z. Gong, F. Yang, Removal of COD, phenols and ammonium from Lurgi coal gasification wastewater using A 2 O-MBR system, J. Hazard Mater., 235 (2012) 78–84.
[28] A. Aleboyeh, N. Daneshvar, M.B. Kasiri, Optimization of CI Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology, Chem. Eng. Process Intensification, 47(5) (2008) 827–832.
[29] M.O. Nkiko, A.I. Adeogun, N.A. Babarinde, O.J. Sharaibi, Isothermal, kinetics and thermodynamics studies of the biosorption of Pb (II) ion from aqueous solution using the scale of croaker fish (Genyonemuslineatus), J. Water Reuse Desal., 3(3) (2013) 239–248.
[30] O.T. Can, M. Kobya, E. Demirbasand, M. Bayramoglu, Treatment of the textile wastewater by combined electrocoagulation, Chemosphere, 62(2) (2006) 181–187.
[31] F. Ghanbari, M. Moradi, A comparative study of electrocoagulation, electrochemical Fenton, electro-Fenton and peroxi-coagulation for decolorization of real textile wastewater: electrical energy consumption and biodegradability improvement, J. Environ. Chem. Eng., 3(1) (2015) 499–506.
[32] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, J. Hazard Mater., 84(1) (2001) 29–41.
[33] I. Linares-Hernández, C. Barrera-Díaz, G. Roa-Morales, B. Bilyeu, F. Ureña-Núñez, A combined electrocoagulation–sorption process applied to mixed industrial wastewater, J. Hazard Mater., 144(1) (2007) 240–248.
[34] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res., 37(18) (2003) 4513–4523.
[35] Ş. İrdemez, Y.Ş. Yildiz, V. Tosunoğlu, Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes, SEPPURIF Technol., 52(2) (2006) 394–401.
[36] Ş. Gül, Ö. Özcan-Yıldırım, Degradation of reactive red 194 and reactive yellow 145 azo dyes by O_3 and H_2O_2/UV-C processes, Chem. Eng. J., 155(3) (2009) 684–69.
[37] V. Khandegar, A. K. Saroha, Electrocoagulation for the treatment of textile industry effluent, J. Environ Manage: review, 128 (2013) 949–963.
[38] A.R. Khataee, M. Zarei, M. Pourhassan, Bioremediation of malachite green from contaminated water by three microalgae: neural network modeling, Clean–Soil, Air, Water, 38(1) (2010) 96–103.
[39] W. Den, C. Huang, H.C. Ke, Mechanistic study on the continuous flow electrocoagulation of silica nanoparticles from polishing wastewater, Ind. Eng. Chem. Res., 45(10) (2006) 3644–3651.
[40] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid. Interface Sci., 100 (2003) 475–502.
[41] P. Cañizares, F. Martínez, C. Jiménez, J. Lobato, M.A. Rodrigo, Coagulation and electrocoagulation of wastes polluted with dyes, Environ. Sci. Technol., 40(20) (2006) 6418–64240.
[42] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters- N, J. Hazard Mater., 129.(1) (2006) 116–122.
[43] A. Records, K. Sutherland (Eds.), Decanter centrifuge handbook, Elsevier. (2001).
[44] S. Lu, R.J, Pugh, E. Forssberg, Interfacial separation of particles, Elsevier., Vol 20, (2005).
[45] M.M. Nourouzi, T.G. Chuah, T.S. Choong, Optimisation of reactive dye removal by sequential electrocoagulation–flocculation method: comparing ANN and RSM prediction, Water Sci. Technol., 63(5) (2011) 984–994.
[46] I.H. Cho, K.D. Zoh, Photocatalytic degradation of azo dye (Reactive Red 120) in TiO_2/UV system: optimization and modeling using a response surface methodology (RSM) based on the central composite design, Dyes Pigm., 75(3) (2007) 533–543.
[47] M.G. Moghaddam, M. Khajeh, Comparison of response surface methodology and artificial neural network in predicting the microwave-assisted extraction procedure to determine zinc in fish muscles, Food Nutr. Sci., 2(8) (2011) 803.
[48] D. Salari, A. Niaei, F. Aghazadeh, S.A. Hosseini, F. Seyednajafi, Catalytic remediation of 2-propanol on Pt-Mn/γ-Al_2O_3 bimetallic catalyst during catalytic combustion-Experimental study and response surface methodology (RSM) modeling, J. Environ Sci. Health A., 47(3) (2012) 351–357.
[49] A. Morshedi, M. Akbarian, Application of response surface methodology: design of experiments and optimization: a mini review, J. Fund. Appl. Life Sci., 54 (2014) 2434–2439.
[50] M. Taheri, M.R.A. Moghaddam, M. Arami, Optimization of Acid Black 172 decolorization by electrocoagulation using response surface methodology, Iranian J. Environ. Health Sci. Eng., 9(1) (2012) 23.
[51] Q. K. Beg, V. Sahai, R. Gupta, Statistical media optimization and alkaline protease production from Bacillus mojavensis in a bioreactor, Process Biochem., 39(2) (2003) 203–209.
[52] M. Muthukumar, D. Sargunamani, N. Selvakumar, J. V. Rao, Optimisation of ozone treatment for colour and COD removal of acid dye effluent using central composite design experiment, Dyes Pigm., 63(2) (2004) 127–134.
[53] J. B. Parsa, H.R. Vahidian, A.R. Soleymani, M. Abbasi, Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption, Desalination, 278 (2011) 295–302.
[54] V.A. Sakkas, M.A. Islam, C. Stalikas, T.A. Albanis, Photocatalytic degradation using design of experiments: a review and example of the Congo red degradation, J. Hazard Mater., 175(1–3) (2010) 33–44.
55] B. Merzouk, B. Gourich, A. Sekki, K. Madani, C. Vial, M. Barkaoui, Studies on the decolorization of textile dye wastewater by continuous electrocoagulation process, Chem. Eng. J. 149(1) (2009) 207–214.
[56] F. Ozyonar, S. Aksoy, Removal of Salicylic Acid from Aqueous Solutions Using Various Electrodes and Different Connection Modes by Electrocoagulation, Int J. Electrochem. Sci., 11 (2016) 3680–3696.
[57] I. Arslan-Alaton, I. Kabdaslı, I.B. Vardar, O. Tünay, Optimization of electrocoagulation conditions for the treatment of simulated reactive dye bath effluent, J. Hazard Mater., 164 (2009) 1586–1594.
[58] J.C. Donini, J. Kan, J. Szynkarczuk, T.A. Hassan, K.L. Kar, The operating cost of electrocoagulation, Can J. Chem. Eng., 72(6) (1994) 1007–1012.
[59] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, SEP PURIF Technol., 37(2) (2004) 117–125.
[60] M. Kobya, E. Senturk, M. Bayramoglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard Mater., 133(1) (2006) 172–176.
[61] M. Kumar, F.I.A. Ponselvan, J.R. Malviya, V.C. Srivastava, I.D. Mall, Treatment of bio-digester effluent by electrocoagulation using iron electrodes, J. Hazard Mater., 165(1) (2009) 345–352.
[62] R.G. Brereton, Applied Chemometrics for Scientists, John Wiley and Sons, Ltd, UK, (2007) 396.
[63] N. Barrak, R. Mannai, M. Zaidi, M. Kechida, A.H. Helal, Experimental Design Approach with Response Surface Methodology for Removal of Indigo Dye by Electrocoagulation., J. Gep., 4(11) (2016) 50–61.
[64] P. Rantakumar, S. Chaudhary, K.C. Khilar, S.P. Mahajan, Removal of arsenic from water by electro coagulation, Chemosphere., 55(9) (2004) 1245–1252.
[65] E. Bazrafshan, A.H. Mahvi, S. Nasseri, M. Shaighi, Performance evaluation of electrocoagulation process for diazinon removal from aqueous environment by using iron electrodes, Iran. J. Environ. Health. Sci. Eng., 2(4) (2007) 127–132.
[66] T.K. Kim, Perk's, E.B. Shin, S. Kim, Decholorization of disperse and reactive dyes by continuous electro coagulation process, Desalination, 150 (2002) 165–175.

[67] B. Zhu, D.A. Clifford, S. Chellam, Comparison of electro coagulation and chemical coagulation pre-treatment for enhanced virus removal using microfiltration membranes, Water Res., 39(20) (2005) 3098–3108.
[68] C. Phalakornkule, S. Polgumhang, W. Tongdaung, Performance of an electrocoagulation process in treating direct dye: batch and continuous upflow processes, World Acad. Sci. Eng. Technol., 57 (2009) 277–282.
[69] D. Ghosh, H. Solanki, M.K. Purkait, Removal of Fe (II) from tap water by electrocoagulation technique, J. Hazar Mater., 155(1) (2008) 135–143.
[70] D.C. Montgomery, Design, Analysis of Experiments, John Wiley and Sons, Inc., New York (1997).
[71] A. Singh, A. Srivastava, A. Tripathi, N.N. Dutt, Optimization of Brilliant Green Dye Removal Efficiency by Electrocoagulation Using Response Surface Methodology, World J. Environ. Eng., 4(2) (2016) 23–29.
[72] M.Y. Mollah, P. Morkovsky, J.A. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, Present and future perspectives of electrocoagulation, J. Hazard Mater., 114(1) (2004) 199–210.
[73] A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine, Electro-coagulation of reactive textile dyes and textile wastewater, Chem. Eng. and Process: Process Intensification, 44(4) (2005) 461–470.
[74] G.S. Halford, R. Baker, J.E. McCredden J.D. Bain, How many variables can humans process, Psychological science., 16.(1) (2005) 70–76.
[75] D. Ghosh, C.R. Medhi, H. Solanki, M.K. Purkait, Decolorization of crystal violet solution by electrocoagulation, J Environ Prot. Sci., 2 (2008) 25–35.
[76] P.M. Lakshmi, P. Sivashanmugam, Treatment of oil tanning effluent by electrocoagulation: Influence of ultrasound and hybrid electrode on COD removal. Sep. Purif. Technol., 116 (2013) 378–384.
[77] M.S. Mahmoud, J.Y. Farah, T.E. Farrag, Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes, Egypt J. Pet., 22(1) (2013) 211–216.
[78] A. Kuleyin, E.B. Balchioglu, Investigation of the removal of crystal violet dye by electrocoagulation method, Fresenius Environ. Bull., 18 (2009) 1597–1602.
[79] L.A. Sarabia, M.C. Ortiz, Response surface methodology, Comprehensive Chemometrics, 1 (2009) 345– 390.
[80] A.R. Amani-Ghadim, S. Aber, A. Olad, H. Ashassi-Sorkhabi, Optimization of electrocoagulation process for removal of an azo dye using response surface methodology and investigation on the occurrence of destructive side reactions, Chem. Eng. Process: Process Intensification, 64 (2013) 68–78.
[81] R.H. Myers, D.C. Montgomery, C.M. Anderson-Cook, Response surface methodology: process and product optimization using designed experiments, A Wiley-Interscience Publications, 2015.
[82] E.C. Harrington, The desirability function, Ind. Qual. Control, 21(10) (1965) 494–498.
[83] J.P. Wang, Y.Z. Chen, Y. Wang, S.J. Yuan, H.Q. Yu, Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology, Water Res., 45(17) (2011) 5633–5640.
[84] G. Derringer, R. Suich, Simultaneous optimisation of several response variables, J. Qual. Technol., 12 (1980) 214–219.
[85] M.E.R. Carmona, M.A.P. da Silva, S.G.F. Leite, Biosorption of chromium using factorial experimental design, Process Biochem., 40(2) (2005) 779–788.
[86] M. Kobya, E. Demirbas, M. Sozbir, Decolorisation of aqueous reactive dye Remazol Red 3B by electrocoagulation, Color Technol., 126(5) (2010) 282–288.
[87] C. Phalakornkule, S. Polgumhang, W. Tongdaung, B. Karakat, T. Nuyut, Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent, J. Environ. Manage., 91(4) (2010) 918–926.
[88] İ.A. Şengil, S. Kulac, M. Özacar, Treatment of tannery liming drum wastewater by electrocoagulation, J. Hazard Mater., 167(1) (2009) 940–946.