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Factorial experimental design of Orange II photocatalytic discolouration

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Abstract

Photo-discolouration of Orange II solutions at different concentrations was carried out in a 1 l concentric reactor irradiated with a 254 nm mercury lamp (125 W) in the presence of Degussa TiO_2 P-25 dispersions. Experimentation involving discolouration of Orange II has been carried out using factorial design methodology for the simulation of the three critical variables affecting the dye discolouration: concentration of Orange II, pH and concentration of TiO_2. A single polynomial function corresponding to optical absorbance of Orange II (Y) was constructed for the treatment of the experimental data obtained in the immersion photo-reactor. The function (Y) allowed the prediction of the residual discolouration after 20 min photo-treatment. By following this model, a minimum of well-chosen experiments was performed to optimise Orange II photo-discolouration. The modelling takes into account that in the chemical system one reaction parameter determines the setting of another and vice-versa (interactive effects). The correlation factor between the experimental and predicted values by the polynomial expression for the discolouration of Orange II was better than 95%. In a typical photo-reactor run at pH 3, the concentration of TiO_2 could be decreased to values <0.5 g/l without affecting the discolouration kinetics.

Keywords: Dyes; Experimental design; Heterogeneous photo-catalysis; Orange II; TiO_2

1. Introduction

Optimising procedures for water treatment, and in particular of dye containing wastewater, is an enormous challenge. This is a task made complex by the wide variety of dyestuff commercially available. Most of the commercial synthetic dyes are used because they are chemically and biologically stable. These dyes strongly inhibit natural biological degradation of organic compounds occurring through bacterial processes, since they affect the availability of readily degradable nutrients necessary in the bacterial metabolism. Biological degradation processes compete with adsorption of the dye in the activated sludge [1]. This is the reason why advanced oxidation technologies have been growing during the last decade since they are able to deal with the problem of dye destruction in aqueous systems. Advanced oxidation technologies (AOT's) such as Fenton and photo-Fenton catalytic reactions [2], H_2O_2/UV processes [3] and TiO_2 mediated photo-catalysis [4,5] have been studied under a broad range of experimental conditions in order to reduce the colour and organic load of dye containing effluent waste waters.

Photocatalysis using TiO_2 as photo-catalyst degrade toxic organic compounds [6,7], reduce metal-ions [8], improve the biodegradability in cellulose effluents [9] and decolour a great variety of dyes in solution [10,11] or in solid mixtures [12]. When titania suspensions are irradiated, electrons are excited from the valence to the conduction band, generating positive holes and electrons:

$$TiO_2 + h\nu\ (<390\,\text{nm}) \rightarrow TiO_2(e^- + h^+) \qquad (1)$$

The energy band gap for TiO_2 Degussa P-25, the most used photocatalyst, is around 3.2 eV (390 nm). Electrons and holes can recombine (Eq. (2)) or react with other molecules, such as oxygen, generating reactive superoxide anions (Eq. (3)).

$$TiO_2(e^- + h^+) \rightarrow TiO_2 + \text{heat} \qquad (2)$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \qquad (3)$$

The positive holes can react with electron donors in the solution to produce hydroxyl radicals (Eqs. (4) and (5)) or would directly oxidise organic molecules (OM) at the semiconductor surface (Eq. (6)).

$$TiO_2(h^+) + H_2O_{(ads)} \rightarrow TiO_2 + H^+ + OH_{(ads)}^{\bullet} \qquad (4)$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + OH_{(ads)}^{\bullet} \qquad (5)$$

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$$TiO_2\,(h^+) + OM \rightarrow \text{degradation intermediates} \rightarrow TiO_2 + OM^{\bullet +} \quad (6)$$

The hydroxyl radicals generated in the process are strong oxidants and react quickly with the organic matter adsorbed on the catalyst (Eq. (7)), forming oxidised intermediates, and if the treatment time is adequate complete mineralization is achieved. The typical mechanism involving hydroxyl oxidative radical reactions go through the steps: electron transfer, hydrogen abstraction and addition to aromatic rings/double bonds.

$$OM + HO_{(ads)}{}^{\bullet} \rightarrow \text{degradation intermediates} \rightarrow CO_2 + H_2O + \text{salts} \quad (7)$$

To optimise the degradation parameters in a photo-reactor most studies have been focused on a univariate approach. In this case, one parameter is varied each time maintaining the others constant during the experiment. An alternative to such approach is the experimental factorial design, a statistical tool that allows the simultaneous change of several variables. This methodology, known also as multivariate analysis, has been previously used in the experimental design of Fenton reaction [13,14] and in the photo-catalytic treatment of industrial effluents [15]. The degradation technique employed in this study requires a low energy lamp source and mild reaction conditions making it environmentally attractive.

The present study focuses on the multivariate design for the degradation of Orange II dye, studying the effect of the variables pH, dye concentration and TiO_2. Innovative software is used based on a factorial combination of the input variables as described below. This approach precludes the use of cumbersome successive experimental optimisation to achieve discolouration of the dye as a function of the selected parameters.

2. Experimental

2.1. Materials

Orange II solutions were prepared dissolving the appropriate amount of dye (Fluka, sodium salt) in distilled water in the range of 0.05–0.1 mM. The pH of this solution was adjusted by addition of HNO_3 or NaOH to do attain the desired pH values in the range 3–5.6. Before irradiation, the solutions were equilibrated for 30 min in the dark under stirring to reach equilibrium with TiO_2. Degussa TiO_2 P-25 was used as received.

2.2. Photochemical reaction

Photochemical experiments were carried out in a concentric cylindrical photo-reactor with a mercury lamp Philips HPLN-125 W. The experimental set-up is shown in Fig. 1. The reaction temperature was maintained constant by means of a recirculating water thermostat at 20 ± 1 °C. Oxygen was bubbled to the reactor through a sintered glass Frite placed at the bottom of the reaction cylinder at a rate of 400 ml/min. The amount of catalyst used was in the range from 0.5 to 1.0 g/l. Runs were performed under stirring in the photo-reactor.

In a typical experiment, the samples were taken from the reactor at different reaction times by means of a 10 ml syringe and then filtered in a Millipore (0.45 μm) filter to avoid particulate entering the optical detection cell or the TOC instrument.

2.3. Analytical procedures

The course of the reaction was followed by UV–VIS spectra using a Shimadzu UV-1603 spectrophotometer. The

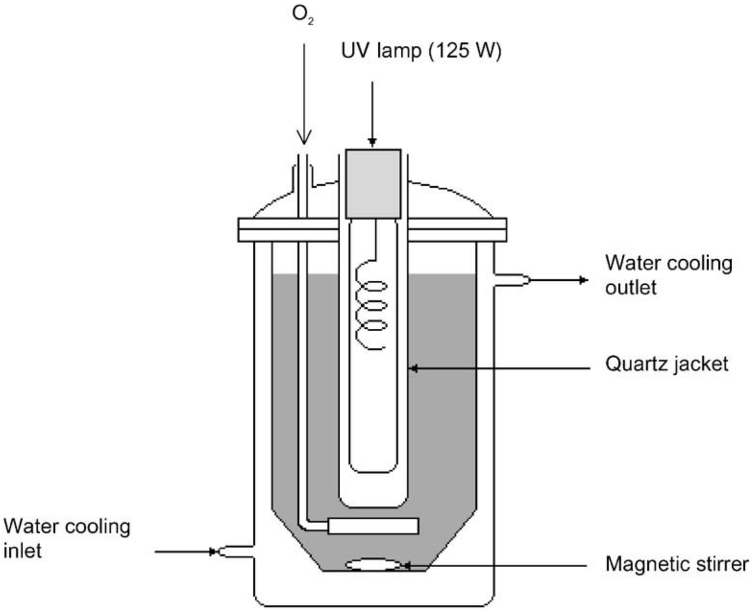

Fig. 1. Scheme of the slurry reactor used during photocatalytic experiments.

kinetics of the reaction were obtained measuring the optical absorbance at λ = 486 nm. Total organic carbon (TOC) measurements were carried out in a Shimadzu 5000 TOC analyser.

The pK_a values were determined by titration of TiO_2 Degussa P-25 suspension (0.5%) with 0.01 M HCl in a Metrohom 716 DMS Titrino. The titration was started at pH 10 and went down to pH 3 to determine the equivalence points. The measurements were repeated three times to assess the experimental error.

2.4. Multivariate experimental design

Experimental design was carried out following the methodology described by Box et al. [16]. The polynomial and response surfaces were worked out through the software FATORIAL provided by Prof. R. Bruns from the State University of Campinas, Brazil [17].

3. Results and discussion

3.1. Spectral changes observed during the dye degradation in the photo-reactor

The changes in the absorption spectra of Orange II solutions during the photocatalytic run at different irradiation times are shown in the Fig. 2. The decrease of the absorption peak of Orange II at λ = 486 nm in Fig. 2 indicates a rapid degradation of azo dye. Complete discolouration of the initial orange colour was observed after 30 min. No coloured intermediate species were generated in solution during the photo-catalytic process as seen from the family of curves shown in Fig. 2.

3.2. Experimental design methodology towards the construction of a single polynomial expression

Experimental design methodology for the simulation of the variation of the critical reaction parameters is a modern approach in industrial reaction design [16,17]. By following this methodology, modelling is possible and it requires only a minimum number of experiments. It is not necessary in the modelling procedure to know the detailed reaction mechanism since the mathematical model is empirical. The magnitude of the interaction between the variables is reflected in the value of the coefficients of the single polynomial expression used to fit the experimental data as shown in Eq. (8).

Table 1 show the experimental results for the response factor (Y) corresponding to the percent of remaining colour in solution observed at the peak of Orange II (λ = 486 nm) after 20 min photocatalysis varying the concentration of Orange II, of TiO_2 and the pH values in a defined range. Since the different input variables presented different dimensional

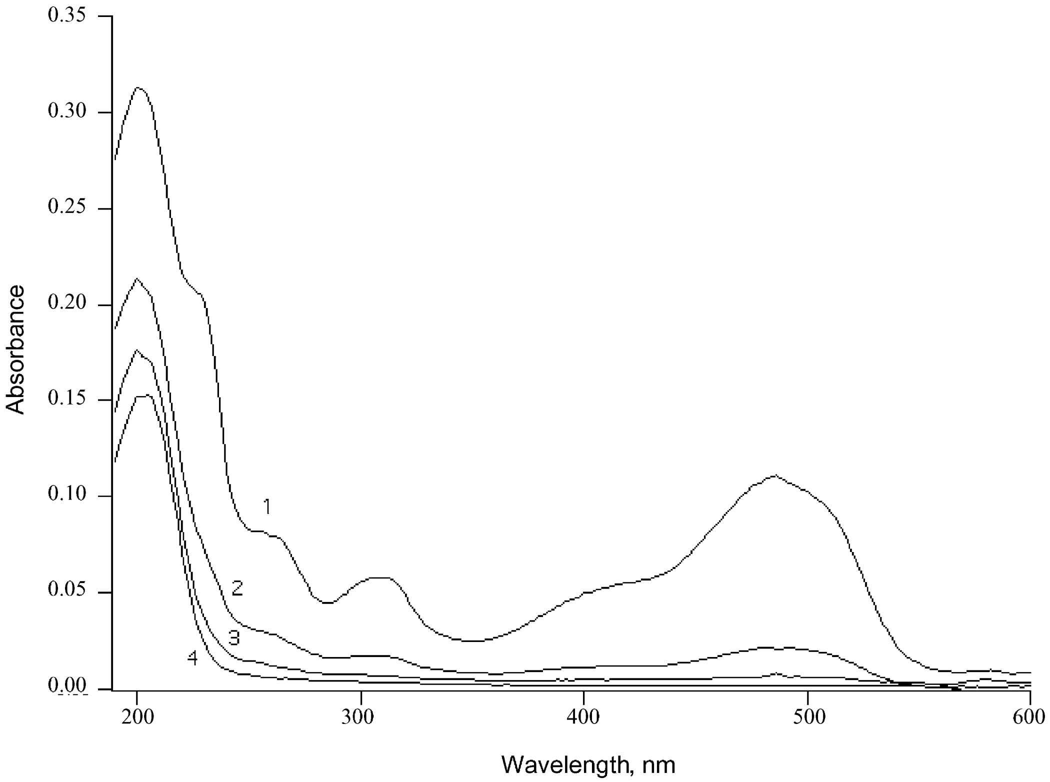

Fig. 2. Spectral changes observed in a solution of Orange II (0.1 mM) irradiated with a mercury lamp light at pH 3, TiO_2 1 g/l at times: (1) zero, (2) 20 min (3) 40 min and (4) 120 min.

Table 1
Numerical results of the factorial experimental design of Orange II discolouration (for experimental details see text)

Experiment	Orange II (x_1)	TiO_2 (x_2)	pH (x_3)	Y^a (Experimental)	Y^a (Calculated)
1	0.05 (−1)	0.5 (−1)	3.0 (−1)	11.3	11.3
2	0.10 (+1)	0.5 (−1)	3.0 (−1)	44.0	39.9
3	0.05 (−1)	1.0 (+1)	3.0 (−1)	10.1	7.6
4	0.10 (+1)	1.0 (+1)	3.0 (−1)	40.0	38.7
5	0.05 (−1)	0.5 (−1)	5.6 (+1)	46.6	43.5
6	0.10 (+1)	0.5 (−1)	5.6 (+1)	66.1	64.2
7	0.05 (−1)	1.0 (+1)	5.6 (+1)	32.2	32.0
8	0.10 (+1)	1.0 (+1)	5.6 (+1)	59.6	55.3
9	0.033 (−1.68)	0.75 (0)	4.3 (0)	14.9	16.2
10	0.117 (+1.68)	0.75 (0)	4.3 (0)	55.1	59.9
11	0.075 (0)	0.33 (−1.68)	4.3 (0)	37.7	41.0
12	0.075 (0)	1.17 (+1.68)	4.3 (0)	27.7	30.5
13	0.075 (0)	0.75 (0)	2.12 (−1.68)	14.0	16.6
14	0.075 (0)	0.75 (0)	6.49 (+1.68)	54.1	57.6
15	0.075 (0)	0.75 (0)	4.3 (0)	40.4	43.7
16	0.075 (0)	0.75 (0)	4.3 (0)	43.1	43.7
17	0.075 (0)	0.75 (0)	4.3 (0)	48.7	43.7

[a] Y: residual colour % after 20 min irradiation.

units, these variables can only be compared if they are normalised to a common unit. Therefore, coded variables were a need during the modelling procedure. The coded values taken for the calculations appear in Table 1 in parenthesis for Orange II (x_1), TiO_2 (x_2) and pH (x_3). Only in this way, the input variables can be used in the single polynomial expression in Eq. (8) below. The model allows the fitting of the experimental data within an error range <5% with respect to the experimental values. The fourth column in Table 1 presents the experimental values obtained for the response factor (Y) and the fifth column presents the calculated values by way of the modelling procedure. The variance obtained from the software for a 95% confidence level was 96.7%.

In the modelling procedure, the first eight runs are placed in the eight vertices of a cube, the next six runs displaced outside of the cube and the three central points are arranged in an spherical-like arrangement (centre of the cube) following the matrix that is solved with the FATORIAL software [17]. In this way a single polynomial expression was obtained (Eq. (8)) where, x_1, x_2 and x_3 represent the dye concentration, the TiO_2 concentration and the initial pH, respectively.

$$\begin{aligned} Y(\%) = {} & 43.71(\pm 2.70) + 12.97x_1(\pm 1.27) - 3.14x_2(\pm 1.27) \\ & +12.20x_3(\pm 1.27) - 2.00x_1^2(\pm 1.40) \\ & -2.81x_2^2(\pm 1.40) - 1.96x_1x_3(\pm 1.66) \\ & -1.96x_2x_3(\pm 1.66) \qquad (8) \end{aligned}$$

Considering just the first order effect of each variable in Eq. (8), the most suitable experimental conditions to decrease the remaining colour within the 20 min of reaction are: low concentration of the dye, high concentration of catalyst and low pH. A relatively modest quadratic effect is observed for the dye and catalyst concentrations. Also, synergy effect seems to be taking place between the dye and pH (x_1x_3) and for TiO_2 concentration and pH (x_2x_3). Values in parenthesis represent the error associated with each coefficient. When the error was equal or higher than the coefficients of the polynomial, this parameter in the present modelling does not appear above in Eq. (8).

3.3. 3-D Response surfaces obtained from the single polynomial expression

As expected, a kinetically faster degradation of Orange II occurs at a low dye concentration. The polynomial of Eq. (8) shows that the dye concentration presents a negligible quadratic effect and a low second order relationship with pH. For a 3-D graphical representation showing the interaction between any pair of variables, it is necessary to fix the value of the third variable. Taken a low concentration of Orange II (0.05 mM), the polynomial expression in Eq. (8) has been used to calculate the response surfaces in Fig. 3 showing the residual colour (Y) % as a function of the TiO_2 concentration and pH values. In the present study the variation of the residual colour in percentage after 20 min photocatalytic treatment was the response function calculated as function of the variables: pH, Orange II and the TiO_2 concentration. Real numerical values of both variables are used and noted in the axes of Fig. 3. This figure shows that when initial pH of the solution is high >5.6, it is necessary to use TiO_2 >1 g/l to attain 70% discolouration of Orange II. But at pH values <3, the amount of catalyst had no significant effect on the discolouration. An almost complete discolouration was observed in all the range of TiO_2 concentration. This means that at low pH value, the amount of TiO_2 can be reduced at values below 0.5 g/l and still obtain efficient discolouration of the azo-dye in the photo-reactor.

Fig. 4 shows the residual colour (Y) % as a function of pH and the concentration of Orange II keeping

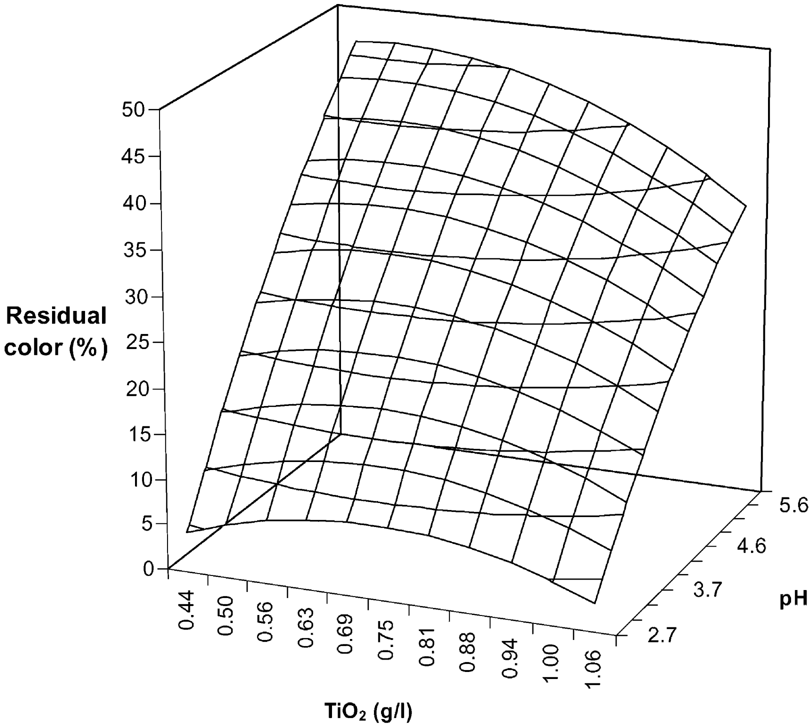

Fig. 3. Response surfaces showing the residual colour (Y) % of a solution Orange II (0.05 mM) as a function of the pH and TiO_2 in solution after 20 min irradiation with a Philips HPLN-125 W lamp ($\lambda > 254$ nm).

the concentration of TiO_2 at an average concentration of 0.75 g/l. Complete discolouration is seen from Fig. 4 to be favoured in dilute Orange II concentrations at acidic pH values. At high concentration of Orange II and less acidic pH value, only a 20% discolouration was attained because the first order effect became more important than the effect due to synergy. In the range of pH used, the dye has always a negative charge. This explains that the discolouration process would be favoured by the attraction of the positive sites existing on the TiO_2 surface. The pK_a values, determined for Degussa TiO_2 P-25 were found to be 5.5 and 8.4 [18]. The point of zero charge of this material is 6.95. At pH 3 the TiO_2 is positively charged due to the surface species ($TiOH_2^+$) and would interact strongly with

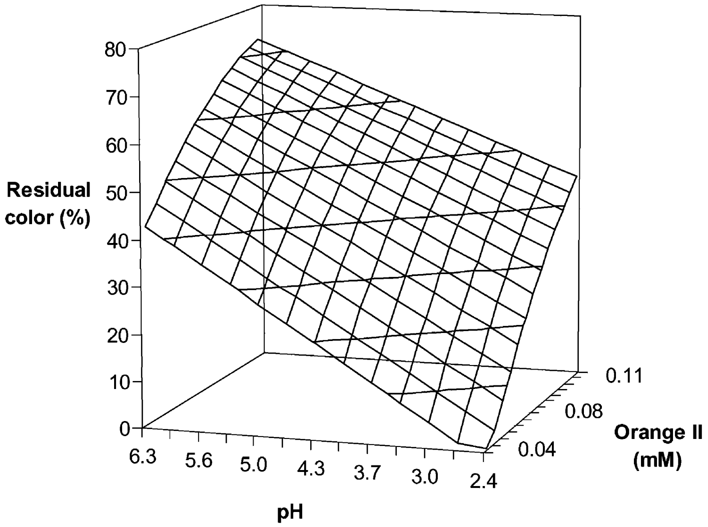

Fig. 4. Response surfaces for the residual colour (Y) % of a solution Orange II (0.05 mM) as a function of the pH and initial Orange II concentration used after 20 min irradiation with a Philips HPLN-125 W lamp ($\lambda > 254$ nm).

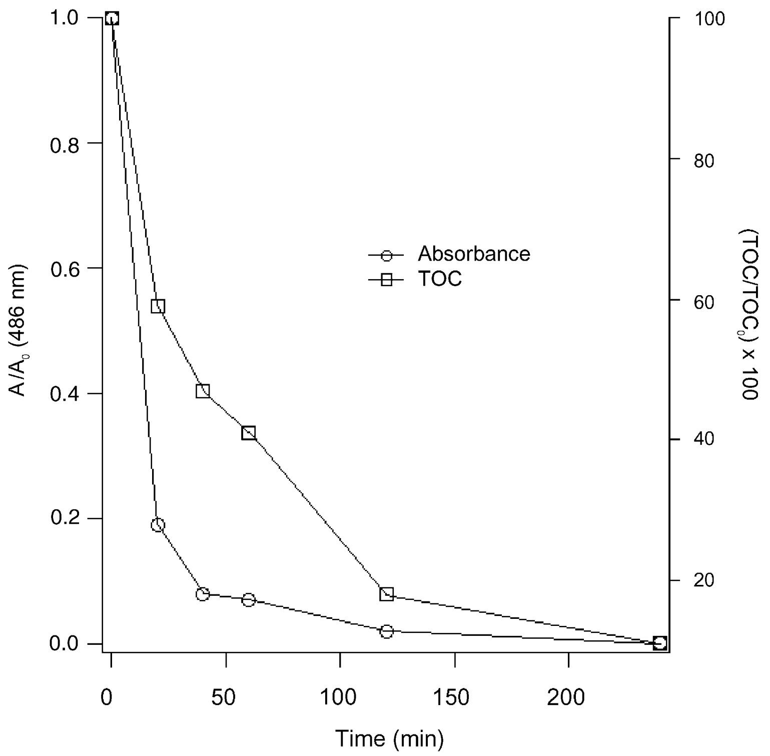

Fig. 5. Discolouration and mineralisation under UV light irradiation with a Philips HPLN-125 W lamp ($\lambda > 254$ nm) as a function of time for a solution of Orange II (0.1 mM) at pH 3 in the presence of 1 g/l TiO_2.

Orange II, which at this pH is a negative species. This is the reason for a favourable adsorption of the dye on the titania surface leading to a better photocatalytic degradation of Orange II.

The effect of pH on the photocatalytic degradation of Reactive Orange 16 on TiO_2, a reactive azo-dye with a similar structure than Orange II, has been recently reported [19]. Low rates of dye destruction were observed at pH values in the acidic range increasing at pH ~6 but did not follow a consistent trend. In the case of Orange II, the degradation trend found in the pH range 2–5.6 follow the trend reported in Fig. 3. The pK_{a1} value originating from the H^+ loss of the –OH group of Orange II has been reported to be 11.4 [20]. The second value for pK_{a2} corresponding to H^+ loss of the sulfonic group in Orange II cannot be determined since it can only be measured by electrochemical methods in non-aqueous solvents. This latter value is commonly taken to be ~1.0 as found for other azo-dyes with a similar number of sulfonic groups and structure. This suggests a favourable dye degradation at very acidic pH consistent with the range of pH reported in the present work.

In a typical run Orange II, a rapid discolouration was observed due to TiO_2 photocatalysis along a smaller reduction in the TOC as shown in Fig. 5. About 90% discolouration was attained at 30 min while the TOC decrease only attained 90% after 120 min irradiation.

Acknowledgements

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