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Experimental design approach applied to the elimination of crystal violet in water by electrocoagulation with Fe or Al electrodes

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ABSTRACT

An experimental design methodology was applied to evaluate the decolourization of crystal violet (CV) dye by electrocoagulation using iron or aluminium electrodes. The effects and interactions of four parameters, initial pH (3–9), current density (6–28 A m^{-2}), substrate concentration (50–200 mg L^{-1}) and supporting electrolyte concentration (284–1420 mg L^{-1} of Na$_2$SO$_4$), were optimized and evaluated. Although the results using iron anodes were better than for aluminium, the effects and interactions of the studied parameters were quite similar. With a confidence level of 95%, initial pH and supporting electrolyte concentration showed limited effects on the removal rate of CV, whereas current density, pollutant concentration and the interaction of both were significant. Reduced models taking into account significant variables and interactions between variables have shown good correlations with the experimental results. Under optimal conditions, almost complete removal of CV and chemical oxygen demand were obtained after electrocoagulation for 5 and 30 min, using iron and aluminium electrodes, respectively. These results indicate that electrocoagulation with iron anodes is a rapid, economical and effective alternative to the complete removal of CV in waters. Evolutions of pH and residual iron or aluminium concentrations in solution are also discussed.

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1. Introduction

Crystal violet (CV) belongs to the triarylmethane dye family and is largely used in the paper, leather, cosmetic, and food industries. The textile industry consumes large quantities of these dyes for nylon, wool, cotton, and silk, as well as for colouring oil, fats, waxes, varnish, and plastics [1]. Furthermore, triphenylmethane dyes are applied as staining agents in bacteriological and histopathological applications. These compounds in wastewater cause colouration and also represent a serious risk to aquatic life. In addition, their presence in drinking water constitutes a potential human health hazard.

Biological processes are the most economical option for eliminating organic pollutants. However, due to the toxicity of the dye, the application of such substances is restricted. Physicochemical methods based on the production and use of hydroxyl radicals called advanced oxidation processes (AOPs) (e.g. H$_2$O$_2$ + UV,

UV + O$_3$, H$_2$O$_2$ + O$_3$, TiO$_2$ photocatalysis, Fenton's reagent, photo-Fenton), have been successfully tested for the elimination of dye compounds [2,3]. However, these methods often lead to secondary products that are not significantly eliminated by the same technique and can be more hazardous than the original compound [4–6]. Additionally, due to the hydroxyl radical scavenger effect, these processes have limited applications in waters containing large quantities of inorganic ions.

Electrocoagulation (EC), using iron or aluminium electrodes, has been effectively tested in the treatment of a variety of dye effluents [7–9]. This technique is very attractive from an economical point of view since the equipment is easy to install and operate, it reduces the production of sludge, it does not use chemical products as coagulant agents, the process is easy to control and the reaction time is short.

Two mechanisms have been proposed for iron electrocoagulation which can be summarised as follows [7,8]:
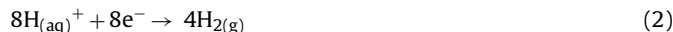
Mechanism 1

Anode:

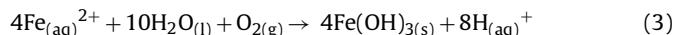$$4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{2+} + 8e^- \tag{1}$$

* Corresponding author at: Grupo de electroquímica, Instituto de química, Facultad de ciencias exactas y naturales, Universidad de Antioquia, A.A. 1226 Medellín, Colombia. Tel.: +57 4 219 56 00; fax: +57 4 219 56 66.
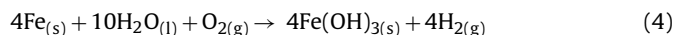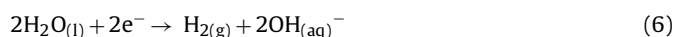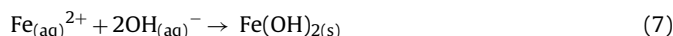E-mail address: rtorres@matematicas.udea.edu.co (R.A. Torres-Palma).

Cathode:

$$8H_{(aq)}^+ + 8e^- \rightarrow 4H_{2(g)} \tag{2}$$

Bulk solution:

$$4Fe_{(aq)}^{2+} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}^+ \tag{3}$$

Overall:

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \tag{4}$$

Mechanism 2

Anode:

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^- \tag{5}$$

Cathode:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^- \tag{6}$$

Bulk solution:

$$Fe_{(aq)}^{2+} + 2OH_{(aq)}^- \rightarrow Fe(OH)_{2(s)} \tag{7}$$

Overall:

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \tag{8}$$
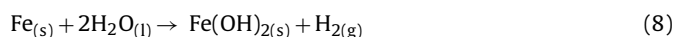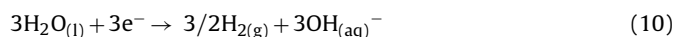
When aluminium electrodes are used, the most commonly accepted mechanism can be summarised by the following reactions [9]:

Anode:

$$Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^- \tag{9}$$

Cathode:

$$3H_2O_{(l)} + 3e^- \rightarrow 3/2H_{2(g)} + 3OH_{(aq)}^- \tag{10}$$

Overall:

$$Al_{(s)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3/2H_{2(g)} \tag{11}$$
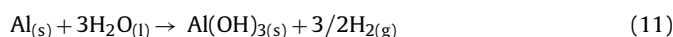
Both iron and aluminium hydroxides, generated during electrocoagulation with iron or aluminium electrodes, respectively, can remove dye molecules by sedimentation or H_2 flotation prior to surface complexation or electrostatic attraction of the formed particles [7].

When compared with traditional flocculation and coagulation processes, electrocoagulation has, in theory, the advantage of removing small colloidal particles, since they have a higher probability of being coagulated due to the electric field that sets them in motion. Furthermore, excessive amounts of coagulants can be avoided, due to their in situ generation by electro-oxidation of a sacrificial anode.

In the present work, we have studied the influence of important electrocoagulation parameters (initial pH, current density, substrate concentration and supporting electrolyte concentration) using two types of sacrificial anodes, iron and aluminium electrodes, on the elimination of a triarylmethane dye model, CV, using an experimental design methodology. This methodology provides a systematic way of working that allows conclusions to be drawn about the variables (or combinations of variables) that are most influential in the response factor while carrying out the minimum number of experiments [10].
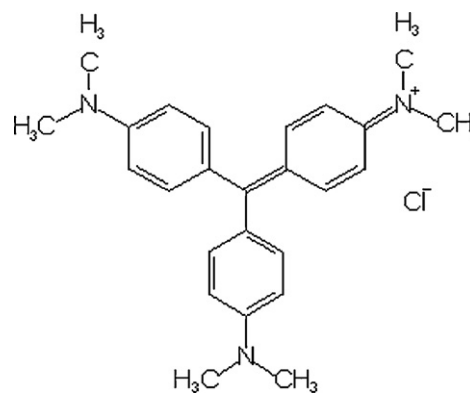

Fig. 1. Chemical structure of crystal violet.

2. Experimental

2.1. Reagents

Crystal violet (Fig. 1) was purchased from Aldrich. Anhydrous sodium sulphate, sulphuric acid and sodium hydroxide were provided by Merck. Distilled water was used throughout for the preparation of aqueous solutions.

2.2. Electrochemical cell

The experimental set-up is shown in Fig. 2. All experiments were performed, under galvanic conditions and magnetic stirring, in a 1000 mL acrylic cell containing the dye dissolved in distilled water (500 mL). Seven monopolar electrodes, four cathodes and three anodes, each one of $0.012\,m^2$, were interspersed in the cell. The anodic electrodes consisted of iron or aluminium plates, while the cathodic electrodes were stainless steel plates. The spacing between electrodes was 1.1 cm. The electrodes were connected to a digital dc power supply (Thurlby Thandar Instruments).

Even though NaCl is the most common supporting electrolyte used for electrocoagulation process, its use remains controversial due to the possible formation of organic chlorine by-products. In a recent paper [11], it was shown that Na_2SO_4 is the best supporting electrolyte for the electrocoagulation process, from an economical, effective and environmental point of view. Therefore, Na_2SO_4 was selected as the support electrolyte in this work.

The electrolytic medium was made basic or acidic as required by the addition of aqueous NaOH or H_2SO_4, respectively; and once the current density was chosen, the coagulation was started and samples were taken at different time intervals. The samples were allowed to settle for 15 min in a vessel before analysis after which the solution was filtered and the filtrate was analyzed. The solution in the electrolytic cell was sampled periodically for UV, pH, atomic absorption and chemical oxygen demand (COD) analysis.
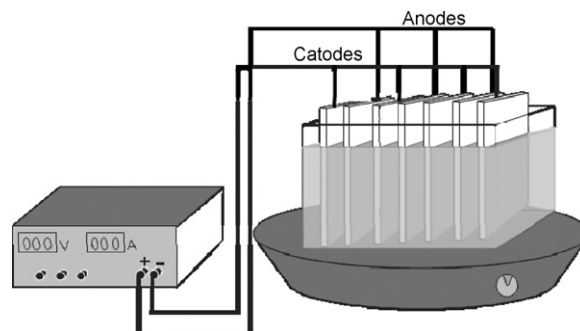

Fig. 2. Electrochemical reactor.

Before each experiment was carried out, the electrodes were subjected to a chemical cleaning procedure. The aluminium plates were washed with acetone to remove any possible grease on the surface, and then dipped in a nitric acid solution. The iron plates were dipped in a solution containing hydrochloric acid and hexamethylene tetramine during 5 min to remove impurities on the electrode surfaces, then rinsed with abundant distilled water and dried.

2.3. Analysis

Quantitative analysis of the CV was done by UV–visible in a LKB biochrom NOVASPEC spectrophotometer set at 590 nm. Chemical oxygen demand, COD, was measured according to the method described by Thomas and Mazas [12], using a dichromate solution as the oxidizer in a strong acid medium. The test solution (2.5 mL) was transferred into the dichromate reagent and digested at 150 °C for 2 h. The optical density for the colour change of dichromate solution was determined at 445 nm with the spectrophotometer. The pH measurements were carried out using a Thermo Orion (model 710 A+) pH meter.

Concentrations of iron and aluminium ions in the aqueous phase were analyzed using an atomic absorption spectrometer GBC 932 Plus with air–acetylene flame for the Fe and nitrous oxide–acetylene for the Al. Hollow cathode lamps were set at 248.3 and 396.2 nm for Fe and Al analysis, respectively. Samples periodically taken from the reactor were allowed to settle for 15 min, filtered to eliminate sludge formed during electrolysis and after suitable dilution, were directly measured by atomic absorption spectrometry. Each experiment was performed in triplicate.

2.4. Experimental design

In order to extract information from the data and to better understand the situations indicated, it is necessary to know the most appropriate experimental design technique to use. A two-level factorial design (2^k) was selected, due to the fact that this design technique is very useful in experiments studying the effect of several variables, and how these variables interact with each other, over a response (response factor) [13–15]. The full factorial design is considered to be the most suitable design when the study is directed towards gaining knowledge of the influence of the variables on the process.

The statistical software package used was Statgraphics Centurion XV®. This is a package for experimental design used to obtain graphs and statistical parameters, reduced models and the necessary tools for data processing in general.

The variables studied were: current density, initial pH, support electrolyte (Na_2SO_4) concentration, and CV concentration. A total of 19 experiments were carried out for both aluminium and iron electrodes (anodes). A two-level full factorial design with three replicate centre points was used. The replicate centre points serve to evaluate the experimental error and the curvature of the evolution of a response factor, that is whether or not the evolution of the response factor is linear within the experimental range studied [16]. The conditions in each experiment were modified using different combinations of the two selected levels. The levels of the four variables studied for each experimental system are shown in Table 1.

3. Results and discussion

3.1. Preliminary test of CV electrocoagulation

A typical electrocoagulation experiment to remove CV with Al anodes is shown in Fig. 3. As can be seen, the electrochemical pro-

Table 1
Levels of selected variables for each experimental system.

Variables	Low level, −1	High level, +1
Initial pH	3	9
Crystal violet ($mg\,L^{-1}$)	50	200
Na_2SO_4 ($mg\,L^{-1}$)	284	1420
J ($A\,m^{-2}$)	6	28

cess removes 23, 47 and 69% of the pollutant after 10, 20 and 30 min of treatment, respectively. Thus, at the beginning of the process, the CV decreases linearly with time. Indeed, the linear coefficient of determination after 30 min, R^2, is 0.9973. This indicates that under the working conditions an almost linear production of coagulant and bubbles takes place, which benefits both the formation and growth of flocs. The same behaviour was observed when iron electrodes were used. Thus, the slope of the curve CV vs time, at the initial step (the initial removal rate, V_o), was selected as the response factor for the experimental design using iron and aluminium anodes.

3.2. Experimental design for the electrocoagulation of CV with iron and aluminium electrodes

Table 2 shows the matrix design obtained with the Statgraphics Centurion XV® computer program for both experimental systems, when using the iron and the aluminium electrodes. It includes the conditions and results obtained for each experiment and the response factor defined as initial removal rate, V_o ($mg\,L^{-1}\,min^{-1}$), after 5 and 30 min of treatment for iron and aluminium electrodes, respectively. Table 2 also indicates the coefficient of determination (R^2) involved in the response factor.

The results in Table 2 show that the initial removal rate is always higher for the iron electrode than for the aluminium electrode under the same experimental conditions (using low or high levels of each variable). This behaviour can be explained by considering the recent investigations of Trompette and Vergnes [17] which indicated that the sulphate anions are passive agents for aluminium surfaces, complicating the formation of coagulant aluminium cations and therefore reducing the efficiency of the electrocoagulation process.

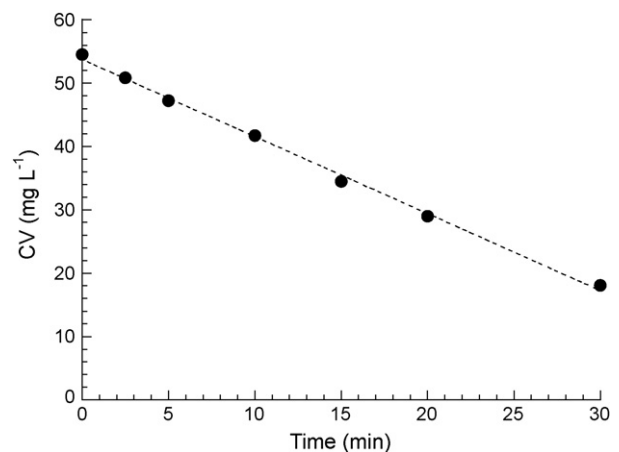
Fig. 3. Evolution of crystal violet (CV) concentracion as a function of time during electrocoagulation process with aluminium electrodes. Initial pH 9; 28 A m^{-2}; 1420 mg L^{-1} of Na$_2$SO$_4$; 54 mg L^{-1} of crystal violet; 500 mL.

Table 2
Design matrix and experimental results (V_o) for iron and aluminium anodes during electrocoagulation of crystal violet.

Experimental	Initial pH	CV (mg L^{-1})	Na$_2$SO$_4$ (mg L^{-1})	J (A m^{-2})	Fe electrode		Al electrode	
					V_o (mg L^{-1} min^{-1})	R^2	V_o (mg L^{-1} min^{-1})	R^2
1	6	125	852	17	15.629	0.9951	2.551	0.9983
2	3	200	1420	6	7.3934	0.9973	0.924	0.9953
3	3	200	284	28	20.226	0.9857	4.864	0.9963
4	9	200	1420	28	34.621	0.9854	5.237	0.9960
5	3	50	284	28	10.308	0.9590	1.118	0.9969
6	3	50	284	6	3.4361	0.9828	0.292	0.9925
7	3	200	284	6	15.671	0.9929	0.869	0.9961
8	9	50	1420	28	11.844	0.9980	1.216	0.9973
9	9	50	284	6	3.6443	1.0000	0.665	0.9999
10	6	125	852	17	19.783	0.9937	2.509	0.9958
11	3	200	1420	28	35.298	0.9802	4.779	0.9947
12	3	50	1420	6	3.2102	0.9921	0.493	0.9980
13	9	50	1420	6	3.384	0.9922	0.638	0.9933
14	9	200	284	28	37.771	0.9986	4.410	0.9958
15	9	200	1420	6	12.703	0.9799	1.472	0.9951
16	3	50	1420	28	7.0724	0.9887	1.555	0.9942
17	9	200	284	6	16.052	0.9993	1.723	0.9984
18	9	50	284	28	18.827	0.9986	1.449	0.9944
19	6	125	852	17	18.335	0.9979	2.529	0.9976

3.3. Effect of operating parameters on the electrocoagulation of crystal violet

Besides the electrode type, the most important variables during the electrocoagulation process are the initial pH, the current density, the concentration of supporting electrolyte and the pollutant concentration. In order to evaluate the individual impact of the variables on the system, Fig. 4 shows the main effects plot (data means) representing the effect of each variable on the response factor. This type of representation shows the contribution to the response factor of changing one of the variables chosen. The slope of the plot is indicative of the importance of the variable. In Fig. 4, positive and negative slopes indicate beneficial or detrimental effects, respectively, on the electrocoagulation efficiency: the higher the slope magnitude (absolute value), the greater the effect of the parameter.

In Fig. 4A, it is observed that in the range of variables studied, the initial pH, the CV concentration and the current density (J) have a positive effect on the efficiency of the electrocoagulation process with iron anodes. As expected, by increasing the CV concentration and the J, there is an evident increase in the elimination rate, while the initial pH shows less influence at the confidence level selected. Furthermore, the influence of Na$_2$SO$_4$ concentration (2–10 mM) on the response factor is almost insignificant. Regarding the aluminium experiments (Fig. 4B), a similar trend is observed. However, as previously discussed, the influence of each variable on the response factor is always higher when the iron electrode is used.

The negligible effect of the sodium sulphate concentration indicates that 2 mM (or 284 mg L^{-1}) of the supporting electrolyte provides the conductivity necessary to reduce the ohmic potential to minimal levels.

The low effect of the initial pH agrees with previous published papers. Chen et al. [18], evaluated the treatment of restaurant wastewater by electrocoagulation and they found that the initial pH effect is not very significant in the range 3–10. Also, Merzouk et al. [19], studying the decolourization of a textile dye with aluminium electrodes, found that when the initial pH was varied between 4.1 and 9, a colour removal between 80 and 90% was obtained after ~20 min of treatment. The effect of the initial pH can be explained as follows. At low initial pH (~3), cationic monomeric species of iron or aluminium predominate. However, the increase of the pH during the course of treatment generates various monomeric and polymeric species that finally transform into insoluble amorphous Al(OH)$_{3(s)}$ and Fe(OH)$_{3(s)}$ through com-

plex precipitation/polymerization kinetics [19,20]. Formation of iron and aluminium hydroxides occurs in the 4–9 range of pH. As a result a slight effect of the initial pH is observed.

The increase in the efficiency of the process with an increase of the current density can be explained by a higher production of coagulant and bubbles, which benefits both the formation and growing of flocs. The rise in the pollutant removal with the increase of initial
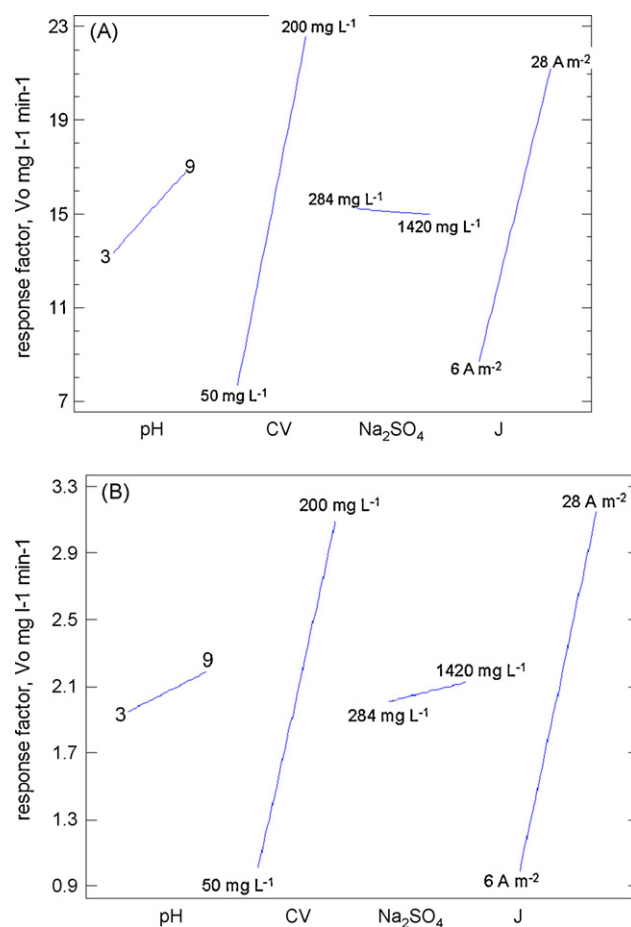

Fig. 4. Main effects plot for (A) iron and (B) aluminium electrodes during the electrocoagulation of crystal violet.
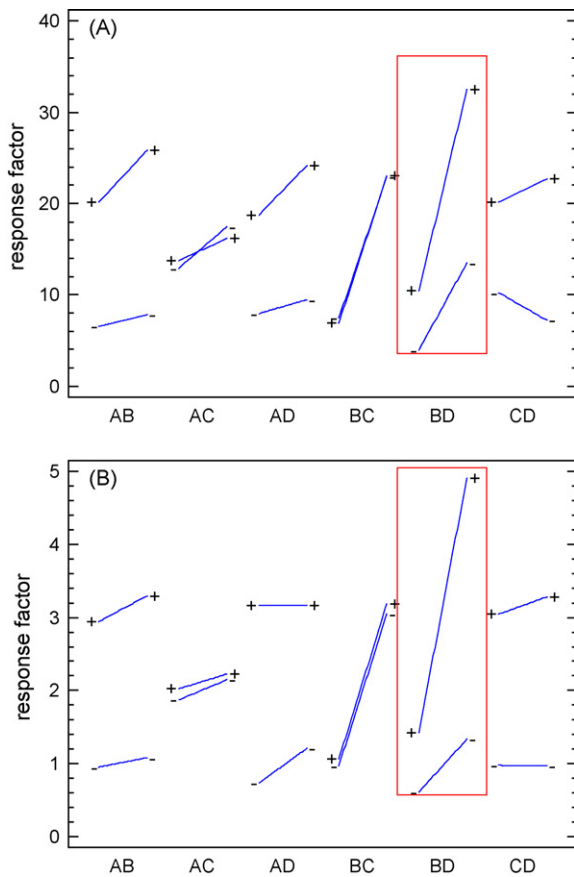
Fig. 5. Interaction plots for (A) iron and (B) aluminium electrodes during the electrocoagulation of crystal violet. A, initial pH; B, CV concentration; C, Na$_2$SO$_4$ concentration; D, current density.

CV concentration suggests that the process is mainly controlled by the generation of coagulant from the electrode.

3.4. Effect of interaction among the operation parameters on the efficiency of the electrocoagulation process

Fig. 5 illustrates interaction plots showing the existence or otherwise of interaction among the variables. An interaction between variables occurs when the change in response from the low level to the high level of one variable is not the same as the change in response at the same two-levels of a second variable, i.e. the effect of one variable is dependent on the second variable. Parallel or almost parallel plots in this kind of figure would mean that the interaction between the variables is not significant, whereas plots which are crossed or tending to cross would show a significant interaction between the variables. In addition, the greater the degree of departure from parallel plots, the stronger is the effect on the response factor.

As Fig. 5A and B indicate, the most significant interaction in both electrodes occurs between the CV concentration and current density variables, i.e. BD interaction. The influence on the response factor is as follows. For low current densities, the initial CV concentration has little influence on the response factor. However, for high current densities the increase in the initial CV concentration produces a significant improvement in the response factor. These results are also reflected in Table 2.

Table 3
ANOVA table for electrocoagulation of crystal violet with iron anodes.

Source	Sum of squares	Mean square	P-Value
A: initial pH	47.9979	47.9979	0.0815
B: CV	1000.59	1000.59	0.0044
C: Na$_2$SO$_4$	0.223351	0.223351	0.8435
D: J	649.669	649.669	0.0068
AB	18.9334	18.9334	0.1751
AC	4.57553	4.57553	0.4171
AD	15.1457	15.1457	0.2062
BC	0.384772	0.384772	0.7963
BD	157.746	157.746	0.0270
CD	31.1788	31.1788	0.1179
ABC	20.3189	20.3189	0.1660
ABD	2.87964	2.87964	0.5054
ACD	21.0328	21.0328	0.1616
BCD	38.3223	38.3223	0.0991
ABCD	48.8482	48.8482	0.0802

3.5. Analysis of variance and formulation of a reduced model for the electrocoagulation process of CV with iron and aluminium electrodes

The experimental results obtained for each experimental system were statistically analyzed by analysis of variance (ANOVA) using the software described previously. In Tables 3 and 4 the ANOVA results are shown.

The confidence level chosen in this study was 95%, which means that the significance level (α) for analyzing the ANOVA table was 0.05. Therefore, a value of the p-value parameter lower than 0.05 for a term of the ANOVA table means that this term is significant and must be considered in the model [16]. Tables 3 and 4 show that during crystal violet electrocoagulation with iron or aluminium electrodes, the significant terms are the J, the CV concentration and the interaction between these two variables. The ANOVA analysis confirms the results obtained in the preceding section and indicates that a reduced model involving the effect of J, CV concentration and the interaction between these parameters could be used to optimize the electrocoagulation process with both electrodes.

The reduced empirical models are described by a first order polynomial expression; the results obtained showed that there is no curvature. The main tools to study the reduced models were based on the study of the residual. The coefficients of the reduced model in the polynomial expression are calculated by multiple regression analysis, using the above-mentioned statistical software, and represent the weight of each variable. As mentioned, reduced models for iron (Eq. (12)) and aluminium (Eq. (13)) electrodes can be obtained taking into account the variables (J and CV

Table 4
ANOVA table for electrocoagulation of crystal violet with aluminium anodes.

| Source	Sum of squares	Mean square	P-Value
A: initial pH	0.229441	0.229441	0.4115
B: CV	17.7494	17.7494	0.0036
C: Na$_2$SO$_4$	0.053361	0.053361	0.6775
D: J	19.2545	19.2545	0.0032
AB	0.050176	0.050176	0.6864
AC	0.005329	0.005329	0.8939
AD	0.231361	0.231361	0.4097
BC	0.001764	0.001764	0.9388
BD	7.63417	7.63417	0.0119
CD	0.058564	0.058564	0.6635
ABC	0.141376	0.141376	0.5093
ABD	0.047524	0.047524	0.6942
ACD	0.037636	0.037636	0.7256
BCD	0.051529	0.051529	0.6826
ABCD	0.172225	0.172225	0.4701
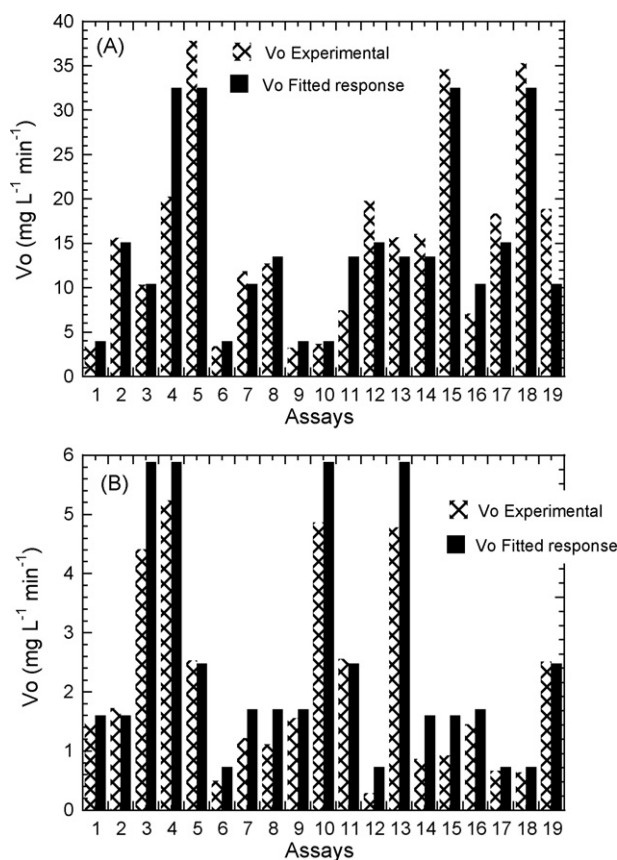
Fig. 6. Comparison between experimental and estimated (from the reduced model) removal rates during the electrocoagulation of crystal violet with (A) iron and (B) aluminium electrodes.

Fig. 7. Evolution of crystal violet concentration, chemical oxygen demand and iron as a function of time during the electrocoagulation process. Initial pH, 5.8; 28 A m^{-2}; Na$_2$SO$_4$ 284 mg L^{-1}; 200 mg L^{-1} of crystal violet; 500 mL. (A) iron anodes and (B) aluminium anodes.

concentration) and the interaction between them:

$$V_o \,(\mathrm{mg\,L^{-1}\,min^{-1}}) = 0.148692 + 0.0407388 \times [\mathrm{CV}]$$
$$+ 0.10354 \times J + 0.00380597 \times [\mathrm{CV}] \times J \tag{12}$$

$$V_o \,(\mathrm{mg\,L^{-1}\,min^{-1}}) = 0.396477 - 0.000190303 \times [\mathrm{CV}]$$
$$- 0.00493182 \times J + 0.000837273 \times [\mathrm{CV}] \times J \tag{13}$$

Fig. 6 shows comparisons between the experimental values obtained in each experiment (Table 2) and the estimated values for the initial removal rate of CV calculated by Eqs. (12) and (13). It can be observed that the estimated values are similar to the experimental ones in most of the experiments. Indeed, the correlation percentage between the outcomes and their predicted values are 83 and 96% for iron and aluminium anodes, respectively. It is important to emphasize that this research work is addressed mainly towards gaining knowledge of the influential variables in the studied system. The reduced models can therefore satisfactorily describe the electrocoagulation technology applied to the elimination of crystal violet in waters.

3.6. Analysis of crystal violet electrocoagulation under our optimal conditions

The above experiments show that in the range of variables studied, the initial pH, the supporting electrolyte concentration and the interactions involving these parameters do not have a significant effect on the electrocoagulation process. It was also observed that
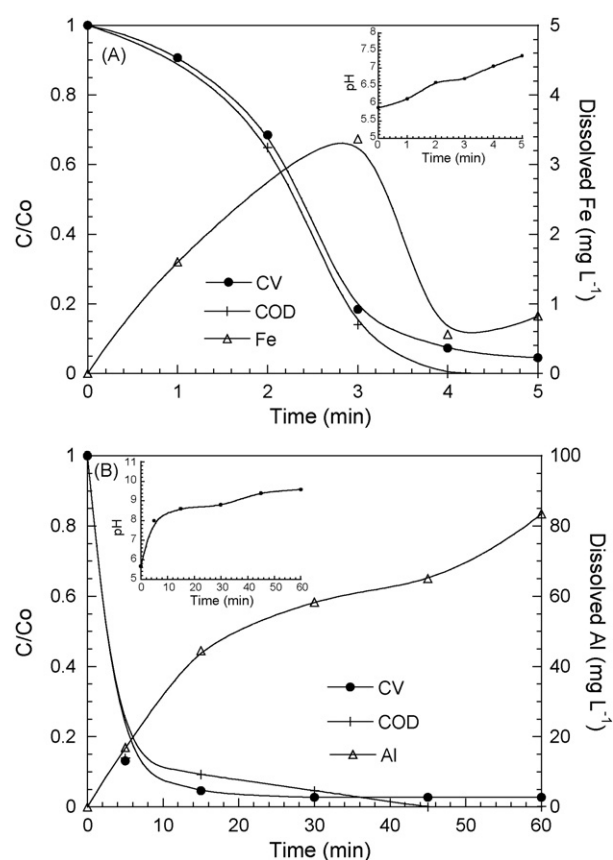
higher substrate concentrations and J favour the process. Consequently, two new sets of experiments were carried out, with iron or aluminium anodes, at the lowest Na$_2$SO$_4$ concentration (2 mM or 284 mg L^{-1}), natural initial pH, and the highest initial CV concentration (200 mg L^{-1}) and J (28 A m^{-2}). The results depicted in Fig. 7A and B show the evolution of CV concentration and the COD during 5 and 60 min of treatment for anodes of iron and aluminium, respectively. It can be observed from these figures that ~85% of both initial CV concentration and COD are removed after 3 and 5 min with iron and aluminium electrodes, respectively. This confirms the better performance of the iron electrodes in the treatment of water contaminated with CV. At the end of the treatments, both anodes led to almost total CV and COD removal. Additionally, this process was found to be a low energy consumption methodology. For example, when iron anodes were used, only 0.4 Wh L^{-1} (5 min) was needed to remove practically all of the initial pollutant.

In addition, the evolution of the CV and COD curves for the two anodes (Fig. 7A and B) follows a similar trend, indicating that the elimination of CV implies an equivalent reduction of COD. This suggests that the electrocoagulation by iron or aluminium is the only process implicated in the removal of the pollutant, and not the oxidation of the substrate by the electrode surface or by oxidants such as hydroxyl radicals, hypochlorite or Cl$_2$.

Residual concentrations of anode materials in solution after the treatment need to be controlled in order to make sure that the level of the metallic ions complies with the environmental regulations. Fig. 7A and B also shows the residual concentration of iron and aluminium ions, respectively, during the processes, measured with atomic absorption. When iron electrodes were used, 3.3 mg L^{-1} of iron ions were present after 3 min of electrolysis, and a concentra-

tion lower than 1 mg L^{-1} was observed at the end of the experiment. Using aluminium anodes, 17 mg L^{-1} of aluminium ions were found after 5 min of the process, whereas after 30 min of treatment, when practically 100% of both CV and COD had been removed, the solution contained 58 mg L^{-1} of aluminium. The concentration of Al and Fe ions is strongly dependent on the pH value of the solution. As can be seen in the inset of Fig. 7A and B, due to the OH$^-$ generated (Eqs. (6) and (10)) or the H$^+$ consumed (Eq. (2)), the initial pH of the solutions increases with the course of time at the beginning of the processes. When using aluminium anodes, the initial pH increased from 5.9 to 8 in 5 min. At the same time, when iron electrodes were used, the initial pH of the solution increased to around 7.4. After this time, the pH of the solution became more stable (data not shown for the iron electrode), showing the well-known buffering capacity of the electrocoagulation system [21]. The observed iron ions profile (inset Fig. 7A) is consistent with a recent work by Mouedhen et al. [22]. The low iron concentration in solution is attributed to the poor solubility of iron species in the range of the solution pH [23]. In turn, the minimum solubility of Al ions occurs at pH $\sim$ 6.3 [24] and as the pH increases, the formation of the soluble Al(OH)$_4^-$ is favoured. Thus, when Al electrodes are used, the aluminium ion concentration increases during the electrocoagulation process (inset Fig. 7B). These results suggest the use of iron anodes for the treatment of CV by electrocoagulation.

4. Conclusions

In this work, an experimental design approach was applied to optimize the elimination of CV in water by electrocoagulation with iron or aluminium electrodes. After the evaluation and optimization of the four variables studied, initial pH, J, CV and sodium sulphate concentration, for the two kinds of anodes, the iron anodes were shown to have the highest efficiency in removing the pollutant. Using this electrode, practically all of the initial CV concentration and the COD were removed after 5 min of treatment with an energy consumption of 0.4 Wh L^{-1}. Residual concentration of iron ions in the solution was lower than 1 mg L^{-1}, and the final pH of the solution was close to neutral. Thus, the results presented in this work indicate that electrocoagulation can be effectively used for the removal of this kind of pollutant in waters.

Acknowledgements

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