

Insights into degradation mechanism of Orange G by photo-Fenton oxidation: Determination of Optimal conditions and identification of by-products

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Introduction

Azo dyes have been widely used in several industries and are recognized as toxic, carcinogenic and non-biodegradable. Several advanced oxidation processes, such as Fenton, electro-Fenton or photo-Fenton have been used for the degradation of dyes with good removal efficiency [1-2]. Despite these achievements, just few ones highlighted the fate of degradation by-products. This work is proposed as a breakthrough in the well-established degradation mechanism of OG oxidation by photo-Fenton process.

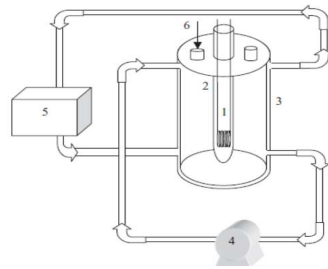


Fig. 1. Photochemical experimental setup

Materials and Methods

Chemicals

Orang G dye, hydrogen peroxide (30%) and iron sulfate $Fe_2(SO_4)_3$ were purchased from Sigma Aldrich (France).

Experimental setup

- (1) Low pressure mercury vapour lamp emitting at 253.7 nm
- (2) Quartz tube
- (3) Reaction vessel
- (4) Pump for sample homogenisation
- (5) Cooling tap water
- (6) Sampling

Orange G oxidation

As the processing time increase, the absorbance related to the azo-bond at 478 nm decreases, with almost complete disappearance after 3 min of treatment, suggesting its fast cleavage and OG oxidation (Fig. 2a). Nevertheless, the observed degradation is not related to effective mineralization because only 9.5% TOC removal is achieved after 15 min. To improve the process efficiency, an optimization of operational parameters is carried out.

Results and discussions

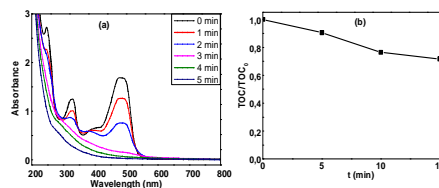


Fig.2. OG discoloration (a) and mineralization (b) as a function of treatment time. $[Fe^{3+}]_0 = 0.2 \text{ mM}$; $[H_2O_2]_0 = 4 \text{ mM}$

By-products analysis

Fig.6a. presents identified short chains carboxylic acid using 0.2 mM of Fe^{3+} , 3 mM of H_2O_2 and 0.2 mM of OG. The fast conversion of these acids is observed, suggesting their mineralization into CO_2 , H_2O and inorganic anions. In Fig 6b. the concentration of released anions are followed under optimal conditions of degradation using 0.1 mM of OG, with the expected sulfate concentration of 0.2 mM for a total conversion of sulfur. The other identified by-products like aromatics intermediates and the techniques for their identification are highlighted in table 1.

Effect of initial H_2O_2 concentration

As shown in Fig.3a., an increase of concentration from 1 to 6 mM, is favorable for OG degradation as more hydroxyl radical is produced. Fig.3b displays the mineralization results with an enhancement of TOC removal from 61.07% to 92.17% after 3 h of treatment. Further increase of H_2O_2 amount decreased the rate of degradation kinetics due to hydroxyl radicals consumption by H_2O_2 excess according to the following equation : $H_2O_2 + HO^* \rightarrow HO_2^* + H_2O$ (1)

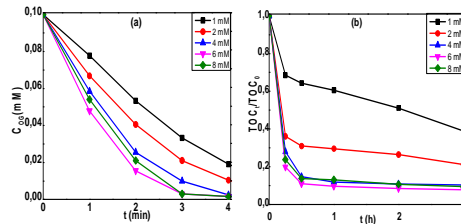


Fig. 3. Degradation (a) and mineralization (b) kinetics of OG as a function of H_2O_2 concentration $[Fe^{3+}]_0 = 0.4 \text{ mM}$.

Effect of initial Fe^{3+} concentration

Fig. 4a shows that complete degradation of OG is obtained at 0.4 mM of Fe^{3+} . In Fig.4b. TOC removal is improved from 82.94 to 92.17% by increasing Fe^{3+} concentration from 0.1 to 0.4 mM. Using 0.6 mM Fe^{2+} leads a decrease in TOC removal, due to the scavenging effect of the excess of photo-generated Fe^{2+} as : $Fe^{2+} + HO^* \rightarrow Fe^{3+} + HO^-$ (2)

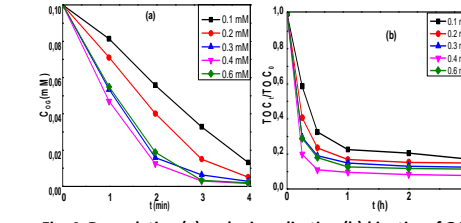


Fig. 4. Degradation (a) and mineralization (b) kinetics of OG as a function of the Fe^{3+} concentration; $[H_2O_2]_0 = 6 \text{ mM}$

Effect of initial Fenton reagents ratio

The above mentioned side reactions (1) and (2) decrease photo-Fenton efficiency, due to their high rate constants ($k_1 = 2.7 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_2 = 3.0 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$). To minimize their occurrence an experimental Fenton reagents ratio is established using apparent rate constants. From Fig.5a. given analytical equations are $k_{app, H_2O_2} = 0.0376 * ([H_2O_2]/[Fe^{3+}]) + 0.4659$ and $k_{app, Fe^{3+}} = -0.0074 * ([H_2O_2]/[Fe^{3+}]) + 1.0658$. The intersection of these straight lines correspond to a ratio of 13.33, which is founded to be the optimum value. From Fig.5b. 4.95 , 65.77 and 95.93 % of TOC removal are obtained after 3h of treatment using respectively UV alone, UV/ H_2O_2 (6 mM) and photo-Fenton at the optimal established ratio.

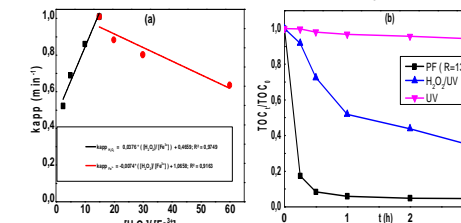


Fig. 5. (a) Apparent rate constant (k_{app}) of degradation as a function of $[H_2O_2]_0 / [Fe^{3+}]_0$ ratio and (b) comparative studies

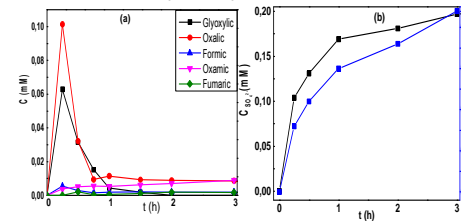


Fig. 6. (a) Carboxylic acids and (b) released anions profiles of concentration during Photo-Fenton process.

Table 1: Identified by-products

N°	Chemical Name	Techniques	Retention time (min)
1	Phtalic anhydride	HPLC	2.80
2	Phtalic acid	HPLC	2.95
3	Phenol	GC-MS	14.37
4	Hydroquinone	HPLC	3.48
5	P-Benzoquinone	HPLC / GC-MS	4.01
6	Oxamic acid	HPLC	14.94
7	Oxalic acid	HPLC	11.72
8	Fumaric acid	HPLC	16.74
9	Glyoxylic acid	HPLC	10.27
10	Formic acid	HPLC	14.10
11	Acetic acid	GC-MS	4.11

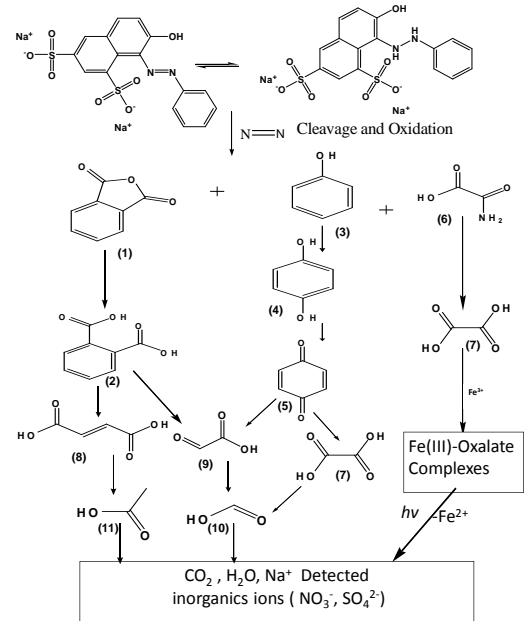


Fig. 7: Proposed reaction pathways of OG oxidation with hydroxyl radicals

Conclusion : The optimum ratio of Fenton reagents for photo-Fenton OG oxidation is founded to be 13.33. Under this condition complete degradation is registered after 4 min and 95.93 % of mineralization after 3 h of treatment. By-products identification were carried and a plausible mechanism oxidation is proposed.

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