Optimization of the solution parameters during the degradation of Orange II in a photo-reactor mediated by Fe-Nafion membranes

M. A. Manzano, A. Riaza, J. M. Quiroga and J. Kiwi

ABSTRACT

The Fenton and photo-Fenton mediated degradation process of Orange II was investigated in a flow photo-reactor. The degradation was monitored as a function of the wavelength of the applied light, recirculation flow rate, amount of H$_2$O$_2$ and the initial concentration of Orange II. Optimization of the photo-Fenton degradation mediated by Fe-Nafion membranes indicated that an Orange II (0.25 M) solution discolored above 95% within 2.5 hours at an H$_2$O$_2$/Orange II ratio of 20. A concomitant mineralization of 40% of Orange II was observed after 5 h reaction. Homogeneous photo-Fenton processes were able to fully discolor Orange II within 1 hour and concomitantly fully mineralize the dye in the presence of Fe(III) (2 ppm) and an H$_2$O$_2$/Orange II ratio of 20. Surfactants such as linear alkylbenzene sulphonates (LAS) and K-perfluoroalkyl sulphonate (FT 800) slowed down the Orange II abatement in photo-Fenton processes.

Key words | advanced oxidation process, azo-dye, fluorinated compounds, surfactants, textile wastewater

INTRODUCTION

Dyeing and finishing operations produce large quantities of wastewater in the textile industry containing dyestuff, surfactants and other contaminants. Traditional techniques for the treatment of these effluents have been used for a long time such as: coagulation, adsorption on activated carbon, chemical oxidation and biological treatment (Liu et al. 2007; Peralta-Hernández et al. 2008).

Fenton’s reagent has been used for the decoloration and mineralization of hazardous organic pollutants and dyes in a large number of studies (Malik & Saha 2003; Swaminathan et al. 2003; Hsueh et al. 2005; Liu et al. 2007; Ramirez et al. 2007). During photo-Fenton processes, the yield of highly oxidative radicals OH’, HO$_2$’ increases compared to dark processes due to the photo-reduction of the ferric to ferrous-ion a step generating additional oxidative radicals as outlined below in reaction (3).

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \]  
\[ \text{Fe}^{3+} + \text{H}_2\text{O} + \text{h}^+ \rightarrow \text{Fe}^{2+} + \text{HO}^- + \text{H}^+ \]  

This study addresses the optimization of the solution parameters during the reactor heterogeneous and homogeneous photo-Fenton degradation processes of Orange II solutions using one of the advanced oxidation technologies (AOT’s). The laboratory reactor experimental results could be useful for the up-scaling to pilot plant treatments for dye degradation processes.

Orange II is a textile dye found frequently in textile effluents associated with a diversity of surfactants. It is not toxic but not biodegradable and found in many furtive emissions of textile dyes manufacturing sites in Spain, Portugal and Turkey. Perfluorinated membranes of Nafion®117 resisting the attack of the radicals generated in solution have been used as supports for Fe-ions.
These Fe-ions do not leach out during the dye degradation process. Linear alkylbenzene sulphonates surfactant (LAS) found also in textile wastewater are used as auxiliary products in textile production and treatment (Castillo & Barceló 2001). Also we explore the effect of the anionic surfactant K-perfluoroalkyl sulphonate (FT 800) used in the finishing of textiles as a textile hydrophobic surface agent during the Orange II degradation (Olsen et al. 2004).

METHODS

Reagents

Orange II, the sodium salt of the acid 4-(2-hydroxy-1-naphtalene) azo-benzene-sulphonic (Scharlau, CAS Number 633-96-5), is a colored mono-sulphated dye due to the azo group (–N = N–) (Augugliario et al. 2002). Ultra-pure FeCl₃·6H₂O (Scharlau, CAS Number 7705-08-0) was used as the source of iron ions and the Cl⁻ anion was shown recently not to preclude Fenton processes (Nadtochenko & Kiwi 1998). Other reagents like H₂O₂ 33% p/v (Panreac, CAS Number 7722-84-1), NaOH (Scharlau, CAS Number 1310-73-2), sulphuric acid 95–97% (Scharlau, CAS Number 7664-93-9) and Milli-Q water were used throughout. The Nafion®117 membrane (thickness 0.007 in., Aldrich, CAS Number 92308-23-1) was used to fix the Fe(III)-ions catalyzing the Fenton reactions. These membranes contain hydrophilic sulfonated groups in the perfluorinated structure allowing to fix 1.82% Fe by weigh (Sabhi & Kiwi 2001). LAS (Merk, CAS Number 25155-30-0) and K-perfluoroalkyl sulphonate FT800 (Bayer, CAS Number 2795-39-3) anionic surfactant were used without further purification.

Analytical techniques

Spectrophotometric measurements were carried out using a Jenway 6405 UV/Visible spectrophotometer. The Total Organic Carbon (TOC) measurements were carried out to monitor Orange II mineralization using a Shimadzu 5050A TOC Analyzer which determined the TOC value trough the difference between total carbon (TC) and the inorganic carbon (IC).

The H₂O₂ in solution was determined by means of the Merkoquant® test which detects peroxides between 1 and 100 mg/L of H₂O₂ and also between 100 and 1,000 mg/L (Merck, 110081 and 110337). The test is valid within pH 2 and pH 7 to determine quantitatively organic or inorganic peroxide or hydro-peroxide groups. Anionic perfluorinated surfactants were quantified by methylene blue active substances method, MBAS (APHA-AWWA-WPCF 1995). Fluorides in solution were analyzed by capillary electrophoresis (Waters Quanta 4000 CIA System, Bedford, MA, USA) in accordance with Waters method N601 and American Society for Testing and Materials (ASTM) D1066. The pH of solutions was measured with Crison micropH 2001 (Ag/AgCl reference electrode).

Flow reactor studies

Figure 1 shows the assembly employed. The photo-reactor was provided for with a Philips TL-D 36W/18 SLV light centred at 366 (λ-distribution between 350 and 400 nm) and could be used also with a second lamp Blue SLV (36 W) centred at 440 nm (λ-distribution between 400 and 500 nm). The lamps were centred along the focal axis of the reactor.

The reactor was used in batch mode operation. A peristaltic pump was used for the recirculation of the
Orange II solution in the photo-reactor loop shown in Figure 1. The reactor volume was 1,100 mL and the total volume of the solution recycled in the photo-reactor was 1,470 mL. Samples for analyses were taken from the mixer flask. Tubing in the reactor assembly was made out of PTFE.

The Nafion 117 membranes were placed in the inside of the cylindrical reactor wall. During reactor operation, the reactor was filled with the Orange II solution and the pH adjusted to 2.8 before adding the H$_2$O$_2$. The mixing flask was sealed with cold water acting as a coolant source to avoid losses by evaporation during reactor operation. The points reported in part B and C in Figure 2 are an average of 3 experimental measurements.

RESULTS AND DISCUSSION

Heterogeneous catalysis

The degradation of Orange II was followed spectrophotometrically at the Orange II peak at 484 nm. Table 1 report the parameters examined during the photo-reactor runs.

Continuous addition of hydrogen peroxide

In contrast with the initial addition of H$_2$O$_2$, the scavenging of the hydroxyl radicals by excess H$_2$O$_2$ was investigated to avoid the OH-scavenging reaction (4) by gradual addition of H$_2$O$_2$ during reactor operation. (Walling 1975;

![Figure 2](https://iwaponline.com/wst/article-pdf/60/4/833/448942/833.pdf)

Figure 2 | Reactor decoloration of Orange II solutions on Nafion-Fe membranes (1.82% by wt): (A) as a function of the light source, (B) as a function of the reactor recirculation rate, (C) as a function of the H$_2$O$_2$ added, (D) as a function of the Orange II concentration and (E) as a function of the position of the Nafion-Fe membrane in the reactor.
Sychev & Isak 1995).

\[
\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^-
\]  

(4)

Figure 2A shows the decoloration as a function of the light sources that were available and could be inserted in the reactor. Figure 2B investigates the Orange II decoloration as a function of the suitable recirculation rates generally used in the photoreactor. Figure 2C shows the decoloration as a function of the amount of \( \text{H}_2\text{O}_2 \) added continuously during reactor operation. Figure 2D shows the Orange II decoloration as a function of the initial Orange II concentration. Finally, Figure 2E shows the decoloration of Orange II as a function of the two possible insertion geometries in the cylindrical reactor.

Figure 2A shows the dependence of the degradation of Orange II on the light wavelength, when using the lamp centred at 366 nm, followed by a lower performance by the lamp centred at 440 nm. At 440 nm, the iron-complexes absorption decreases compared to 366 nm, decreasing the photo-conversion of ferric to ferrous-ions (reaction 3) (Walling & Amranth 1982; Faust 1994). For this reason the lamp centred 366 nm was selected from now on and will be used during the next steps of this work as the reactor irradiation source.

In Figure 2B, recirculation flows of 100, 300 and 450 mL/min were tested during Orange II degradation in the photo-reactor. A flow of 100 mL/min was not sufficient to allow optimal contact of the solution with the reactor lamp. A 300 mL/min flow improved this situation by cutting the residence of the Orange II solution in the tubing part of the reactor assembly. At 450 mL/min there was not enough residence time of the Orange II solution in the photoreactor to allow optimal degradation.

Figure 2C shows that an addition of 100 \( \mu \text{L} \) \( \text{H}_2\text{O}_2 \)/min was not enough to obtain the maximum degradation rate. When the flow was set at 500 \( \mu \text{L} \)/min scavenging of \( \text{OH}^- \) sets in (see reaction 4) due to excess \( \text{H}_2\text{O}_2 \). An input of 300 \( \mu \text{L} \)/min produced suitable results since the scavenging of \( \text{OH}^- \) radicals by \( \text{H}_2\text{O}_2 \) was significantly lower. At the end of the run (input of 300 \( \mu \text{L} \)/min) the \( \text{H}_2\text{O}_2 \) was completely consumed as detected by the experimental technique used in this study. This is the reason the later value was selected for the subsequent runs during the course of this study.

Figure 2D shows the degradation of Orange II 0.25, 0.5, 0.75 and 1 mM solutions. Since a small excess \( \text{H}_2\text{O}_2 \) was added from the beginning of the reaction, the degradation was complete for the different Orange II concentrations tested within 24 hours.

Figure 2E shows the Orange II degradation when the membrane was placed (a) around the cylindrical light source and (b) around the inner wall of the tubular reactor. The degradation results were observed to be similar in both cases, but the option b) showed a higher degradation rate within the first 300 min of reaction. This geometrical arrangement was therefore used throughout this study.

### Table 1 | Solution parameters explored during Orange II degradation

<table>
<thead>
<tr>
<th>Variable (units)</th>
<th>Values</th>
<th>Optimal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength of the illumination source (nm)</td>
<td>440, 366 and darkness</td>
<td>366</td>
</tr>
<tr>
<td>Recirculation flow (mL/min)</td>
<td>150, 300 and 450</td>
<td>300</td>
</tr>
<tr>
<td>Hydrogen peroxide flow rate (( \mu \text{L}/\text{min} ))</td>
<td>100, 300 and 500</td>
<td>300</td>
</tr>
<tr>
<td>Initial concentration of Orange II (mM)</td>
<td>0.25; 0.5; 0.75 and 1</td>
<td>Effective at any concentration</td>
</tr>
<tr>
<td>Position of membrane into the photo-reactor</td>
<td>Around the cylindrical light source and around the inner wall of the tubular reactor</td>
<td>Around the inner wall of the tubular reactor</td>
</tr>
<tr>
<td>Initial addition of hydrogen peroxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar ratio ([\text{H}_2\text{O}_2]/[\text{Orange II}]) for Orange II low concentration (0.25 mM)</td>
<td>10, 20, 40 and 60</td>
<td>20</td>
</tr>
<tr>
<td>Molar ratio ([\text{H}_2\text{O}_2]/[\text{Orange II}]) for Orange II high concentration (1 mM)</td>
<td>10, 20, 40 and 60</td>
<td>20</td>
</tr>
</tbody>
</table>
Initial addition of hydrogen peroxide

Runs were carried with 366 nm lamp and at a recirculation rate of 300 mL/min. The dosing of hydrogen peroxide was studied by varying the H2O2/Orange II molar ratio (R): 10, 20, 40 and 60 for two concentration range: (a) for low concentrations of Orange II (0.25 mM) and (b) for higher concentrations of Orange II (1 mM) respectively. The results for the degradation of Orange II for the two concentrations ranges (a) and (b) were similar since in both cases 100% decoloration of Orange II was attained within 3 hours. Figure 3A and B show the results obtained.

The electricity input to achieve decoloration was 61.2 kWh/m³. At Orange II 0.25 M and 1 M concentration, the decoloration curve within the same time shows that the saturation of the solution in terms of incoming photons was not reached for the concentrations of Orange II selected. In both cases the H2O2 added was enough and in small excess during the oxidative process.

Continuously added H2O2 vs initial addition of H2O2 and membrane stability

A 96% decoloration was achieved using an Orange II/H2O2 of R20 for an Orange II concentration 0.25 mM after 150 min. When the same quantity of H2O2 was added continuously in aliquots of 300 μL/min within 150 min, the decoloration of the dye reached only 57%. Therefore, the H2O2 is to be added at the beginning of the runs during this study. The Nafion®117 Fe membrane (1.82% Fe by wt) did not leach out Fe-ions into the solution after multiple runs up to the detection limit of the Quantofix® of 2 ppm Fe-ions in solution.

Homogeneous catalysis

This study was carried out using a lamp with 366 nm and a 0.25 mM Orange II solution with a R20 molar relationship. Four concentrations of Fe-ions were tested in solutions: 0, 0.5, 2 and 10 ppm. The results obtained are presented in Figure 4. Decoloration proceeds within one hour with an electricity consumption of 24.5 kWh/m³.

The decoloration kinetics of Orange II improves in the reactor up to a Fe-concentration of 10 ppm. When using 2 ppm of iron (III) in solution, the complete decoloration of Orange II was possible. This Fe concentration was therefore selected as appropriate for the present study. Without ferric ions, only a low degree of Orange II degradation was observed due to the H2O2 present.
Heterogeneous vs homogeneous catalysis: mineralization and kinetics

Mineralization

Figure 5 shows the percentage of mineralization taking place during homogeneous and heterogeneous catalysis.

The mineralization kinetics was favored in the case of homogeneous catalysis. This is consistent with the observation that all the H$_2$O$_2$ was consumed after 90 minutes reaction in the homogeneous case vs only 42% in the heterogeneous Fenton process.

Kinetic study

The kinetic study of the mineralization was analyzed in terms of 1st and 2nd order kinetics as according to Chan & Chu (2003). The regression coefficients obtained are shown in Table 2. Figure 5 shows the lines plotted using the Chan and Chu model, indicating an excellent agreement between the experimental results and the values predicted by the selected model.

The parametric equation of the Chan-Chu kinetic model is presented next. The main characteristic is the physical meaning of its parameters $\rho$ and $\sigma$ through the values of $-1/\rho$ and $1/\sigma$, respectively. The first is related to the initial oxidation capacity while the second is related to the final oxidation capacity or theoretical oxidation percentage:

$$\frac{t}{1 - C/C_0} = \rho + \sigma t$$

Where $t =$ reaction time; $C_0 =$ initial concentration; and $C$ concentration at instant $t$.

Table 2 | Kinetic values found during Orange II degradation

<table>
<thead>
<tr>
<th></th>
<th>Order 1</th>
<th>Order 2</th>
<th>Chan-Chu Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterogeneous</td>
<td>0.8237</td>
<td>0.9116</td>
<td>0.9962</td>
</tr>
<tr>
<td>Homogeneous</td>
<td>0.9906</td>
<td>0.3734</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

Originally, this model was applied to the homogeneous degradation of atrazine using Fenton reagent and photo-Fenton mediated oxidation of PCBs (Riaza-Frutos et al. 2007). It describes the two stages of the reaction satisfactorily through two parameters: the initial slope or rate of the oxidation process ($-1/\rho$) and the final oxidation capacity during the process ($1/\sigma$). These parameters are sensitive to the concentration H$_2$O$_2$ present.

The slopes in homogeneous processes were indicative of the higher rate of mineralization taking place. The oxidation capacity ($-1/\rho$) was higher for the homogeneous catalysis with values of $2.5 \times 10^{-2}$ vs. a value of $3.75 \times 10^{-3}$ for heterogeneous processes. For the heterogeneous catalysis, 40% mineralization was reached whereas the model ($1/\sigma$) predicts 63%. Regarding the homogeneous catalysis, the model predicts 100% mineralization because ($1/\sigma$) reaches a value above 1 (1.11) since the model calculates it on infinite time. This result is in agreement with the experimental data after 300 minutes where the percentage of mineralization achieved was 100%.

Effect of surfactants during Orange II decoloration in homogeneous Fenton processes

Figure 6 shows the surfactants LAS and K-perfluorooalkyl sulphonate FT800 hinder the decoloration of Orange II in the photo-reactor.

Both of the surfactants are used in the textile industry (Castillo & Barceló 2001; Olsen et al. 2004) and were added in Figure 6 at concentrations corresponding to the critical micelle concentration. These values are in the range used commonly in studies on surfactants in textile wastewater (Feitkenhauer & Meyer 2002; Arslan-Alaton & Alaton 2007). Figure 6 shows that LAS hinders the Orange II decoloration in a more significant way than FT800.

The fluorinated surfactant was resistant to the highly oxidative radicals attack generated by the Fenton system since no F-ions could be detected in solution using the
MBAS method (described in the Experimental Section). These results agree with the results reported for FT800 by Hidaka et al. (1992) and Sun et al. (1993). In the case of LAS the radical attack decreased its concentration from 98.7 ppm to 51.2 ppm as detected by the MBAS method.

The C–C bond energy (347 KJ/mol) is lower than the bond energy for C–F (441 KJ/mol) for the fluorinated surfactants. The lower bond energies for LAS besides a lower steric barrier hindering the diffusion of the radicals towards Orange II seems to explain the pattern for the effect of the surfactants reported in Figure 6.

CONCLUSIONS

The decoloration of Orange II during heterogeneous processes mediated by Nafion-Fe membranes were shown to be effective under 366 nm light for solutions 0.25 to 1 mM Orange II and to be almost complete within 2½ hours. An excess of the initially added H2O2 favored the reaction. In homogeneous photo-Fenton systems, the oxidation of Orange II shows that only 2 ppm of Fe were necessary on photo-Fenton reactions for the complete oxidation of Orange II in the presence of H2O2. The decoloration was completed within 1 hour. Surfactants added to Orange II solution were shown to hinder decoloration of the dye during photo-reactor operation.

REFERENCES


