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Research article

Semi-empirical chemical model for indirect advanced oxidation of Acid Orange 7 using an unmodified carbon fabric cathode for H_2O_2 production in an electrochemical reactor

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ABSTRACT

A commercial Unidirectional Carbon Fabric piece was used to design an electrode for the cathodic O_2 reduction reaction in a divided (by a Nafion® 117 membrane) parallel plate reactor. The anode was a commercial stainless steel mesh. Under this approach it is feasible to produce H_2O_2 at low energy (2.08 kWh kg^{-1} H_2O_2) in low ionic acidic medium. In the catholyte side the H_2O_2 can be activated with Fe^{2+} to develop the Fenton reagent. It was found that Acid Orange 7 (AO7) indirect oxidation (in the concentration range of 0.12–0.24 mM) by Fenton chemistry follows a first order kinetic equation. The energy required for 0.24 mM AO7 degradation is 1.04 $kWhm^{-3}$. From each experimental AO7 oxidation the main parameters (*a*, *mM* and *k*, min^{-1}) of the first order kinetic equation are obtained. These parameters can be correlated with AO7 concentration in the concentration range studied. Based on this method a semi-empirical chemical model was developed to predict the AO7 abatement, by means of Fenton chemistry. Good AO7 oxidation predictions can be made in the concentration range studied. A detailed discussion of the energy required for oxidizing AO7 and the accuracy of the chemical model to predict its oxidation is included in this paper.

1. Introduction

Although most of the existing carbon materials were not developed for electrochemical applications, in the last 50 years these manufactured materials have been applied for developing novel environmental electrochemical processes. Its acceptability resides in its mechanical, chemical and physics properties. Moreover, carbon is not a scarce material; it is rather an economic stuff, in general presents a minimum of both health hazards and environmental effects. Among the first carbon electrochemical applications the Cu^{2+} cathodic reduction on a carbon porous electrode, can be mentioned (Bennion and Newman, 1972). In 1976 the reticulated vitreous carbon (RVC) was developed for several non-electrochemical applications; however, shortly after some electrochemical applications employing this material were already documented. Due to its electrochemical characteristics RVC was very attractive for studying its electrochemical performance as a 3D-electrode. The most important electrochemical processes in which RVC was involved, were reviewed many times (Wang, 1981; Pletcher and Walsh, 1992; Friedrich et al., 2004). Since several decades ago, graphite was as well involved in electrochemical subjects. For example as a cathode for H_2O_2 production (Sudoh et al., 1985). In biofuel cells graphite fibers wound, around a conductive metal core, was used as anode (Logan et al., 2007); while, in other similar application it was used as both cathode and anode (Gregory et al., 2004). Lately, new kinds of carbon materials have been investigated like the production of e-textiles by means of the incorporations of metals (Singh et al., 2010), conductive polymers or layer graphene/graphite (Woltornist et al., 2015) on the surface of fabric materials. The resulting materials can be applied to biosensors, heat generation, wearable electronics, communication, medicine, and energy (Woltornist et al., 2015; Lee et al., 2013). In this way, in a recent work it is shown that Pt-modified and Pt/polyaniline-modified carbon fiber fabric electrodes were prepared for electrochemical application, mainly focused to textile wastewater treatment (Fernández et al., 2015).

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Unidirectional Carbon Fabric (UCF) is a conductive material, developed by Fibre Glast Developments for a wide range of industrial applications, including auto racing, boat hulls, hockey sticks, bicycles and aerospace. The objective of this work is to test this carbon fabric in environmental electrochemical applications. Due to its physical properties (conductivity and flexibility) this material can be used to design an electrode for the cathodic oxygen reduction reaction (ORR) in a divided parallel plate reactor. It is feasible to produce H_2O_2 as a function of the carbon fabric surface (geometrical design). The H_2O_2 can be activated in the presence of Fe^{2+} upon its electrogeneration to produce the Fenton reagent. Therefore this approach can be used to textile wastewater treatment. In this work a synthetic wastewater was prepared by dissolving an azo dye in a slightly acidic solution. The Acid Orange 7 (AO7) was chosen as a model pollutant, organic molecule to evaluate the electrochemical performance of an unmodified UCF cathode. The quest for feasible, environmental processes to abate AO7 (in general azo dyes) from textile wastewater is justified and lately this subject has then attracted increasing academic interest (Fernando et al., 2014; Lau et al., 2014; Zhou et al., 2014; Scialdone et al., 2014).

In this work, a simple semi-empirical chemical model was developed to predict the AO7 abatement, in a range of AO7 concentrations studied, by means of Fenton chemistry. The fraction of H_2O_2 activated ($OH^{\bullet}$ production) by Fe^{2+}, provides a measure of the efficiency of the AO7 oxidation process. AO7 oxidation follows a pseudo first order kinetics but it can be visualized as a first order kinetics. The AO7 degradation by Fenton chemistry follows an exponential decay *vs* time. In such decay, the rate velocity (k) is a function of the initial AO7 concentration. Therefore, for a given range of AO7 concentration the function $k = f(AO7_0)$ can be determined. For a given electrolysis time, it is possible to evaluate (by means of Faraday's law) the amount of H_2O_2 electro-produced and the fraction of AO7 oxidized. Theoretical values are compared against experimental ones and a detailed discussion of the energy required for oxidizing AO7 and the accuracy of the chemical model to predict its oxidation is included in this paper.

2. Theoretical approach

2.1. H_2O_2 production

ORR is a complex electrochemical reaction. On carbon, it takes place simultaneously by both 4-electron and 2-electrons pathways (Wiesener and Ohms, 1990). The ORR on a UCF surface will produce a mixture of H_2O_2/H_2O, according to equations (1) and (2).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

It is possible to decrease the energy for H_2O_2 production if a low energy anodic reaction is chosen. Thus, on a Fe-anode the spontaneous electro-production of Fe^{2+} is expected in an acidic anolyte. However, at a sufficiently positive anode potential, Fe^{2+} can be oxidized to Fe^{3+}, according to

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (3)$$

Reaction (3) is a less energy demanding reaction than O_2 evolution. For a given electrolysis time (t, *in seconds*), the amount of H_2O_2 is evaluated by Faraday's law and the cumulative current efficiency (ϕ) for H_2O_2 production, see equation (4).

$$n_{H_2O_2} = \frac{I_{Cell} t}{2F} \phi \quad (4)$$

Where $n_{H_2O_2}$ are the H_2O_2 moles electro-produced on a UFC surface, I_{Cell} is the cell current (A), F is Faraday's constant (C mol^{-1}).

2.2. AO7 oxidation

The interactions of soluble iron cations (Fe^{II}/Fe^{III}) with H_2O_2 give a near-stoichiometric generation of a strong oxidant. Although the identification of such strong oxidant is still controversial (Bossmann et al., 1998; Kremer, 1999), it is accepted that it is the $OH^{\bullet}$. The fraction of the organic conversion (or the fraction of the hydrogen peroxide activated) provides a measure of the efficiency of the AO7 oxidation process. In a simplified mechanism the reduction of H_2O_2 can be visualized by means of the following reaction:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (5)$$

In a simple chemical model, equation (5) can represent the H_2O_2 activated by soluble iron cations. By means of equation (5) it is possible to represent the stoichiometric 68-electrons AO7 oxidation reaction, if sulfur and nitrogen are transformed in sulfuric acid and ammonium, respectively, see equation (6).

$$C_{16}H_{11}O_4N_2SNa + 34H_2O_2 \rightarrow 16CO_2 + NaHSO_4 + 2NH_3 + 36H_2O \quad (6)$$

Except for the first minute of AO7 oxidation, the dye abatement follows an apparent first order kinetic equation and can be adjusted to the following equation:

$$[AO7]_t = a\left(e^{-kt}\right) \quad (7)$$

Where $[AO7]_t$ is the AO7 concentration (mM), at any time t during the electrolysis time; a (mM) is a constant but does not represent the initial AO7 concentration and k (min^{-1}) is the rate constant of the reaction.

From a set of absorbance values *vs* electrolysis time, measured during the oxidation of different AO7 concentrations, it is possible to fit the experimental data to a first order kinetic equation. Evidently, the absorbance values were first converted to concentration values by means of the Lambert–Beer law. From each experimental AO7 oxidation a pair of a (mM) and k (min^{-1}) are obtained. These parameters can be correlated with AO7 concentration in the concentration range studied. For a given unknown AO7 concentration a pair of a and k are obtained from the previous correlation. If such parameters are substituted in equation (7) and the time starts to increase, a theoretical AO7 oxidation is obtained. At any time, the AO7 concentration and its absorbance in the catholyte can be evaluated. Other useful information can be obtained as well, such as H_2O_2 electro-produced and the energy required at any time.

3. Experimental

3.1. Solutions and chemicals

All experiments were performed at room temperature. The electrolytes were prepared using laboratory tap water. The chemicals used in this work were reagent grade quality (Aldrich–Sigma or JT Baker). AO7 (molecular weight, 350.3 g mol^{-1}) was supplied by Ciba Specialty Chemicals. The anolyte was 1.5 L of 0.8 M H_2SO_4, while the catholyte consisted of 1.5 L of 0.05 M Na_2SO_4 (pH 2,