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Catalysis Today 107–108 (2005) 68–76

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Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent

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Abstract

The experimental design methodology was applied having in mind the optimization of the azo dye Orange II degradation using the Fenton's reagent (mixture of H_2O_2 and Fe^{2+}). The variables considered were the temperature, H_2O_2 concentration and Fe^{2+}:H_2O_2 ratio, for a dye concentration of 0.3 mM and pH 3. The multivariate experimental design allowed to develop quadratic models for: (i) color removal and (ii) total organic carbon (TOC) reduction (both after 2 h of reaction), which were adequate to predict responses in all the range of experimental conditions used. Under the optimum conditions, performances of 99.7 and 70.7% for color and TOC removal, respectively, were experimentally reached. It was found that both H_2O_2 concentration and temperature have an important effect in the organic matter degradation efficiency.

Keywords: Experimental design; Orange II; Fenton's reagent; Hydrogen peroxide; Oxidation

1. Introduction

The textile industry, of great importance in the Portuguese economy, produces large quantities of effluents that contain significant concentrations of organic matter. These wastewaters often contain some color after treatment, being then directly launched into the rivers and others water courses. However, more problematic than the aesthetic aspect is the environmental impact that a discharge of this type of compounds has, because some of them are toxic for certain species [1]. Therefore, the removal/degradation of dyes from wastewaters is a great challenge for the related industries.

The main currently used techniques for decontamination of waters proceeding from the textile industry involve adsorption processes with activated carbon. However, these processes may be costly, inefficient and often produce a high amount of secondary wastes. Ozone and hypochlorite oxidations are efficient decolorizing methods, but they are not desirable because of the high cost of equipment, operating costs and the secondary pollution arising from the residual chlorine [2].

Recent progress in the removal of dyes has led to the development of advanced oxidation processes (AOPs). Among them, the oxidation using Fenton's reagent has proved to be a promising and attractive treatment method for the effective decolorizing and degradation of dyes, as well as for the destruction of a large number of hazardous and organic pollutants [1–4]. Besides, the process is simple and non-expensive, taking place at low temperatures and atmospheric pressure [5]. Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide, and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H_2O_2 [6]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (1)$$

However, to achieve high performances, the experimental conditions must be optimized. And this is not an easy task since in Fenton oxidation several parameters affect the oxidation efficiency, like the pH of the reaction medium, the temperature, the hydrogen peroxide concentration and

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doi:10.1016/j.cattod.2005.07.060

the amount of catalyst used, usually expressed as the Fe^{2+}:H_2O_2 ratio. Although many researchers have usually only focused on the single-factor-at-a-time approach, studying the effect of each experimental parameter on the process performance while keeping all other conditions constant, this approach does not take into account cross-effects from the factors considered and leads to a poor optimization result. When a multifactor system is present, it is more appropriate to employ statistically based optimization strategies to achieve such goal, with the minimum number of experiments [7,8]. Indeed, an alternative to the above-mentioned strategy is the experimental design approach, which implies the use of statistical tools that allow the simultaneous change of several variables (multivariate analysis) [7]. The experimental design methodology is a modern approach, which has been widely used in several applications (e.g., [9–11]), also allowing the modeling of the process. In fact, the design of experiments (DOE) is used to identify or screen the important factors affecting a process or product and to develop statistically significant empirical models.

This study concerns the degradation of the non-biodegradable azo dye Orange II by Fenton's reagent. As azo dyes are extensively used in textile dyeing and finishing processes [12], Orange II was selected as the test chemical to represent the concerned dye group because it is inexpensive and very used in the textile, pulp and paper industries. It is also a main goal of the present work to find the optimum conditions to maximize both color and total organic carbon (TOC) removal, and so a DOE tool will be used.

2. Materials and methods

Chemical oxidation of an aqueous solution of the azo dye Orange II was conducted in a stirred jacketed glass batch reactor, with 0.3 L capacity, being the temperature controlled through a Huber thermostatic bath (Polystat CC1 unit). The reactor was equipped with a Falc F30ST magnetic stirrer for continuous stirring of the reaction mixture, and a thermometer was used to assess the temperature in the aqueous phase. The absorbance and the pH were continuously monitored, using a Philips PU8625 UV/VIS spectrophotometer and a pH-meter from EDT instruments (RE 357 TX), respectively. For on-line absorbance measurements (at $\lambda_{max} = 486$ nm), a flow-through cell was used, being the recirculation of the solution made with the help of a Watson-Marlow 5055 peristaltic pump, at a flow-rate of 100 mL/min. Data acquisition (at a frequency of 0.2 s^{-1}), with displaying and saving capabilities in a PC, was performed using a home-designed interface with the software Labview 5.0, from National Instruments.

The dye, Orange II ($C_{16}H_{11}N_2NaO_4S$) from Fluka p.a., was used as received. In all experiments a reaction volume of 0.2 L was used, with a 0.3 mM dye concentration (to which corresponds a total organic carbon content of 58.6 mg/L) and the runs were carried out at pH 3.0. This pH value was set based on previous experimental results [13] and agrees with literature findings, as it is usually accepted that acidic pH levels near 3 are usually optimum for Fenton oxidation [1,2,14]. Therefore, in all the runs the initial pH was adjusted to 3.0 through addition of 1 M NaOH or 0.1 M H_2SO_4 solutions. Then, solid iron sulfate ($FeSO_4 \cdot 7H_2O$, from Panreac) was added, followed by the hydrogen peroxide solution (30%, w/w, from Merck), with intermediate pH adjustment when necessary. Time zero coincides with the H_2O_2 addition, and experiments were run up to 120 min.

Total organic carbon was measured by catalytic oxidation followed by IR spectrometry for CO_2 quantification using a Shimadzu 5000A instrument, model TOC-5000 CE, equipped with an automatic sample injector. TOC values represent the average of at least two measurements. For such analysis samples were withdrawn from the reactor at several times, and reaction was stopped by adding excess Na_2SO_3, which instantaneously consumes the remaining hydrogen peroxide.

A design of experiments approach was used to model and optimize the process performance. The model considered to describe our data was a second-order polynomial, and the corresponding coefficients were calculated from the experimental responses by means of least squares regression, using the JMP501 software [15].

3. Results and discussion

Fig. 1 shows the dye molecule, which is basically consisted by an azo (N=N) linkage, a benzene ring and a naphthalene ring, all of them exhibiting different absorbance peaks. Indeed, the chromophore containing azo linkage has absorption in the visible region, while the benzene ring and the naphthalene ring absorb in the UV region. Besides, the naphthalene ring absorption wavelength is higher than that of the benzene ring. The exact values can be seen in Fig. 2, which shows the UV–vis spectra recorded before and after oxidation. The spectrum recorded for the original dye solution is the expected one [16,17], with the characteristic absorbance peaks at around 228, 310 and 486 nm. Fig. 2 also puts into evidence that the treated dye sample was almost colorless and did not show significant absorbance in the visible region, indicating that color removal was practically complete (for the employed conditions). Indeed, the disappearance of the absorbance signal at 486 nm reflects, unequivocally, an almost complete decolorizing and the breakdown in the chromophore group. However, the

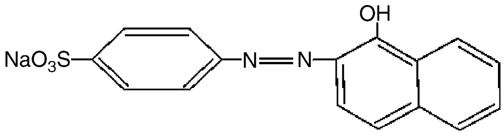

Fig. 1. Chemical structure of the Orange II dye.

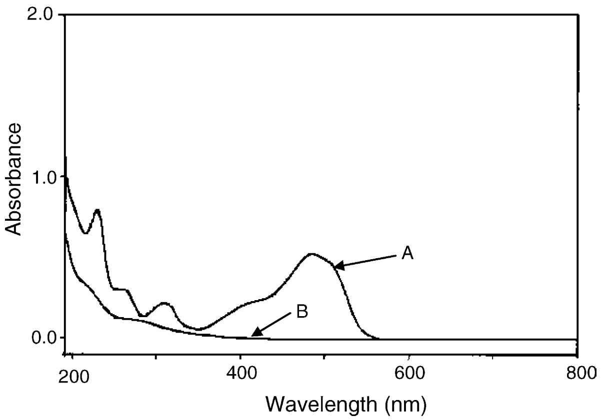

Fig. 2. UV–vis absorption spectra of Orange II before (A) and after (B) oxidation, in the following conditions: $T = 28.9$ °C, $[H_2O_2] = 10.0$ mM and $Fe^{2+}:H_2O_2$ ratio = 0.125 (w/w); initial pH 3.0.

spectrum in the UV region shows that the dye was not mineralized completely, though absorption reduced over the UV range. The diminution of the absorbance peak at 228 nm is related to the cleavage of the benzene group present in the original structure of the dye (cf. Fig. 1).

Blank experiments showed that neither decolorizing nor mineralization of Orange II occurs in the presence of Fe^{2+} ions alone (Fig. 3a and b). Color removal was also negligible in the presence of only H_2O_2 (Fig. 3a), but in such conditions a slight TOC reduction was noticed (Fig. 3b). In this case, i.e. without the iron catalyst, the amount of hydroxyl radicals formed is almost insignificant, but the own oxidant action of H_2O_2 justifies the results obtained. Indeed, although hydrogen peroxide has an oxidation potential (1.78 V) much smaller than that of hydroxyl radicals (2.80 V), it is nevertheless not negligible [5]. The fact that no color removal is observed in such run, though TOC slightly decreases, may be ascribed to the attack of the H_2O_2 molecule to other parts of the dye (e.g., aromatic rings) rather than to the azo double bond (N=N) in the chromophore group. In addition, it is also reasonable to take into account the dissociation of the hydrogen peroxide molecule to form $OH^{\bullet}$ species, which may attack the azo double bonds or the aromatic rings [2]. However, at low radical concentrations, Dutta et al. [3] found that they preferentially attack the benzene ring of a dye (methylene blue) molecule.

In Fig. 3 are also shown, merely as illustrative examples, some other curves, which illustrate that after 2 h of oxidation decolorizings as high as 99.0% can be achieved, but after 10 min of operation a color removal of 97% was already reached. Simultaneously, it is possible to attain mineralization efficiencies above 70% in 2 h of operation.

For most of the experiments where a significant color (and/or TOC) removal was reached, it is evident that the process is much faster in the first 5–10 min, and then it proceeds at a slower reaction rate. Recently, we have found a similar behavior during cork cooking wastewater mineralization [18], while Malik and Saha [2] also found that direct dyes are decomposed in a two-stage reaction with Fenton's reagent. In the first stage dyes are decomposed rapidly and somewhat less rapidly in the second stage. The main reason for this well-known behavior is that ferrous ions react very quickly with hydrogen peroxide (rate constant is 53 $mol^{-1}\,dm^3\,s^{-1}$) to produce large amounts of hydroxyl radicals (Eq. (1)), which can then react rapidly with the dye (so-called Fe^{2+}/H_2O_2 stage) [2]. Ferric ions produced can react with H_2O_2 to produce hydroperoxyl radicals ($HO_2^{\bullet}$) and restore ferrous ions through the following reaction scheme [19,20]:

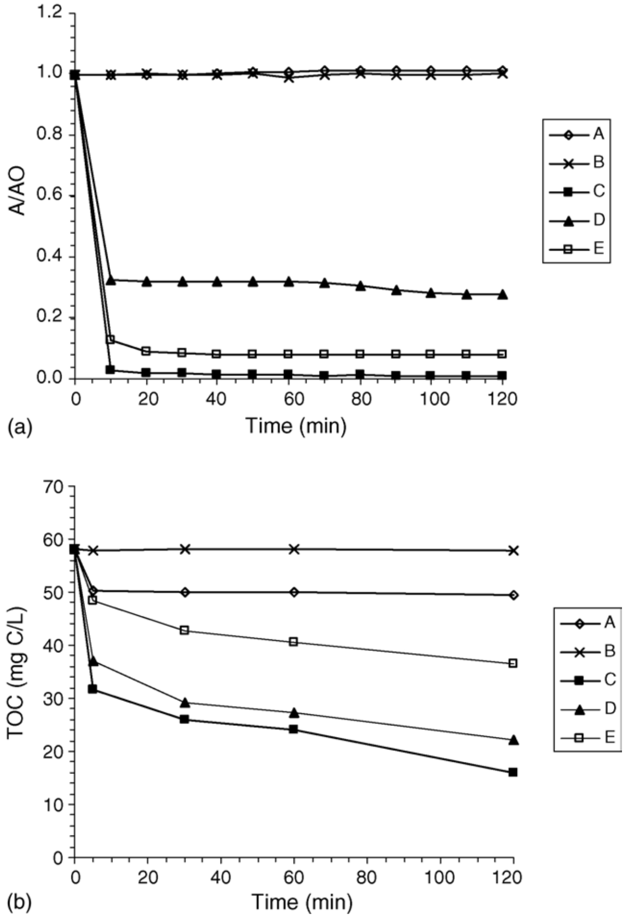

Fig. 3. Color leaching (a) and mineralization (b) of the Orange II solution (0.3 mM) as a function of time, using: (A) H_2O_2 alone ($T = 30$ °C and $[H_2O_2] = 9.0$ mM); (B) Fe^{2+} alone ($T = 30$ °C and $[Fe^{2+}] = 0.7$ mM); (C) run 1; (D) run 2; (E) run 3 (see experimental conditions in Table 1). Experiments were performed at initial pH 3.0. In absorbance curves, the number of experimental points was reduced for a better visualization.

$$Fe^{3+} + H_2O_2 \leftrightarrows Fe{-}OOH^{2+} + H^+ \qquad (2)$$

$$Fe{-}OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \qquad (3)$$

However, the reaction rate for iron regeneration is much slower than that in Eq. (1) (rate constant is now 0.02 $mol^{-1}\,dm^3\,s^{-1}$) [2]. Consequently, the rate of oxidation in the second stage (Fe^{3+}/H_2O_2 stage) is slower than in the first one due to the slow production of Fe(II) from Fe(III). Concluding, we can say that the reaction rate decrease on the second stage of the Fenton oxidation is basically due to the fact that ferrous ions are consumed quickly, but reproduce slowly. Consequently, the oxidation rate of organic compounds is fast when large amounts of ferrous ions are present because large amount of hydroxyl radicals are produced. However, due to the slow Fe^{2+} production/regeneration, the Fenton's reaction slows down. Moreover, the hydroperoxyl radicals produced in the second stage have a much smaller oxidation potential compared to $OH^{\bullet}$ [5], thus also justifying the slower oxidation rate in the second step. Finally, there are several competitive reactions that also consume hydroxyl radicals, or reactions with the intermediate products formed from the dye decomposition when the process advances, which hinder the decay of the parent compound. In conclusion, there are several factors that contribute to the decrease of the Orange II decomposition rate at higher times of reaction, and this is the reason why several authors proposed two kinetics schemes for the Fenton's reaction of organic compounds. The experimental results of this work also demonstrate this situation.

A central composite design (response surface design) was carried out considering the minimum and maximum levels for temperature (10–50 °C), H_2O_2 concentration (3–15 mM) and Fe^{2+}:H_2O_2 ratio (0.05–0.2, w/w). It is noteworthy that the ranges considered for the three studied variables were chosen based on literature findings [1–3,12,14], as well as in experiments previously performed by our group [13]. Assuming a second-order polynomial model, at least 13 experiments must be carried out to solve the matrix (including the cross-effects between variables and two centre points), for which software JMP 501 was used. Table 1 shows the description of the experiments and the relationship between codified and real values. Low and high levels are denoted by (−1) and (+1), respectively, and the central points as (0). It is noteworthy that the methodology used requires that experiments outside the experimental range previously defined should be performed to allow prediction of the response outside the cubic domain (denoted as +1.682).

As above-mentioned, the objective functions to maximize are both the color and TOC removal (after 120 min of oxidation). These are the responses, which we will call Y_1 and Y_2, respectively. The 13 experiments indicated in Table 1 were then performed in a random order to minimize systematic errors, and the response factors evaluated. Table 2 shows the experimental responses. The coefficients of the quadratic model in the polynomial expression were then calculated by multiple regression analysis, using the above-mentioned DOE software. It must be stressed that such coefficients represent the weight of each variable by itself, the weight of the quadratic effect and the weight of the first-order interactions between the coded variables. Eqs. (4) and (5) represent the two responses, where Y_1 and Y_2 are in %:

$$\begin{aligned}Y_1 = {} & 98.42(\pm 4.47) + 4.52(\pm 2.16)A_2 - 2.73(\pm 2.16)A_3 \\ & - 5.26(\pm 2.69)A_2^2 - 2.71(\pm 2.69)A_3^2 \\ & - 4.00(\pm 2.24)A_1A_2 - 5.75(\pm 2.24)A_1A_3 \\ & - 3.75(\pm 2.24)A_2A_3 \end{aligned} \tag{4}$$

$$\begin{aligned}Y_2 = {} & 56.92(\pm 5.22) + 8.02(\pm 2.52)A_1 + 19.02(\pm 2.52)A_2 \\ & - 2.73(\pm 2.52)A_3 - 5.39(\pm 3.15)A_1^2 \\ & - 11.93(\pm 3.15)A_2^2 - 2.75(\pm 2.62)A_1A_3 \end{aligned} \tag{5}$$

Table 2
Experimental results of the experimental design for Orange II oxidation

Run no.	Experimental results	
	Y_1	Y_2
1	99.0	72.3
2	72.1	62.0
3	92.1	37.0
4	91.6	66.5
5	80.2	22.8
6	97.8	56.4
7	74.7	14.1
8	96.2	61.0
9	86.1	19.1
10	97.9	60.3
11	93.9	47.7
12	98.1	58.2
13	98.4	55.7

Responses considered are: Y_1—color removal (%) and Y_2—TOC removal (%).

Table 1
Codified and experimental values of the experimental design

Run no.	Codified values			Experimental values		
	Temperature	$[H_2O_2]$	Fe^{2+}:H_2O_2	Temperature (°C)	$[H_2O_2]$ (mM)	Fe^{2+}:H_2O_2 (w/w)
1	+1	+1	−1	50	15	0.05
2	+1	+1	+1	50	15	0.2
3	+1	−1	−1	50	3	0.05
4	0	0	+1.682	30	9	0.25
5	+1	−1	+1	50	3	0.2
6	−1	+1	−1	10	15	0.05
7	−1	−1	−1	10	3	0.05
8	0	+1.682	0	30	19.09	0.125
9	−1	−1	+1	10	3	0.2
10	+1.682	0	0	63.63	9	0.125
11	−1	+1	+1	10	15	0.2
12	0	0	0	30	9	0.125
13	0	0	0	30	9	0.125

where

$$A_1 = \frac{X_1 - 30}{20}; \qquad A_2 = \frac{X_2 - 9}{6}; \qquad A_3 = \frac{X_3 - 0.125}{0.075} \tag{6}$$

X_1, X_2 and X_3 denote the variables temperature, H_2O_2 concentration and Fe^{2+}:H_2O_2 ratio, respectively. Since the different factors present different units, they are given in the form of dimensionless coded variables (A_1–A_3) in order to permit comparison between them. It must be remarked that in the cases where the error in Eqs. (4) and (5) was equal or higher than the corresponding coefficient, the associated variable, quadratic effect or first-order interaction was ignored and was not expressed in the models, as usual [7].

As can be seen in Fig. 4, the values predicted by the second-order models agree very reasonably with the experimental data. For instance, in what concerns the color removal, relative errors are always below 9.2% (with an average of 3.2%). Even for the other response, both values are very close, indicating a good correspondence between the model prediction and the experiments (average relative error of 8.9%). In addition, the analysis of variance yielded significance probabilities (F-test) of 95.2 and 95.9% for color and TOC removal, respectively (95% confidence level), thus evidencing the existence of a regression effect [15].

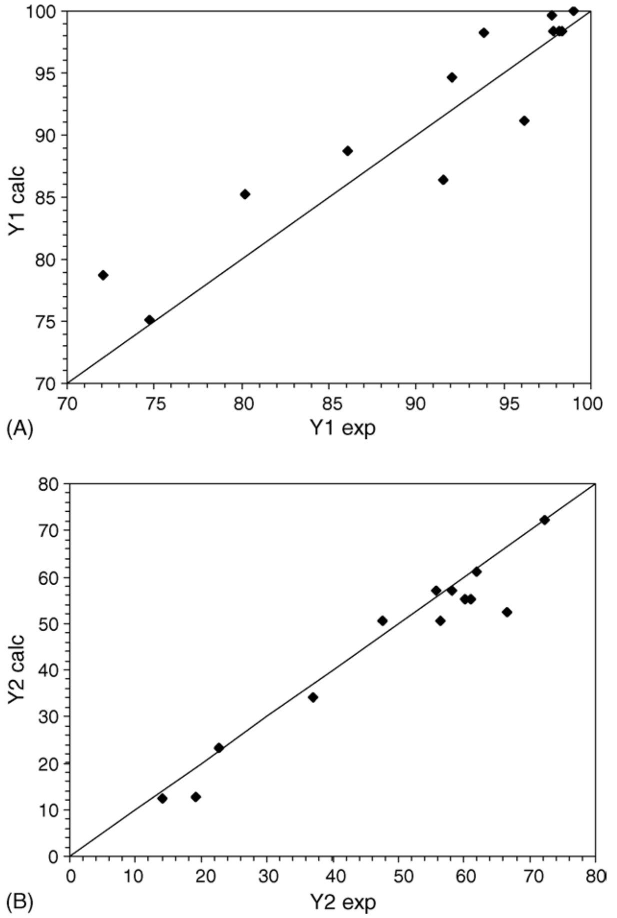

Fig. 4. (A and B) Experimental and calculated results of the experimental design for Orange II oxidation. Responses considered are: Y_1—color removal (%) and Y_2—TOC removal (%).

Considering just the first-order effects of each variable in Eqs. (4) and (5), it is clear that the main factor that affects color removal is the H_2O_2 concentration, while for TOC reduction temperature also plays a significant role. In both cases, all the cross- and quadratic effects are negative, suggesting that optimum values must exist for each parameter, as discussed below.

Fig. 5 presents the response surface modeling in a three dimensional representation to put into evidence the effects of temperature, H_2O_2 concentration and Fe^{2+}:H_2O_2 ratio on the color removal after 2 h of reaction. As a general trend, we can see that depending on the reaction temperature, the H_2O_2 concentration and Fe^{2+}:H_2O_2 ratio may have a positive or negative effect on dye decolorizing (Fig. 5A). Indeed, for low temperatures both parameters seem to affect positively the final performance, while for high temperatures an excessive oxidant load may have a detrimental effect. At the highest temperature ($T = 50$ °C) low catalyst doses are required, possibly because reactions are faster. A similar behavior is noticed when changing the temperature and H_2O_2 concentration, at constant Fe^{2+}:H_2O_2 ratio (Fig. 5B). Thus, we can say that all variables may affect positively or negatively the color removal, depending on the values of the other experimental conditions (cross-effects). This justifies the use of DOE tools for process optimization. It must however be remarked that in some cases the second-order model yields response values slightly above 100%, which is due to the error in the numerical fit and reflects the problem associated with the interpolation once very high color removal efficiencies were attained.

The fact that in some conditions very high H_2O_2 concentration values lead to a decrease in the final color leaching is possibly due to the competition between these species for hydroxyl radicals. Indeed, $OH^{\bullet}$ radicals are quite non-selective, reacting with the organic matter present but also with other species. A maximum value for the decolorizing performance is achieved with a peroxide concentration of ca. 10 mM due to the following reaction [6,14,21]:

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \tag{7}$$

Therefore, at high oxidant loads such scavenging effect becomes more significant, which leads to the non-productive decomposition of hydrogen peroxide and limits the yield of hydroxylated (oxidized) organic compounds. Although other radicals ($HO_2^{\bullet}$) are produced, their oxidation potential is much smaller than that of the $OH^{\bullet}$ species [5]. It must however be stressed that when increasing the H_2O_2 concentration, keeping the Fe^{2+}:H_2O_2 ratio constant, higher catalyst loads are employed, which may also have a scavenging effect, as discussed below (see Eq. (8)). Thus, this effect may also contribute to the decline in the overall efficiency recorded at high oxidant loads.

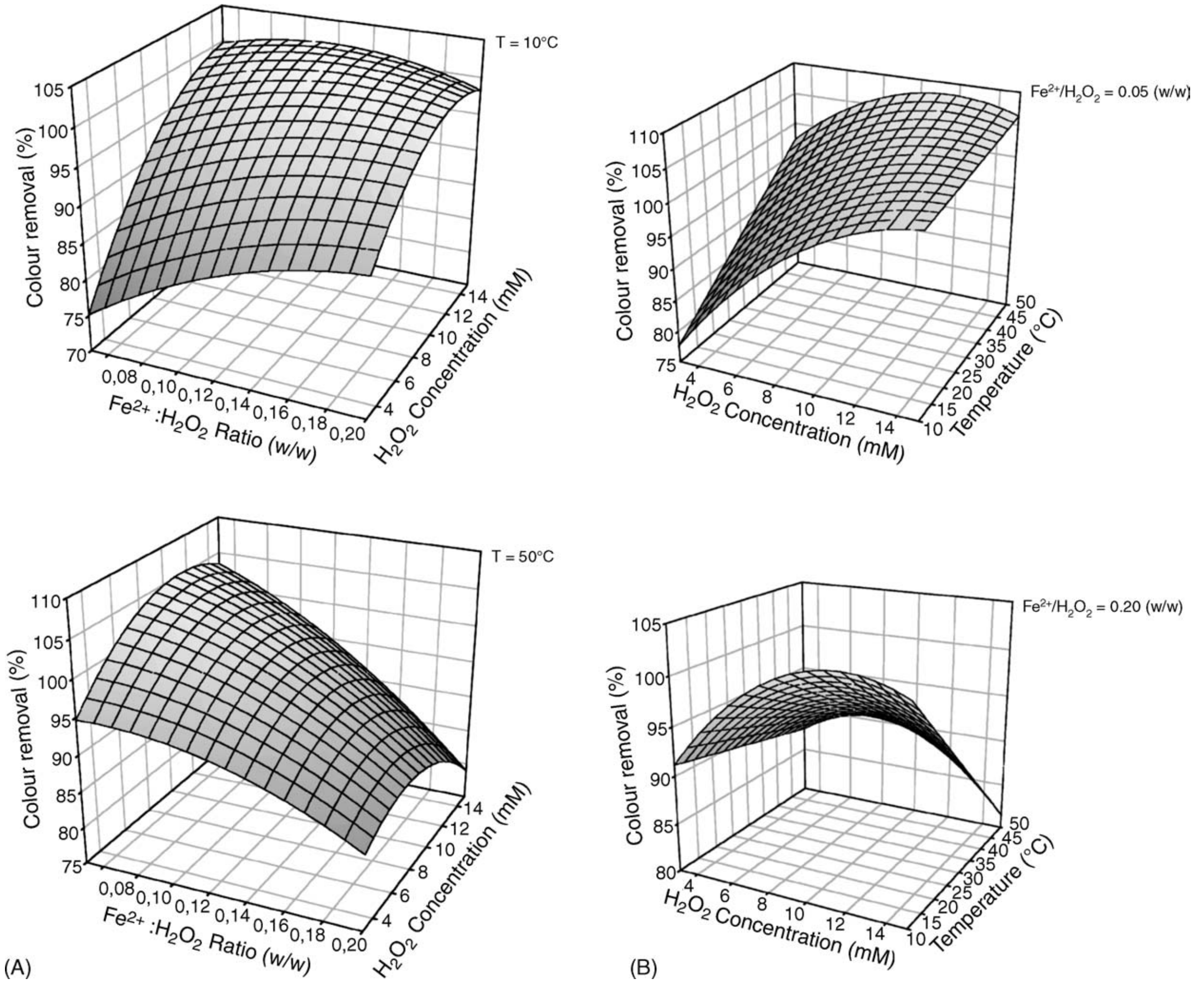

Fig. 5. Response surface showing the color removal (%) of the Orange II solution (0.3 mM) as a function of: (A) Fe^{2+}:H_2O_2 ratio and H_2O_2 concentration (for different temperatures) and (B) H_2O_2 concentration and temperature (for different Fe^{2+}:H_2O_2 ratios); initial pH 3.0.

In this work, it was found that the decolorizing rate (and also the TOC reduction rate) is strongly dependent on the amount of H_2O_2 added. But the effect caused by temperature is also considerable: when the reaction was performed at low temperatures (~10 °C) both rates decreased, due to the Arrhenius dependence of the kinetic constants. However, data shown in Fig. 5A and B refer to the performance achieved after 2 h of oxidation. It is visible that depending on the experimental conditions, the color removal may be positively affected by the reaction temperature, while in some cases high temperatures lead to a decrease in the overall performance. Thus, an optimum value must exist, what is in agreement with other results found in the literature [4,18]. Some authors report that at high temperatures hydrogen peroxide decomposition into oxygen and water becomes very fast, leading to a decline in the overall efficiency [3,4].

Finally, for the Fe^{2+}:H_2O_2 ratio an optimum range was also noticed, and this behavior was also found by other authors in the Fenton process (e.g., [2]). An increase in the Fe^{2+}:H_2O_2 ratio implies higher Fe^{2+} loads, and therefore more $OH^{\bullet}$ radicals are available for oxidation. Excess catalyst may however lead to a loss of $OH^{\bullet}$ species by the following scavenging reaction [6]:

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{8}$$

The polynomial expression in Eq. (5) was used to calculate the response surface illustrated in Fig. 6A and B, showing the TOC removal after 2 h of reaction (initial TOC = 58.6 mg/L). Conclusions are similar to those described for color removal, evidencing that process variables may have a positive or negative effect on the final performance, depending on the other experimental parameters. Once again, optimum values for both H_2O_2 concentration and temperature are found, although shifted for higher values as compared to color removal. This could be expected, once to achieve mineralization more aggressive conditions are required than those employed to simply break the chromophore group.

It is known that complete leaching of Orange II does not mean that the dye is completely oxidized, and so the mineralization and color removal processes were investigated simultaneously. Consequently, the TOC of the reaction

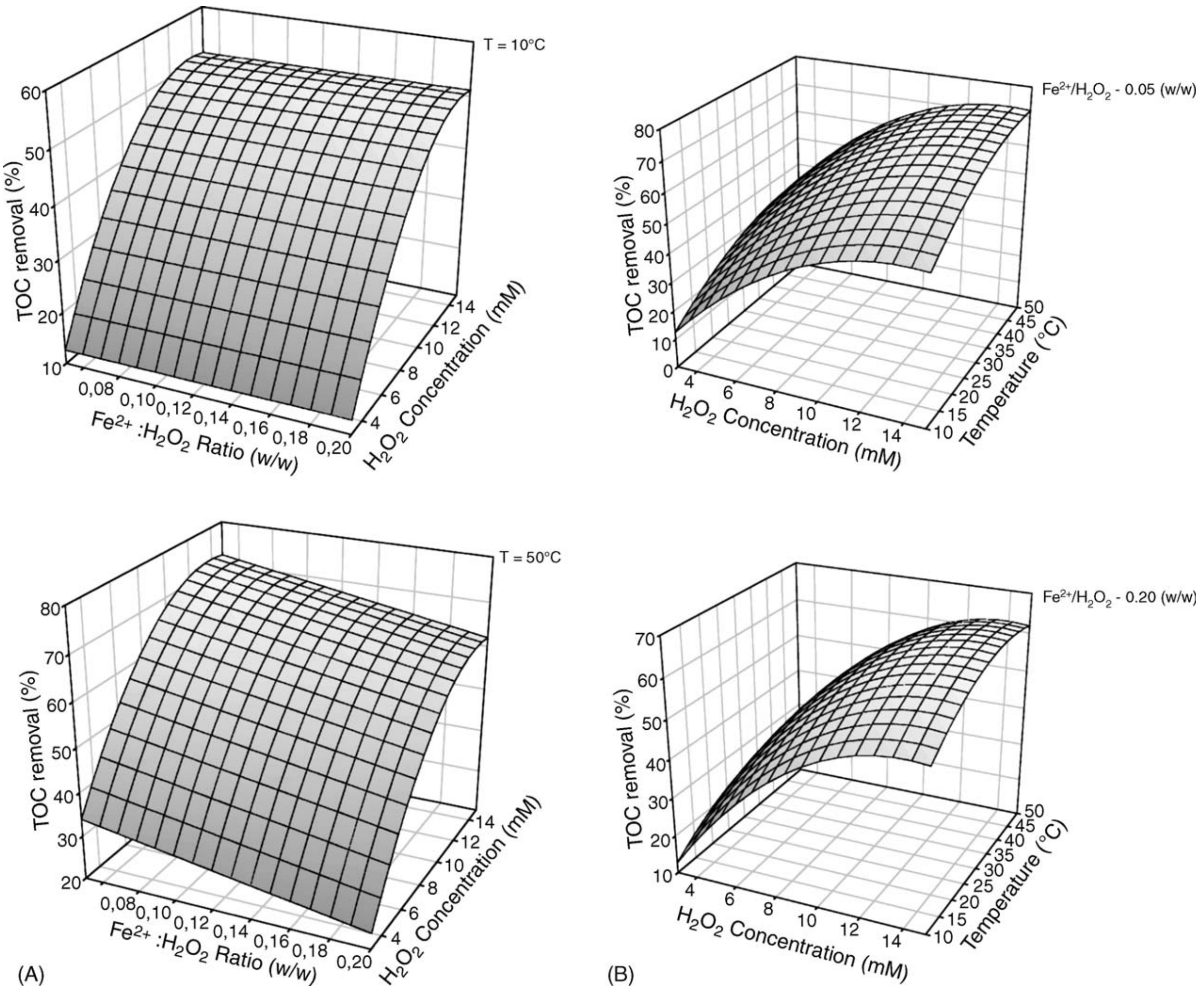

Fig. 6. Response surface showing the TOC removal (%) of the Orange II solution (0.3 mM) as a function of: (A) Fe^{2+}:H_2O_2 ratio and H_2O_2 concentration (for different temperatures) and (B) H_2O_2 concentration and temperature (for different Fe^{2+}:H_2O_2 ratios); initial pH 3.0.

mixture was also measured along time in all experiments, some of them shown in Fig. 7. For run no. 1, a TOC removal of 72% was reached after 2 h, with ∼99% of color removal (Table 2). It must however be stressed that good conditions for mineralization do not necessarily imply good results for color leaching. For instance, in run no. 2, a good TOC reduction was attained (62%), with a very inefficient color removal (see Table 2).

With the goal in mind of process optimization, two more experiments were performed in the optimum conditions found regarding color and TOC removal. These runs also allowed us to check the validity of the developed models. Once Eq. (4) predicts that color can be completely removed in a wide range of the experimental parameters, we decided to use conditions that do not require excessive consumption of reagents neither too high temperatures. For TOC, the optimum values found through non-linear optimization (maximum in Eq. (5)) were employed. The experimental conditions are described in the caption of Fig. 8. It is

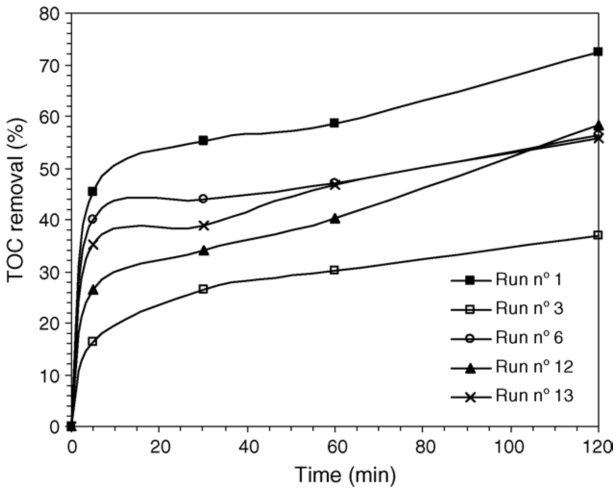

Fig. 7. TOC removal of the Orange II solution (0.3 mM) along time, for some runs (experimental conditions shown in Table 1). Experiments were performed at initial pH 3.0.

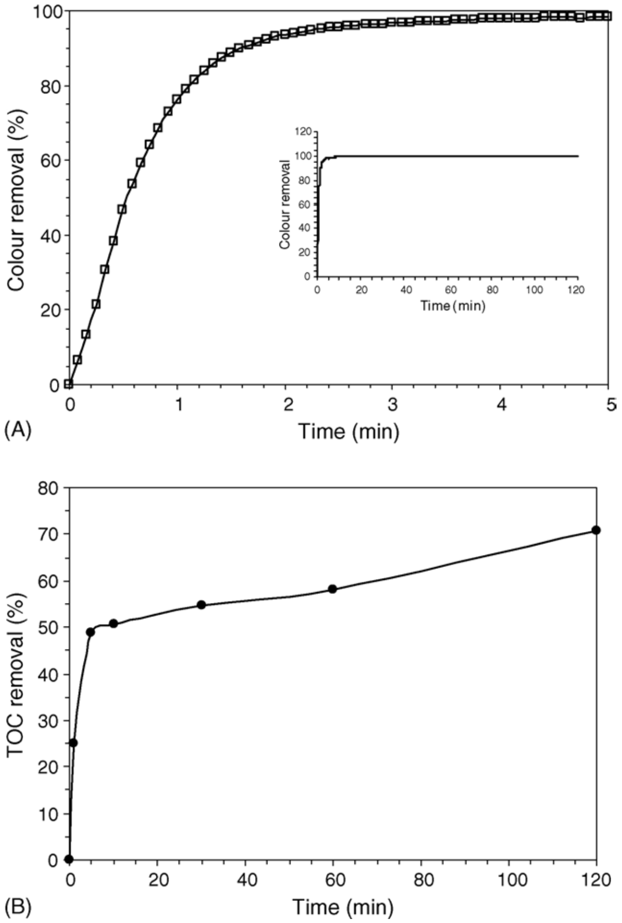

Fig. 8. Color (A) and TOC (B) removal along time using the optimized conditions: (A) color removal with $T = 29\ ^\circ C$, $[H_2O_2] = 10.0$ mM and $Fe^{2+}:H_2O_2$ ratio = 0.08 (w/w) and (B) TOC removal with $T = 50\ ^\circ C$, $[H_2O_2] = 13.8$ mM and $Fe^{2+}:H_2O_2$ ratio = 0.05 (w/w). Experiments were performed at initial pH 3.0. The number of experimental points in absorbance plot was reduced for a better visualization.

noteworthy that a high H_2O_2 load and temperature is required for good TOC reduction, while for color removal reaction conditions do not need to be so severe. For those experiments the model predicts efficiencies of 99.9 and 72.6%, for color and TOC reduction, respectively. It is remarkable that an experimental leaching level of 99.7% was reached after 2 h (see detail in Fig. 8A). In what concerns the TOC removal, a mineralization degree of 70.7% was achieved (Fig. 8B), which only differs 2.7% from the predicted value. However, this figure suggests that higher mineralization degrees could be achieved with longer experiments. As shown in Fig. 8A, color removal is very fast, being possible to achieve a performance above 98% in just 5 min. On the other hand, complete oxidation proceeds at a much slower reaction rate.

The DOE methodology used has shown to be a valuable tool to model a complex process such as the Fenton oxidation, and to achieve optimal experimental conditions without a detailed knowledge of the reaction sequences involved, which are most often complex. In fact, the DOE approach allows the modeling of the process through statistically significant but empirical models, of the ‘‘black-box’’ type. However, a deep knowledge of the process is of crucial importance, particularly in what concerns the reaction mechanism and reaction kinetics (although requiring a mathematical description of the phenomena involved in the process). This will be the aim of future work, which is actually already been carried out in our group. Nevertheless, it is reasonable to assume that mineralization of the dye might yield HSO_4^- and predominantly NH_4^+ (among other compounds) [12], but the formation of intermediate Fe-complexes consisting of Fe-chelates leading to carboxylic acids should be also considered, as found in previous studies. In particular, oxalic, formic and acetic acid along with smaller concentrations of other short non-branched and branched aliphatic acids (C_3–C_7) have been reported [22]. In what concerns possible reaction intermediates, it is also important to remark the nice study presented by Nam et al. [23] using the Fe(III)–EDTA–H_2O_2 system. The authors propose a detailed mechanism for the Orange II degradation, with several intermediates involved, particularly 4-hydroxybenzenesulfonic acid and 1,2-naphtoquinone. Finally, the work by Bandara et al. [12] should be also stressed, although the results concern the use of sunlight-induced reactions. Based on their results, the following mechanism could be suggested for the decomposition of Orange II, taking also into account the above-mentioned equations, particularly Eqs. (1)–(3):

$$C_{16}H_{11}N_2NaO_4S + OH^\bullet \rightarrow C_{16}H_{11}N_2NaO_4S(-OH) + \text{oxidized intermediates} + CO_2 \qquad (9)$$

where the oxidized intermediates might, through subsequent reactions with the OH radicals, lead to aromatic and aliphatic intermediates, and finally to carbon dioxide and water (along with NO^{3-}, NH_4^+, $NaHSO_4^-$ and H^+). Among other compounds, the formation of nitrogen and sulfo-containing products is described by the authors, being also noteworthy the evolution of N_2 when the N=N bond is cleaved [12].

4. Conclusions

A central composite design was used to evaluate the effect of temperature, H_2O_2 concentration and $Fe^{2+}:H_2O_2$ ratio in the Fenton’s oxidation of the azo dye Orange II, at pH 3. The responses considered were the color (Y_1) and TOC (Y_2) removal after 2 h of oxidation. It was found that the second-order models developed for both Y_1 and Y_2 fit quite reasonably the experimental data in the ranges studied.

The dye seems to be decomposed in a two-stage reaction with the Fenton’s reagent, being degraded very quickly in the first 5–10 min (Fe^{2+}/H_2O_2 stage), with a slower reaction rate later on (Fe^{3+}/H_2O_2 stage). The first stage is particularly fast for color removal, being possible to achieve a color leaching above 98% in just 5 min of reaction time, although in some cases efficiencies higher than 90% can be reached in only 1 min.

Data obtained revealed that the Fenton's reagent is promising for degradation of the dye, as leaching efficiencies clearly above 99% and mineralization degrees higher than 70% were reached in 2 h. However, to achieve these results, operating conditions must be carefully selected. Indeed, the surface response plots of the models showed that for both factors (Y_1 and Y_2) optimum values for the process variables exist, what is a typical behavior in the Fenton process. Though TOC reduction requires very aggressive conditions (high H_2O_2 concentration and temperature) color leaching does not requires high stringency. The hydrogen peroxide concentration and the temperature showed to be the variables with higher impact into the final performance. In particular, temperature turns into a key parameter when it is desirable to reduce reagents consumption.

Although the model predicts that color can be completely removed for a wide range of experimental conditions, we decided to test its validity with an additional run where excessive use of reagents and high temperature should be avoided. An additional experiment was also carried out in the conditions found by non-linear optimization regarding TOC reduction (maximum of Y_2). The following performances were achieved:

- Color removal = 99.7%, for $T = 29\ ^\circ\mathrm{C}$, $[H_2O_2] = 10.0$ mM and Fe^{2+}:H_2O_2 ratio = 0.08 (w/w).
- TOC removal = 70.7%, for $T = 50\ ^\circ\mathrm{C}$, $[H_2O_2] = 13.8$ mM and Fe^{2+}:H_2O_2 ratio = 0.05 (w/w).

Acknowledgements

The authors gratefully acknowledge the fruitful discussions and suggestions made by Prof. Adélio Mendes, from FEUP. J. Herney Ramirez also acknowledges Alban – European Union Program of High Level Scholarships for Latin America – for the financial support for his Ph.D. grant (Reference no. I03D-00045CO) and Luis Carlos Matos for his technical assistance.

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