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Degradation of Concentrated Solutions of Non-biodegradable Orange II by Photocatalytic and Electrochemical Methods

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The rate of photodegradation of Orange II was significantly accelerated by the addition of portions of H_2O_2 at appropriate times based on the monitoring of oxygen content and oxidant consumption; in contrast, mineralisation by electrochemical treatment was observed to be relatively inefficient.

Recent studies have shown that Fenton, photo-Fenton[1–5] and electrochemical[6] oxidation of organic compounds are efficient processes. In this study we plan to show that this approach could be applied to degrade concentrated solutions containing azo-dyestuffs[7] such as Orange II. There is a growing interest in removing dyes from water reservoirs for health as well as aesthetic reasons. Since the photo-Fenton system is catalytic instead of stoichiometric in iron, it is of interest to see if this approach could be used with shorter reaction times (in the minutes range) and compete with the more traditional flocculation–coagulation non-destructive techniques to remove the azo-dye.

Irradiation of the solutions as carried out in 60 ml Pyrex flasks with a cutoff at $\lambda \approx 290$ nm. The light source was a Suntest solar simulator where the radiant flux (90 mW cm^{-2}) was measured with a power meter.

Fig. 3 shows the total organic carbon (TOC) decrease for concentrated dye solutions as found in the effluents of azo-dye manufacturing at the production site. Fig. 3 indicates a TOC reduction under light from 450 mg C l^{-1} to 38 mg C l^{-1} in trace a. This is an 88% reduction within 40 min. Diluted dye solutions shown by traces c and d were seen to mineralize within shorter times as expected for a lower substrate concentration.

Concentrated solutions of Orange II (2.95 mM or 0.118 mM in 40 ml solution) needed 4.4 mmol of H_2O_2 for complete mineralisation. This is an oxidant–pollutant ratio of ≈37:1. Therefore, the mineralisation stoichiometry can be suggested as shown in eqn. (1).

$$C_{16}H_{11}N_2NaO_4S + 37\,H_2O_2 + 1/2\,O_2 \longrightarrow 16\,CO_2 + 40\,H_2O + NO_3^- + NH_4^+ + SO_4^{2-} + H^+ + Na^+ \qquad (1)$$

Fig. 5(*a*) presents the results for the degradation of Orange II solutions in dark and light (Suntest simulator) induced reactions at initial pH values of 2, 6 and 10. The concentrations of Orange II, Fe^{3+} and H_2O_2 are the same as those used in Fig. 3, but adding the H_2O_2 on an hourly basis. This allows for a more detailed analysis of the TOC and Orange II concentration reported in Figs. 5(*a*) and (*b*). The initial pH has been regulated with an acid (0.1 M HCl) or a base (0.1 M NaOH) in these unbuffered systems. For a solution with an initial pH 2, Fig. 5(*a*) shows mineralisation (TOC decrease *vs.* time) in the dark to be incomplete and only reach about 68% of the initial TOC value. It is seen that during the degradation the Fenton reagent does not fully mineralize the Orange II until 8 h have elapsed. In the dark, the reaction of H_2O_2 with Fe^{2+} [reaction (2)] competes with the organic intermediates in solution as the reaction runs its course.

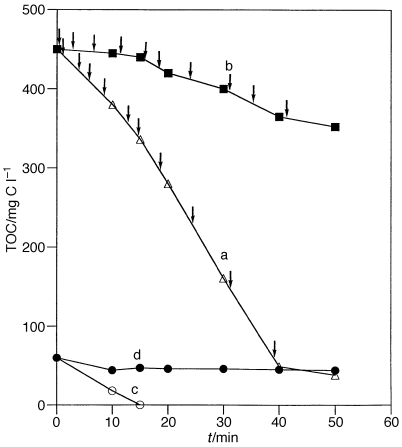

Fig. 3 Photochemical degradation of a solution of Orange II (2.95 mM), H_2O_2 (10 mM) and Fe^{3+} (0.92 mM). TOC *vs.* time during dark (filled symbols) and light induced degradation (open symbols) of concentrated solutions (450 mg C l^{-1}) (a,b) and diluted solutions (60 mg C l^{-1}) (c,d) of Orange II. The arrows indicate the times of H_2O_2 addition

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad k_1 = 58\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \qquad (2)$$

No kinetic data have been found for the reaction between $^{\bullet}OH$ radical and Orange II. Confirmation that the reaction (2) producing OH^- is involved in the generation of intermediates during Orange II degradation was obtained in the following way: a few drops of NaOH (0.1 M) were added to a solution containing Orange II (initial pH ≈3). The initial orange color of the solution changed to red upon NaOH addition. The spectrum of the red compound turned out to be identical to the spectrum of a solution with an initial pH 3 irradiated for 1 h. This change is ascribed to reaction (3). The red form undergoes further decomposition during photo-assisted Fenton reaction.

Fig. 5(*b*) presents the high-pressure liquid chromatography data for the disappearance of Orange II in the three solutions used for the results given in Fig. 5(*a*). The evolution of the pH values during the degradation is shown in Fig. 5(*c*). This figure shows the variation of pH as a function of time for three unbuffered solutions with initial pH values of 2, 6 and 10. The rather complex shape for the

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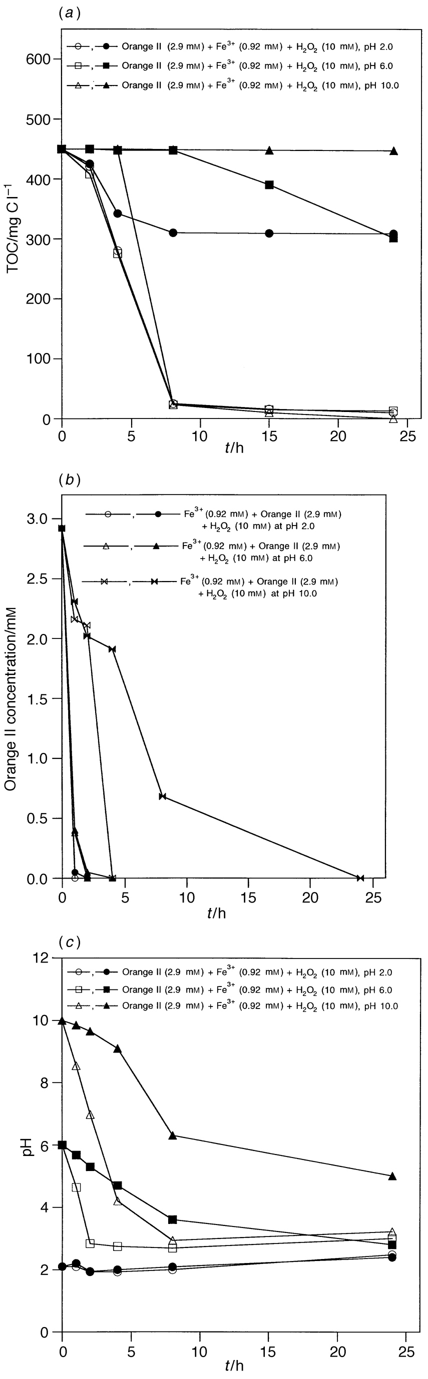
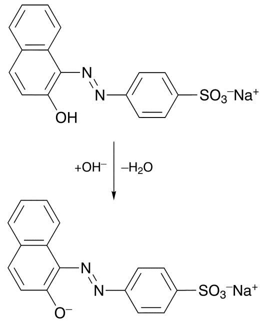


Fig. 5 (*a*) TOC *vs*. time for three concentrated Orange II unbuffered solutions with different initial pH values. Open symbols are for irradiated solutions and filled symbols refer to dark runs. Other details are seen in the caption inside the figure. (*b*) disappearance of Orange II under light (open symbols) and in the dark (filled symbols) for the three solutions. (*c*) Variation of the pH *vs*. time for reactions in the dark (filled symbols) and light induced (open symbols), for different initial pH values of concentrated solutions of Orange II

degradation as a function of time (initial pH 6 and 10) suggests the presence of pH dependent Fe–aqueous complexes with different structures and reactivities.

The results presented in Fig. 5(*c*) suggest that only when the pH has reached acidic values is a meaningful reduction of TOC values observed in solution. At higher pH the $[Fe(H_2O)_6]^{3+}$ species (pK_a 2.79) deprotonates rapidly to $[Fe(H_2O)_5(OH)]^{2+}$ and $[Fe(H_2O)_4(OH)_2]^{+}$ [2,18,19] slowing down the degradation as observed in Fig. 5(*c*). Recently, adduct formation has been observed between $^{\bullet}OH$ and Orange II during dye degradation and the latter process was reported to involve protonated species.[19]



(3)

The disappearance of Orange II at an initial pH of 2.9 by electrolysis *via* a Pt anode and a Zr cathode (100 mA cm^{-2} at a potential of 3.2 V) was also performed in the presence of Na_2SO_4 (50 mg l^{-1}) electrolyte. The abatement of the Orange II by electrochemistry took twice as long as the Orange II degradation performed by photochemical means in a solution about three times more concentrated in azo-dye. Electrochemical treatment of Orange II solutions close to the solubility limit of ≈2 g l^{-1} were observed as a function of the electric charge (A h l^{-1}) used. The rate of electrochemical mineralisation [k_2, see eqn. (4)] was low when compared to photochemical treatment.

$$\text{Orange II} \xrightarrow{k_1} \text{organic intermediates} \xrightarrow{k_2} CO_2 \qquad \text{where } k_1 \gg k_2 \quad (4)$$

The main organic intermediate observed during the electrochemical degradation of Orange II was sulfanilic acid. The electrochemical degradation indicates that non-biodegradable abatement is possible with a mass-free reagent and without added oxidant.

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Techniques used: HPLC, UV–VIS spectroscopy, ion–liquid chromatography

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Figures: 9

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References cited in this synopsis

1 Presented partly in: *International Conference on Oxidation Technologies for Water and Wastewater Treatment*. Goslar, Germany, May 12–15, 1996.
2 R. Helz, G. Zepp and D. Crosby, *Aquatic and Surface Photochemistry*, Lewis Publishing Company, Boca Raton, FL, 1994.
3 O. Legrini, E. Oliveiros and A. M. Brown, *Chem. Rev*., 1993, **93**, 67.
4 J. Kiwi, C. Pulgarin, P. Peringer and M. Gratzel, *New J. Chem*., 1993, **17**, 487.
5 C. Morrison, J. Bandara and J. Kiwi, *J. Adv Oxidation Technol*., 1996, **1**, 160.
6 C. Comninellis and C. Pulgarin, *J. Appl. Electrochem*., 1993, **23**, 108.
11 M. Halmann, *Photochem. Photobiol. A*, 1992, **66**, 215.
18 B. Faust and J. Hoigné, *Atmos. Environ*., 1990, **23**, 235.
19 V. Nadtochenko and J. Kiwi, *J. Chem. Soc., Faraday Trans*., 1997, **93**, 2373.