



# Toxicity removal assessments related to degradation pathways of azo dyes: Toward an optimization of Electro-Fenton treatment



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## HIGHLIGHTS

- Monitoring ecotoxicity as an interesting approach to decrease time treatment and then energy consumption.
- Showing early formation of aromatic products correlated to the increase in solution toxicity
- Improving the degradation kinetic of persistent organic pollutants: 96% after 8 h for Acid Orange 7.

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## ABSTRACT

The degradation pathway of Acid Orange 7 (AO7) by Electro-Fenton process using carbon felt cathode was investigated via HPLC-UV and LC-MS, IC, TOC analysis and bioassays (*Vibrio Fischeri* 81.9% Microtox<sup>®</sup> screening tests). The TOC removal of AO7 reached 96.2% after 8 h treatment with the optimal applied current density at  $-8.3 \text{ mA cm}^{-2}$  and 0.2 mM catalyst concentration. The toxicity of treated solution increased rapidly to its highest value at the early stage of electrolysis (several minutes), corresponding to the formation of intermediate poisonous aromatic compounds such as 1,2-naphthaquinone (NAPQ) and 1,4-benzoquinone (BZQ). Then, the subsequent formation of aliphatic short-chain carboxylic acids like acetic acid, formic acid, before the complete mineralization, led to a non-toxic solution after 270 min for 500 mL of AO7 (1 mM). Moreover, a quantitative analysis of inorganic ions (i.e. ammonium, nitrate, sulfate) produced during the course of degradation could help to verify molar balance with regard to original nitrogen and sulfur elements. To conclude, a clear degradation pathway of AO7 was proposed, and could further be applied to other persistent pharmaceuticals in aquatic environment.

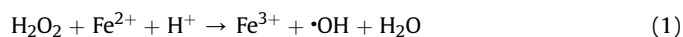
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## 1. Introduction

Textile wastewater is still being of great concern from environmental point of view, in terms of toxicity and persistence. Azo dyes, characterized by the presence of azo group ( $-\text{N}=\text{N}-$ ), represent approximately 70% in mass of all dyestuffs used worldwide, making them the largest group of synthetic colorants which are released into the environment. Many of them are known or possible toxic, carcinogenic and mutagenic substances that need to be treated

before discharge into aqueous medium (Andoralov et al., 2013). Acid Orange 7 (AO7), also called Orange II, is a typical azo dye (Fig. 1).

Electro-Fenton (EF) process has been known as an environmentally friendly electrochemical technology for the degradation of refractory pollutants in aquatic environment (Venkatesan and Santhanalakshmi, 2012). The principal reaction (Equation (1)) of the Fenton oxidation process produces hydroxyl radical through the catalyzed reduction of  $\text{H}_2\text{O}_2$  by  $\text{Fe}^{2+}$  in an acidic medium.



To avoid drawbacks encountered during the Fenton process, mainly  $\text{H}_2\text{O}_2$  transportation potential risk and activity loss, Electro-Fenton (EF) process has been developed. This latter combines the

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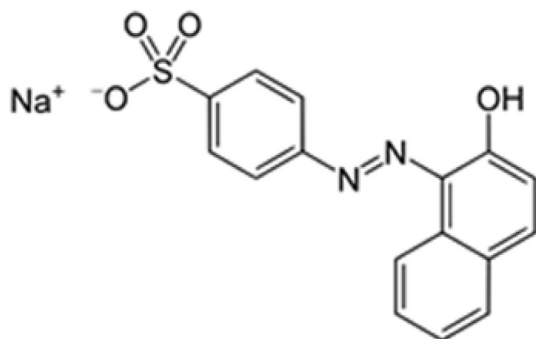


Fig. 1. Molecular structure of Acid Orange 7.

ferrous ion addition with the *in-situ* electro-generation of  $\text{H}_2\text{O}_2$ . The production of  $\text{H}_2\text{O}_2$  in aqueous solution is obtained by electro-reduction of dissolved oxygen (Equation (2)) under an appropriate applied current (or cathodic potential) (Xia et al., 2015). Cathodic electrodes such as vitreous carbon (Arredondo Valdez et al., 2012), carbon felt (Thi Xuan Huong et al., 2015; Le et al., 2015a, 2016, 2015b), carbon sponge (Özcan et al., 2008a), and gas-diffusion electrode (Yu et al., 2015) are commonly used for this purpose.



Thus, hydroxyl radicals can be generated in the solution by addition of a catalytic quantity of  $\text{Fe}^{2+}$  ions (Equation (1)).  $\cdot\text{OH}$  can then attack and initiate the oxidation of pollutant (RH) following Equation (3).



Commercial carbon felt, used in this study, owns several advantages such as no toxicity, good conductivity, low weight, high chemical resistance, high thermal stability, easy handling and low cost (González-García et al., 1999; Brillas et al., 2009). This is why it has been applied in various applications relevant to water treatment by Electro-Fenton (EF) process (Hammami et al., 2007), vanadium redox flow batteries (Lim and Lee, 2015; Oh et al., 2015; Liu et al., 2015), microbial fuel cell (Cui et al., 2015), and electrochemical technologies (Cotillas et al., 2015; Wang et al., 2015). Used as electrode in EF technology, it exhibits other outstanding properties like: (i) high specific surface area, good mechanical integrity, commercial availability and efficient cathodic regeneration of  $\text{Fe}^{2+}$  ( $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ ), which make it an attractive cathode material for EF process (Zhou et al., 2014); (ii) Adaptable to many various EF systems with different shapes as well as areas of electrodes from small ( $2 \text{ cm}^2$ ) (Le et al., 2015b, 2016) to big size ( $60 \text{ cm}^2$  here); and (iii) its physico-chemical stability allows to decline significantly the cost for the EF technology, since it can be continuously used for many cycles (at least 10 cycles) without any decrease of the treatment efficiency.

In the recent studies, AO7 has been chosen as a refractory pollutant which was treated by the advanced oxidation processes (AOPs), such as using electrochemically generated  $\cdot\text{OH}$  radicals in acidic aqueous medium by a boron-doped diamond or platinum anode could reach 98% TOC (Total Organic Carbon) removal after 9 h of electrolysis (Aquino Neto et al., 2014). Hydroxyl radicals was also created from Fenton's reagent at the carbon-felt cathode to the removal of nearly 92% TOC from initial AO7 pollutant after 8 h treatment (Murata et al., 2009). Besides that, AO7 could be

decolorized and degraded by an eco-friendly method through the enzymatic mechanisms involved bacteria (Andoralov et al., 2013). The radiolytic degradation of Acid Orange 7 (AO7) in aqueous solutions was investigated to find by-products concerning N–N and C–N cleavages from mother-molecular (Crespihlo et al., 2006).

Chemical degradation pathways of dyes by Electrochemical Advanced Oxidation Processes (EAOP) have been extensively studied (Le et al., 2015b; Özcan et al., 2008a). However the ecotoxicity study of sub-products generated by the process at different times has not been reported yet. The aim of this work is then to acquire both chemical and eco-toxicological information on the degradation mechanisms of AO7 by Electro-Fenton reaction on carbon felt electrode, while proving that hydroxyl radicals ( $\cdot\text{OH}$ ), a highly powerful oxidizing agent, can mineralize toxic and bio-refractory organic pollutants into non or less toxic compounds. To do this, analytical identification and quantification of targeted molecules and their intermediate sub-products will be carried out by HPLC-UV and LC-MS, IC and TOC analysis, together with toxicity assessments performed during the course of EF process.

The results showed that the decomposition of initial pollutants led to the appearance of well identified aromatic compounds at the early stage of the process, followed by the formation of several short-chains carboxylic acids before that complete mineralization into carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) was achieved. Thus, a degradation pathway by the advanced oxidation (Electro-Fenton process) at optimal conditions of oxidant dose or oxidation duration reaching to nontoxic products could be constructed thoroughly and systematically for this model pollutant.

The novelty of this work focuses on the evaluation of the toxicity of by-products related to the degradation pathways of azo dye, Acid Orange 7. The results were proved tightly via various techniques such as HPLC-UV and LC-MS, IC, TOC analysis and bioassays (*Vibrio Fischeri* 81.9% Microtox<sup>®</sup> screening tests). The work one again points out the high efficiency of EF technology for treatment of bio-refractory pollutants where toxic initial compounds are quickly degraded into non-toxic compounds.

## 2. Materials and methods

### 2.1. Chemicals and bacterial strain

The carbon felt was purchased from A Johnson Matthey Co., Germany. AO7 (Orange II sodium salt), sodium sulphate (anhydrous, 99.0–100.5%); sodium hydroxide (99%); sulfuric acid (95–97%); iron (II) sulphate hepta-hydrate (99%); hydroquinone (HQ); 1,4-benzoquinone (BZQ); 2-formyl-benzoic acid (FBA); 1,2-naphthoquinone (NAPQ); 2-hydroxyl-1,4-naphthalenedione (HNQ); 4-hydroxylbenzenesulphonic acid (HBA); 2-naphthol (NOL); oxalic acid (OA); maleic acid (MA); oxamic acid (OMA); fumaric acid (FA) were obtained from Sigma-Aldrich. TOC standard of 1000 mg/L (Sigma-Aldrich Co.) and sodium hydrogen carbonate (99.5%, ACS, Karlsruhe) were used for total organic and inorganic carbon calibration curves assessments. Bacterial strain of *Vibrio fischeri* NRRL B-11177 involved in toxicity tests came from Hach Lange GmbH, Germany. Osmotic adjusting solution (MilliQ water with 22% NaCl) and diluent (MilliQ water with 2% NaCl) were used for the preparation of bacterial solutions.

### 2.2. Degradation of AO7 in Electro-Fenton system

Electro-Fenton experiments were performed at room temperature in a 500 mL undivided cylindrical glass cell with a two-electrodes system (Fig. 2). The applied current was controlled thanks to a power supply (Lambda Electronic, USA) in galvanostatic mode. The carbon felt cathode ( $60 \text{ cm}^2$ ) was used as working

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