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Article

Electrochemical Degradation of the Reactive Red 141 Dye on a β-PbO_2 Anode Assessed by the Response Surface Methodology

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A degradação eletroquímica do corante Vermelho Reativo 141 foi investigada por meio da aplicação da metodologia de superfície de respostas, utilizando reator filtro-prensa com anodo de β-PbO_2. A carga requerida para 90% de descoloração (Q^{90}) e a remoção da demanda química de oxigênio após 30 min de eletrólise (COD^{30}) foram utilizadas para modelar o sistema. As variáveis investigadas foram a densidade de corrente, pH, concentração de NaCl e temperatura. Baixos valores de Q^{90} (0,2-0,3 A h L^{-1}) foram obtidos em condições ácidas (pH 1-3) e em altas concentrações de NaCl (1,0-2,0 g L^{-1}), quando as espécies oxidantes Cl_2 e HOCl estão presentes. Os melhores valores para COD^{30} foram obtidos com altas densidades de corrente e em condições de pH ácido a neutro; entretanto, o consumo energético resultante torna o processo economicamente não viável. Para soluções extremamente ácidas foram obtidos valores reduzidos de consumo de energia, relacionado ao Q^{90}, em torno de 0,79 kW h m^{-3}.

The electrochemical degradation of the Reactive Red 141 dye using a filter-press reactor with a β-PbO_2 anode was investigated through the application of the response surface methodology. The charge required for 90% decolorization (Q^{90}) and the chemical oxygen demand removal percentage after 30 min electrolysis (COD^{30}) were used to model the system. The investigated independent variables were the current density, pH, NaCl concentration, and temperature. Low values of Q^{90} (0.2-0.3 A h L^{-1}) were obtained at acidic conditions (pH 1-3) and high concentrations of NaCl (1.0-2.0 g L^{-1}), when Cl_2 and HOCl are the predominant oxidant species. The best values of COD^{30} were obtained at high current densities and acidic to neutral conditions (pH 5-7); however, the consequent energy consumption makes the process not economically feasible under these conditions. For strongly acidic solutions, specific energy consumptions associated to Q^{90} as low as 0.79 kW h m^{-3} were attained.

Keywords: electrooxidation, dye degradation, Reactive-Red 141 dye, PbO_2 anode, factorial design

Introduction

The contamination of water is one of the greatest current challenges, as it is becoming a scarce natural resource. The textile industry, in particular, stands in a delicate position due to the large volumes of water used and wastewater produced during dyeing process steps.[1] Among the dyes used by this industry, the azo (-N=N-) ones are the most produced and consumed.[2,3] It should be noticed that a considerable amount of synthetic dyes are also discharged in the environment during production. The textile effluents are characterized by intense colors originated by un-reacted dyestuff, high organic loads (due to the presence of auxiliary chemicals), and oscillations in pH and temperature. Those first two characteristics make necessary the treatment of these effluents before their discharge into the environment. On the other hand, increasingly rigid environmental regulations also contribute to a search for better and more efficient treatment methods.[4] The azo dyes, as highlighted by Zidane *et al.*,[5] are a dye class that is not easily treated by conventional wastewater treatment methods.

As summarized by Martinez-Huitle and Brillas,[3] biological, physico-chemical, and chemical methods, among others, are commonly used for the treatment of industrial wastewaters. All these methods have advantages and disadvantages, although no current technology has universal application.[3,6,7] The biological treatment is commonly the most efficient and economic for wastewater chemical oxygen demand (*COD*) abatement, but is

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inefficient and time consuming for most textile effluents since the respective dye molecules are recalcitrant to microbiological degradation;[1,6,7] this recalcitrance makes the method quite inefficient for color removal. Physico-chemical methods for wastewater treatment, such as adsorption, coagulation, or filtration, are efficient for decolorization, but their application is expensive and leads to a high amount of sludge.[3] Chemical methods as well as advanced oxidation processes are also powerful techniques for dye wastewater decolorization, but are associated to high costs as well as operational problems.[3]

Considering the above, electrochemical methods might be a good option due to their versatility, easiness of implementation and pollutant high removal rates, despite electrical energy consumption. In such methods, electrode materials play an important role on the degradation efficiency, mechanism and in the resulting products. Depending on the electrode material used, the anodic oxidation of organic pollutants can be distinguished as occurring by selective oxidation (with "active" anodes) or by combustion (with "non-active" anodes).[3,8] Recently these types of anodes have been referred to as low and high oxidation power anodes, respectively.[9] Low oxidation power anodes are those that interact strongly with hydroxyl radicals (•OH), resulting in a low chemical reactivity for organics oxidation (low current efficiency for organics oxidation). On the contrary, high oxidation power anodes present a weak interaction with •OH radicals, resulting in a high reactivity for organics oxidation (high current efficiency for organics oxidation).[9] Organics oxidation mediated by other electrogenerated oxidants, like Cl_2, ClO^- and HClO, is possible in the presence of chloride ions.[3] Concerning these electrogenerated oxidants, several works have been published on their reaction schemes,[3,10,11] speciation diagrams,[10] and parameters affecting their production[11-14] (*e.g.* anode material, temperature and pH), as well as their role on the dyestuff mineralization.[13,15,16] However, the possible formation of undesirable chloro-organic derivatives, as detected in the electrochemical treatment of a tannery wastewater,[17] might be the main disadvantage of these electrogenerated oxidants.

Pure or doped PbO_2 is a high O_2-overvoltage anode material commonly used in organics electroxidation.[4,18-25] According to the criteria discussed by Kapalka *et al.*,[9] PbO_2 anodes could be classified as medium oxidation power anodes. In some cases, poor performance and problems like scaling and dissolution regarding Ti/PbO_2 electrodes were reported,[11,26] although these problems seem to be related to the substrate preparation. Nevertheless, this anode in many instances has presented good performances in the degradation of organics, sometimes similar to that of a boron-doped diamond electrode.[4,18-25]

Classical and conventional methods of studying the influence of one variable at a time require a considerable number of experiments and are time consuming. Moreover, not all combinations of variables or all their levels are taken into account. Thus, statistical methodologies, such as the Response Surface Methodology (RSM),[27] enable studying and modeling a system with respect to its variables more efficiently, in order to find and optimize the best experimental conditions.

Therefore, this work aimed to find the best experimental conditions, using RSM, for the electrochemical degradation of the Reactive-Red 141 (RR 141) azo dye on a Ti-Pt/β-PbO_2 anode.

Experimental

Chemicals

All chemicals, including $Pb(NO_3)_2$ (a.r., Acros), sodium lauryl sulfate, SLS (99%, Fisher Scientific), H_2PtCl_6 (99.9%, Aldrich), HCl (36.5%, Mallinckrodt), H_2SO_4 (98%, Mallinckrodt), HNO_3 (69-70%, Mallinckrodt), Ag_2SO_4 (a.r., JT Baker), $HgSO_4$ (a.r., JT Baker), NaCl (a.r., JT Baker), Na_2SO_4 (a.r., Qhemis), and RR 141 (Dyestar), were used as received. Doubly deionized water (Millipore Milli-Q system, ≥ 18.2 MΩ cm) was used for the preparation of all solutions.

β-PbO_2 film preparation on a Ti-Pt substrate

Firstly, both sides of Ti plates (3.1 cm × 2.7 cm, 99.9% Aldrich) were sandblasted using 60-70 µm glass microspheres, followed by cleaning for 20 min in an ultrasonic bath containing 2-propanol. Then, platinum films were electrodeposited (250 mA cm^{-2} for 10 min) on these Ti plates, using a conventional one-compartment cell with two Pt foil counter electrodes. The electrodeposition bath consisted of 20 g L^{-1} H_2PtCl_6 in 8.2 mol L^{-1} HCl at 65 ºC.[28]

The β-PbO_2 films were electrodeposited on the platinized Ti substrates in a conventional cell, using a calomel reference electrode and two AISI-304 stainless steel plates as counter electrodes. The deposition bath consisted of 0.1 mol L^{-1} $Pb(NO_3)_2$, 0.5 g L^{-1} sodium lauryl sulfate (SLS), in 0.1 mol L^{-1} HNO_3 at 65 °C.[25] The electrolysis (20 mA cm^{-2}) was carried out for the time necessary to obtain a 50 mg cm^{-2} PbO_2 film, assuming 100% faradaic efficiency. As soon as the electrodeposition was finished, the electrode was transferred to and maintained in a vessel containing deionized water initially at 65 °C, until ambient temperature was reached.

Electrochemical degradation of RR 141

The electrochemical experiments were carried out in a one-compartment filter-press reactor composed of the Ti-Pt/β-PbO_2 electrode (exposed area: 3.1 cm × 1.9 cm, each face) and two nickel plates as anode and cathodes, respectively. The experimental setup and the electrochemical reactor are schematically shown in Figures 1 and 2, respectively. In order to investigate and find the best experimental conditions for the RR 141 electrochemical degradation, RSM by a central composite design (CCD) was used. The investigated variables were: current density, pH, NaCl concentration, and temperature. Five different levels (–2, –1, 0, 1, 2) were studied for each variable. Table 1 shows the range and the levels of these variables. Three replications were carried out at the design center in order to evaluate the pure error and, consequently, the lack of fit. All the experiments were carried out randomly.

Table 1. Range and codification of the independent variables (X_i) used in the experimental design

Independent variables	Coded levels				
	–2	–1	0	1	2
Current density, X_1 (mA cm^{-2})	25	50	75	100	125
pH, X_2	1	3	5	7	9
NaCl concentration, X_3 (g L^{-1})	0	0.58	1.17	1.75	2.34
Temperature, X_4 (°C)	15	25	35	45	55

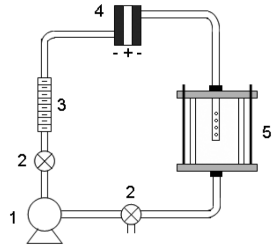

Figure 1. Experimental setup for the electrochemical treatment of the Reactive Red 141 dye: (1) magnetic pump; (2) valves; (3) rotameter; (4) filter-press reactor; (5) reservoir.

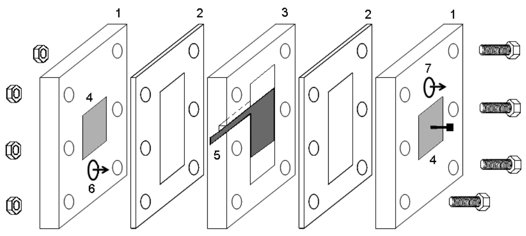

Figure 2. Schematic representation of the filter-press reactor used in the electrolyses of solutions of the Reactive Red 141 dye at laboratory scale: (1) end plates and cathode holder; (2) silicon membrane spacers; (3) middle plate and anode holder; (4) nickel plate cathode; (5) Ti-Pt/β-PbO_2 anode (exposed area: 3.1 cm × 1.9 cm, each face); (6) solution inlet; (7) solution outlet. The inter electrode gap is 5 mm.

The RR 141 concentration in a 0.1 mol L^{-1} Na_2SO_4 solution was fixed at 100 mg L^{-1}. Other fixed parameters were the dye solution volume (0.4 L) and the flow rate (360 L h^{-1}).

Analyses

The electrochemical performance was analyzed through solution color and *COD* removals. The decolorization was monitored *in situ* (at 544 nm) by pumping the dye solution from the electrochemical system reservoir to an UV-Vis spectrophotometer (Ultrospec 2100 pro, from Amersham Pharmacia Biotech), and then back to the reservoir. The charge *per* unit volume of the electrolyzed solution required for 90% decolorization (Q^{90}) was used to model the electrochemical system performance.

The *COD* measurements were carried out after 30 min of electrolysis (COD^{30}) using a 2.5-mL sample of the electrolyzed dye solution. This sample was oxidized by digestion at 150 °C for 2 h in a H_2SO_4 solution with $K_2Cr_2O_7$, Ag_2SO_4, and $HgSO_4$. The sample absorbance was read at 620 nm in a Hach DR/890 model spectrophotometer. The COD^{30} values were calculated using a previously calibrated curve and the modeling was conducted through the percentage of *COD* removal.

The quadratic equation used to model the RSM responses was $Y = \beta_0 + \Sigma\beta_i X_i + \Sigma\beta_{ii} X_i^2 + \Sigma\beta_{ij} X_i X_j$, where $\beta_{0,i,ii,ij}$ are model coefficients and $X_{i,j}$ the independent variables. Detailed description and discussion of this equation can be found in Montgomery's book.[27]

Results and Discussion

The CCD experimental matrix as well as the observed and predicted responses for COD^{30} removal (%) and Q^{90} (A h L^{-1}) are shown in Table 2. The quadratic equations that describe the COD^{30} removal and Q^{90} behaviors are given below. In these equations, non-significant coefficients were excluded based on the results for each model analysis of variance (ANOVA) and the student *t* test (at 95% confidence level).

$$Q^{90}\ (\text{A h L}^{-1}) = 0.545 + 0.003X_1 + 0.134X_2 - 0.140X_3 + 0.084X_4 + 0.006X_1^2 - 0.051X_2^2 + 0.117X_3^2 + 0.053X_4^2 - 0.017X_1X_2 - 0.019X_1X_4 + 0.073X_2X_3 + 0.056X_2X_4 - 0.006X_3X_4$$

$$COD^{30}\ (\%) = 90.0 + 11.9X_1 - 5.6X_3 - 2.0X_4 - 4.2X_1^2 - 10.0X_2^2 - 10.4X_3^2 - 5.1X_4^2 - 4.1X_1X_2 - 3.4X_1X_3 + 2.6X_1X_4 - 5.5X_2X_3 + 10.6X_3X_4$$

According to the *F*-test, the Q^{90} modeling presented a considerable lack of fit ($F_{10,2\ (95\%)} = 170.0$). However, the

Table 2. Central composite design matrix for the eletrooxidation of the Reactive Red 141 dye and respective predicted and observed charges (90% decolorization) and COD removal

Exp	*I*	pH	NaCl	Temperature	Charge / (A h L^{-1})		*COD* removal / %		SEC* / (kW h m^{-3})
					Predicted	Observed	Predicted	Observed	
1	–1	–1	–1	–1	0.676	0.539	56.2	69.4	2.83
2	–1	–1	1	1	0.346	0.343	53.5	41.8	1.57
3	–1	1	–1	1	1.051	1.054	45.0	46.0	4.88
4	–1	1	1	–1	0.598	0.719	38.9	28.3	3.68
5	1	–1	–1	1	0.782	0.723	69.8	68.9	4.30
6	1	–1	1	–1	0.341	0.392	61.6	40.9	2.60
7	1	1	–1	–1	0.732	0.797	92.5	92.7	5.61
8	1	1	1	1	0.839	1.030	64.8	32.0	5.95
9	1	–1	–1	–1	0.754	0.687	89.8	86.7	4.78
10	–1	1	–1	–1	0.720	0.637	75.3	71.4	3.31
11	–1	–1	1	–1	0.263	0.325	41.7	32.7	1.66
12	1	1	1	–1	0.610	0.699	42.5	57.6	4.73
13	–1	–1	–1	1	0.782	0.668	25.9	23.1	3.16
14	1	1	–1	1	0.985	0.907	72.6	85.7	5.57
15	1	–1	1	1	0.346	0.405	83.9	100.0	2.43
16	–1	1	1	1	0.905	0.956	50.8	58.1	4.35
17	0	0	0	0	0.545	0.560	90.0	70.1	3.10
18	0	0	0	0	0.545	0.533	90.0	100.0	3.00
19	0	0	0	0	0.545	0.542	90.0	100.0	3.09
20	–2	0	0	0	0.565	0.634	49.6	54.1	2.62
21	2	0	0	0	0.577	0.470	97.1	100.0	3.23
22	0	–2	0	0	0.073	0.196	50.0	48.7	0.78
23	0	2	0	0	0.611	0.450	50.0	58.8	2.46
24	0	0	–2	0	1.290	1.544	59.4	47.3	8.89
25	0	0	2	0	0.732	0.441	37.1	56.6	2.36
26	0	0	0	–2	0.591	0.560	73.6	79.3	3.58
27	0	0	0	2	0.926	0.919	65.6	67.2	4.55

* Specific energy consumption related to the charge used for 90% decolorization.

observed and the predicted Q^{90} values presented a good correlation as shown in Figure 3a. On the other hand, the COD^{30} removal modeling was satisfactorily adjustable ($F_{10,2\ (95\%)} = 1.1$), with a significant correlation between the observed and predicted percentage values (Figure 3b).

Figure 4 shows some of the response surfaces for Q^{90} as a function of the independent variables: NaCl concentration and pH (Figure 4a), temperature and pH (Figure 4b), and current density and pH (Figure 4c). Among these variables, pH is the most important due to different chloro-species generation. The current density and the NaCl concentration determine the rate and amount of the generated chloro-species, respectively. The temperature determines mainly the oxidants diffusion rate, as well as the chloro-species generation and stabilization.

Figure 4a (data obtained at 35 °C and using 75 mA cm^{-2}) shows that the best operational conditions (low Q^{90} values) occur for very low pH values and high NaCl concentrations. According to the literature,[3,10,16,22] the predominant active chlorine species in these conditions are Cl_2 and HClO:

$$2Cl^-(aq) \rightarrow Cl_2(aq) + 2e^- \qquad (1)$$

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + Cl^-(aq) + H^+(aq) \qquad (2)$$

As these species have a higher oxidation potential than the OCl^- species, which are mainly produced in neutral to basic conditions (pH ≥ 7), the mediated oxidation of the chromophore double bonds is rapidly accomplished.

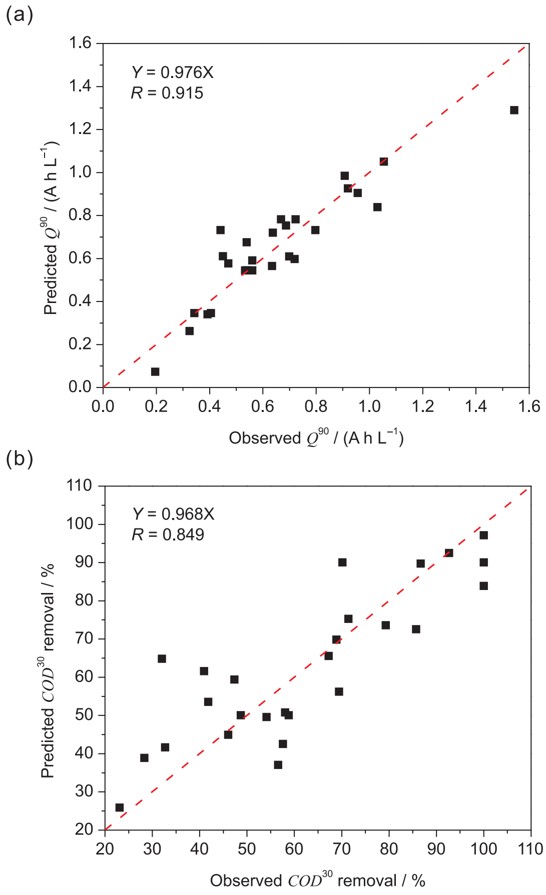

Figure 3. Observed and predicted plot for: (a) charge required for 90% decolorization and (b) *COD* removal after a 30 min electrolysis.

Figure 4b (data obtained using 75 mA cm^{-2} and 1.17 g L^{-1} NaCl) shows that Q^{90} has a region of minimum at 35 °C and very low pH values. This is consistent with the temperature associated to the results presented in Figure 4a. The increase in Q^{90} at temperatures lower than 35 °C is probably due to a decrease in the reaction rate. On the other hand, the increase in Q^{90} at temperatures higher than 35 °C is possibly due to a lower Cl_2 solubility, as well as increased O_2 evolution reaction or waste chemical reactions:[3,12,13,20]

$$2HOCl(aq) + OCl^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq) + 2H^+(aq) \quad (3)$$

$$2ClO^-(aq) \rightarrow 2Cl^-(aq) + O_2(g) \quad (4)$$

$$ClO^-(aq) + H_2(g) \rightarrow H_2O(l) + Cl^-(aq) \quad (5)$$

$$Cl_2(aq) \rightarrow Cl_2(g) \quad (6)$$

That is why Q^{90} increases faster at high temperatures than at low temperatures, as the pH increases.

Figure 4c (data obtained at 35 °C and using 1.17 g L^{-1} NaCl) also shows the best operation conditions at very low

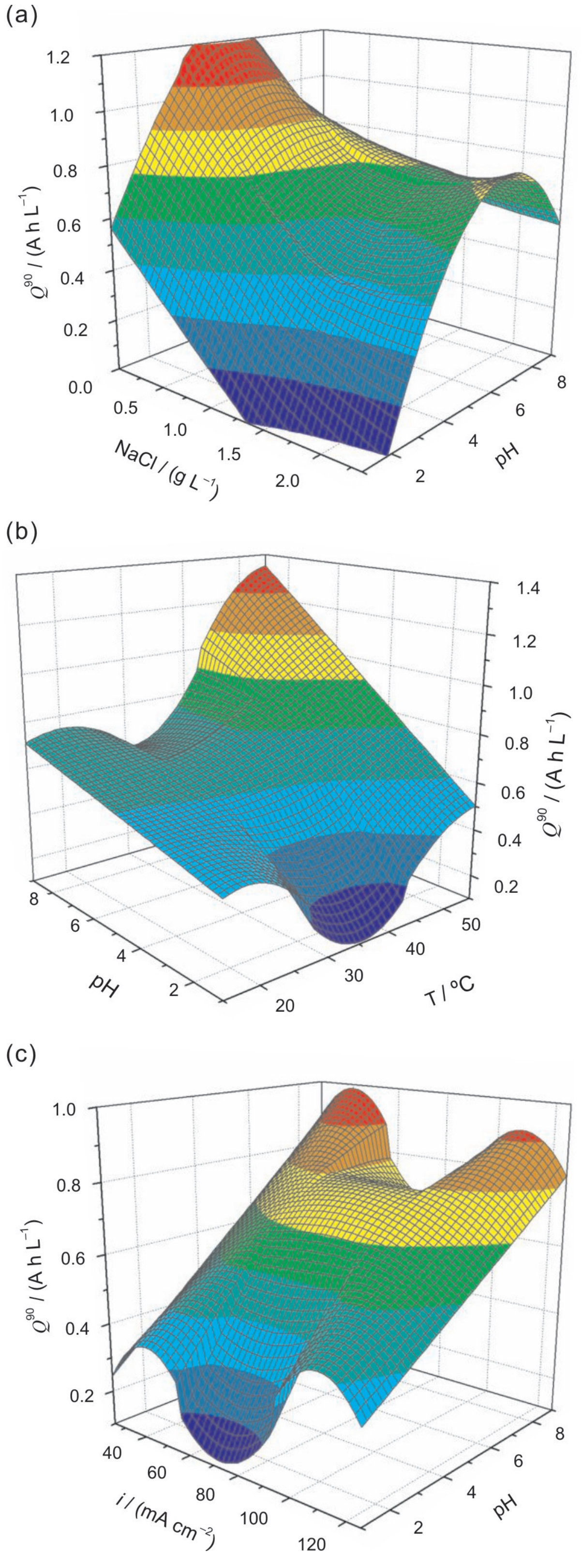

Figure 4. Response surfaces for the charge required for 90% decolorization, as a function of: (a) pH and NaCl concentration (at 35 °C and using 75 mA cm^{-2}), (b) pH and temperature (using 75 mA cm^{-2} and 1.17 g L^{-1} NaCl) and (c) pH and current density (at 35 °C and using 1.17 g L^{-1} NaCl).

pH values, at which, clearly Q^{90} has a minimum value region at about 70 mA cm^{-2}. These conditions are related to Cl_2 and HOCl generation. The high values of Q^{90} at low and high current densities (two maxima) are possibly related to the amount of generated oxidants and to their waste chemical reactions, respectively.

The response surfaces for COD^{30} removal are shown in Figure 5. In order to compare Q^{90} and COD^{30} removal, the response surfaces of the latter are represented as a function of the same independent variables as in Figure 4. Figure 5a (data obtained at 35 °C and using 75 mA cm^{-2}) shows that the best pH conditions for COD^{30} removal are different from those for Q^{90}. The optimal pH region (5 to 7) corresponds to slightly acidic to neutral solutions. Additionally, high NaCl concentrations seem to be unnecessary in the electroxidation of solutions containing the RR 141 dye. Different pH conditions for *COD* and color removals are not new in the literature.[3,12,15,16,26] These results indicate that the dye molecule is slowly mineralized by the Cl_2 and HClO species, mainly due to their low solubility in the solution (reaction 6). On the other hand, neutral to basic conditions (pH ≥ 7) favor the production of high amounts of the OCl^- species:

$$HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq) \tag{7}$$

As this oxidant concentration increase, a greater *COD* removal is more likely to be accomplished despite its lower oxidation potential.

Figure 5b (data obtained using 75 mA cm^{-2} and 1.17 g L^{-1} NaCl) shows that the COD^{30} removal is nearly independent of the pH at the lowest (< 20 °C) and highest (55 °C) temperatures. The highest COD^{30} removals were attained at the lowest temperature because at the highest temperature this removal tends to deteriorate due to the oxidant waste reactions (equations 3 to 6). Hence, the maximum rates of degradation are achieved at around 35 °C and pH 5. It should be recalled that low Q^{90} values were also optimized at conditions around 35 °C.

The COD^{30} removal response surface as a function of pH and current density is shown in Figure 5c (data obtained at 35 °C and using 1.17 g L^{-1} NaCl). The value of COD^{30} removal increases sharply with the current density due to the high rates of oxidants electrogeneration. In these conditions the low pH values lead to the best COD^{30} removal performances owing to the higher concentrations of the Cl_2 and HClO species, which have higher oxidation potentials than the OCl^- species.

The lowest values of specific energy consumption attained for Q^{90} were 0.78 kW h m^{-3}, for strongly acidic solutions (experiment 22: 75 mA cm^{-2}, 1.17 g L^{-1} NaCl,

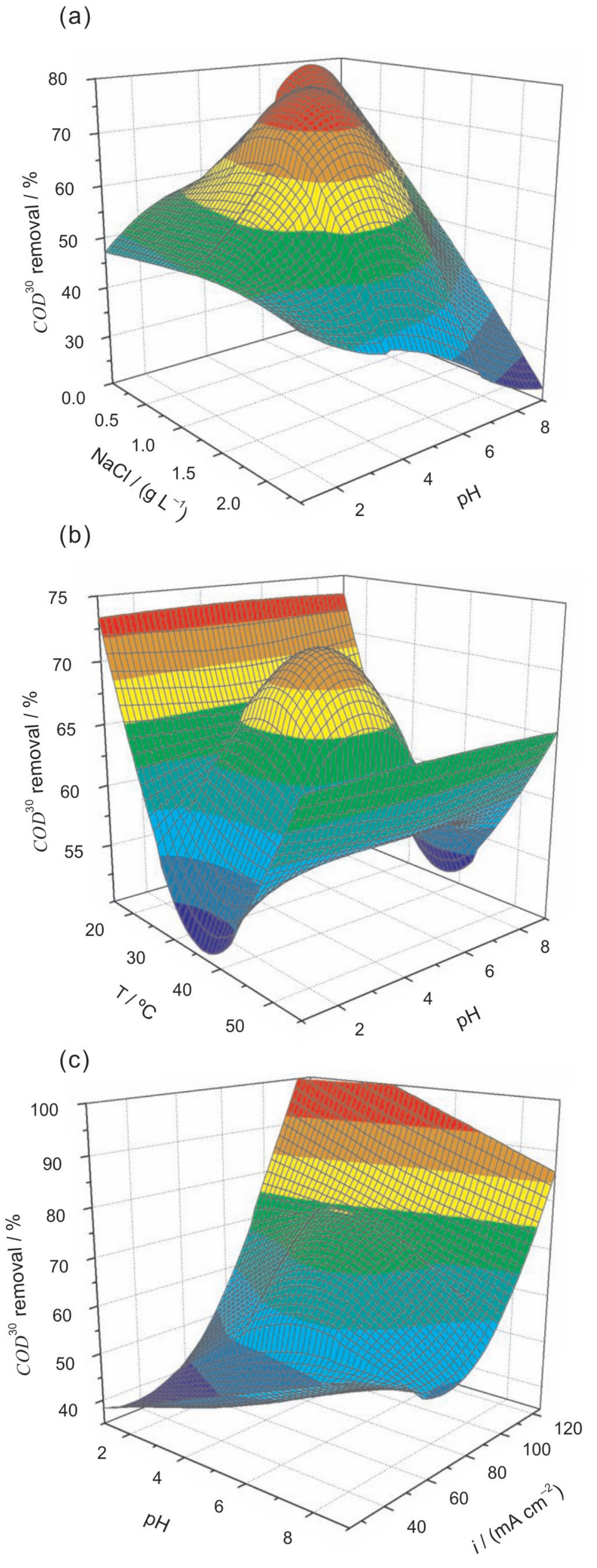

Figure 5. Response surfaces for the *COD* removal percentage after a 30 min electrolysis, as a function of: (a) pH and NaCl concentration (at 35 °C and using 75 mA cm^{-2}), (b) pH and temperature effects (using 75 mA cm^{-2} and 1.17 g L^{-1} NaCl) and (c) pH and current density effects (at 35 °C and using 1.17 g L^{-1} NaCl).

and 35 °C), and about 1.6 kW h m^{-3}, independently of the temperature (experiments 2 and 11: pH 3, 50 mA cm^{-2} and 1.75 g L^{-1} NaCl). These values are much lower than the ones reported by Rajkumar and Kim,[16] who, using a dimensionally stable anode (36 mA cm^{-2}, 100 ppm RR 141, initial pH 6.2-6.5, 1.5 g L^{-1} NaCl and 25 °C), reported a value of 3.453 kW h m^{-3} to attain at least 95% decolorization.

Finally, as it was mentioned before, the possible formation of undesirable chloro-organic derivatives might be a disadvantage of oxidants electrogenerated from chloride ions. This possibility will be investigated in a future work on the electroxidation of the RR 141 dye.

Conclusions

Application of RSM allowed investigating a high number of variables that affect the electrochemical degradation of the RR 141 dye, leading to knowledge of their effects and interactions. The results obtained for the decolorization of the dye solution and its *COD* removal clearly showed that different experimental conditions are needed in each case. In the presence of chloride ions, the pH was the most significant variable affecting these conditions. This fact is strongly related to the nature and amount of oxidant species generated: *i*) Cl_2 and HOCl at acidic conditions (pH 3) for decolorization and *ii*) OCl^- at neutral or basic conditions (pH ≥ 7) for *COD* removal. Finally, RSM applied to the RR 141 electrochemical degradation allowed optimizing the experimental conditions to attain low values of the specific energy consumption, especially when compared to the values reported in the literature.

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