



Degradation of the azo dye Acid Red 1 by anodic oxidation and indirect electrochemical processes based on Fenton's reaction chemistry. Relationship between decolorization, mineralization and products



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ABSTRACT

Solutions of 236 mg dm⁻³ Acid Red 1 (AR1), an azo dye widely used in textile dyeing industries, at pH 3.0 have been comparatively treated by anodic oxidation with electrogenerated H₂O₂ (AO-H₂O₂), electro-Fenton (EF) and photoelectro-Fenton (PEF) at constant current density (*j*). Assays were performed with a stirred tank reactor equipped with a Pt or boron-doped diamond (BDD) anode and an air-diffusion cathode for H₂O₂ generation from O₂ reduction. The main oxidizing agents were hydroxyl radicals produced at the anode from water oxidation in all methods and in the bulk from Fenton's reaction between generated H₂O₂ and 0.5 mmol dm⁻³ Fe²⁺ in EF and PEF. For each anode, higher oxidation power was found in the sequence AO-H₂O₂ < EF < PEF. The oxidation ability of the BDD anode was always superior to that of Pt. Faster and similar decolorization efficiency was achieved in EF and PEF owing to the quicker destruction of aromatics with hydroxyl radicals produced in the bulk. The PEF process with BDD was the most potent method yielding almost total mineralization due to the additional rapid photolysis of recalcitrant intermediates like Fe(III)-carboxylate complexes under UVA irradiation. The increase in *j* always enhanced the decolorization and mineralization processes because of the greater production of hydroxyl radicals, but decreases the mineralization current efficiency. A total of 11 aromatic intermediates, 15 hydroxylated compounds, 13 desulfonated derivatives and 7 short-linear carboxylic acids were identified. NH₄⁺, NO₃⁻ and SO₄²⁻ ions were released during azo dye degradation. From the products detected, a comprehensive reaction sequence for AR1 mineralization is proposed. The relationship between decolorization, mineralization and products formed is finally discussed.

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1. Introduction

Recently, the UNESCO's World Water Development Report [1] manifested the growing concern about dyeing industrial effluents. Large volumes of industrial effluents with high dye contents are discharged into water bodies causing esthetic problems derived from their color and their worrying hazardous effects on living beings. Azo dyes are the most used organic dyes, representing for over 70% of annual dyes consumption [2]. They have the

azo group (–N=N–) as chromophore, associated with aromatic systems containing groups such as –OH and –SO₃H. Azo dyes are highly recalcitrant and are hardly removed by conventional biological and physicochemical methods, thus persisting in the aquatic environment [2,3]. They are toxic to aquatic organisms and humans [4,5] and possess carcinogenic, mutagenic and bactericide properties [1]. The development of powerful and effective oxidation processes to remove azo dyes and their by-products from wastewaters are required to avoid their adverse environmental impact and the danger they imply to public health.

Electrochemical advanced oxidation processes (EAOPs) are based on the *in situ* generation of hydroxyl radical (•OH) to mineralize organic matter in waters [6,7]. The high standard redox potential of this radical ($E^\circ(\bullet\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$) favors its non-selective reaction with most organics giving dehydrogenated or

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hydroxylated derivatives up to complete combustion to CO₂, inorganic ions and water. EAOPs are promising and environmentally friendly technologies that are very effective for organics degradation and easily usable and scalable [6–10]. Although some papers have been recently published dealing with the decolorization and removal of several azo dyes by these methods [11–15], much deeper information about the influence of operating parameters and generated products on the degradation processes of a high number of these pollutants is needed to clarify the possible viability of EAOPs for wastewater remediation.

The most typical EAOP is anodic oxidation (AO), where adsorbed hydroxyl radical (M(•OH)) is generated from water discharge by reaction (1) at an anode (M) with high O₂-overpotential by applying a high current [6,13,16–20].

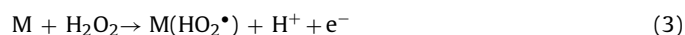


The non-active boron-doped diamond (BDD) anode is currently considered the best anodic material for AO since it generates very high amounts of reactive physisorbed BDD(•OH) radicals as a result of its very weak BDD•OH interaction and great O₂-overpotential [21]. These properties confer BDD the ability of being more effective to remove aromatics including azo dyes than other common anodes such as Pt [22,23] and PbO₂ [24,25].

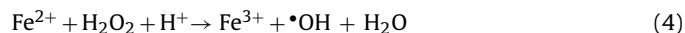
Carbonaceous cathodes like graphite [26], carbon or graphite felts [12,26–30], activated carbon fiber [31], carbon sponge [32], carbon-polytetrafluoroethylene (PTFE) gas (O₂ or air) diffusion [11,15,33–36], carbon nanotubes [37,38] and BDD [14,39,40] have shown a high efficiency for H₂O₂ electrogeneration from the two-electron reduction of injected O₂ from reaction (2):



In an undivided cell for AO, the use of a carbon-PTFE air-diffusion cathode minimizes the possible cathodic reduction of organic pollutants [15,23]. In this EAOP, so-called AO with electrogenerated H₂O₂ (AO-H₂O₂), other weaker reactive oxygen species (ROS) than •OH can be produced at the anode, like hydroperoxyl radical (HO₂•) from H₂O₂ oxidation by reaction (3):

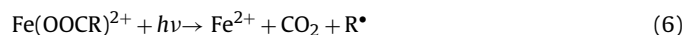


Cathodes with ability for H₂O₂ electrogeneration have also been extensively used in indirect EAOPs based on Fenton's reaction chemistry [7–9]. The most common method is electro-Fenton (EF) [11,12,15,26–30,32,35,36], where •OH is produced in the bulk from the reaction between generated H₂O₂ and low amounts of added Fe²⁺ ion by Fenton's reaction (4) with optimum pH 2.8:



Reaction (4) is catalytic and can be propagated from Fe²⁺ regeneration, pre-eminently by Fe³⁺ reduction at the cathode [27,32].

When an undivided cell is used in EF, organic molecules are mainly destroyed by the combined action of M(•OH) formed at the anode from reaction (1) and •OH produced in the bulk from reaction (4), along with a slower destruction by other weaker ROS such as H₂O₂ and HO₂• [7]. Unfortunately, the EF treatment of aromatics with an air-diffusion cathode does not allow total mineralization of aromatic solutions due to the formation of Fe(III)-carboxylate complexes that are only slowly removed by BDD(•OH) [7,41]. This problem can be solved performing the photoelectro-Fenton (PEF) process, in which the solution treated by EF is irradiated with UVA light [15,31,33,42–45] and the degradation process is enhanced by: (i) the photoreduction of Fe(OH)²⁺, the pre-eminent Fe³⁺ species at pH near 3, to regenerate Fe²⁺ producing more •OH from reaction (5) and (ii) the photolysis of generated Fe(III)-carboxylate complexes by the general reaction (6):



The aim of this paper is to gain a better knowledge on the decolorization and mineralization processes of azo dyes during their EAOP treatments. To do this, the AO-H₂O₂, EF and PEF degradations of an azo dye widely used in the textile industry like Acid Red 1 (AR1, C₁₈H₁₃N₃O₈S₂²⁻, see characteristics in Table 1) were comparatively studied at pH 3.0 using Pt/air-diffusion and BDD/air-diffusion cells. Solutions with 236 mg dm⁻³ AR1 (100 mg dm⁻³ of dissolved organic carbon (DOC)) were checked, since it corresponds to typical azo dye contents found in industrial effluents [34]. The influence of current density (*j*) on the decolorization efficiency and mineralization degree and rate was examined to better explain the role of generated oxidizing agents and/or UVA radiation in all the EAOPs tested. Aromatic intermediates were identified by liquid chromatography-mass spectrometry (LC-MS). Generated carboxylic acids and released inorganic ions were identified and quantified by high-performance liquid chromatography (HPLC). A reaction sequence for AR1 mineralization involving all the products detected is proposed. Finally, the relationship between decolorization, mineralization and products formed is discussed.

2. Experimental

2.1. Chemicals

Reagent grade Acid Red 1 was supplied by Sigma-Aldrich and used as received. Analytical grade anhydrous sodium sulfate and iron(II) sulfate heptahydrate were purchased from Fluka and Sigma-Aldrich, respectively. The solution pH was initially adjusted with analytical grade sulfuric acid supplied by Across Organics. Sodium perchlorate and perchloric acid, used in some trials, were analytical grade purchased from Merck. Carboxylic acids, other chemicals and solvents used in chromatographic techniques were of HPLC, LC-MS and analytical grade purchased from Sigma-Aldrich, Lancaster, Merck and Panreac. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system with resistivity > 18 MΩ cm at 25 °C.

2.2. Electrolytic system

Electrolytic experiments were performed in an open and undivided two-electrode cell of 150 cm³ capacity with an external jacket allowing circulation of thermostated water regulated by a Selecta Digiterm 3000524 thermostat. The anode was a BDD thin film supplied by Adamant Technologies (La-Chaux-de-Fonds, Switzerland) or a Pt sheet of 99.99% purity supplied by SEMPISA (Barcelona, Spain). The cathode was a carbon-PTFE air-diffusion electrode from E-TEK (Somerset, NJ, USA), mounted as described elsewhere [46], allowing H₂O₂ generation from air injection at a flow rate of 300 cm³ min⁻¹. All electrodes had a geometric area of 3 cm² and were separated about 1 cm. The assays were made at constant *j* by connecting the electrodes to an Amel 2053 potentiostat-galvanostat and the potential difference of the cell was directly measured with a Demestres 601BR digital multimeter. To remove the impurities of the BDD anode surface and activate the air-diffusion cathode before the degradation trials, they were polarized in 100 cm³ of a 0.05 mol dm⁻³ Na₂SO₄ solution at 100 mA cm⁻² for 180 min.

All experiments were carried out with 100 cm³ of solutions containing 236 mg dm⁻³ AR1 in 0.05 mol dm⁻³ Na₂SO₄ as background electrolyte at pH 3.0. In EF and PEF, 0.5 mmol dm⁻³ Fe²⁺ were added to the solution as catalyst. The solution pH and the Fe²⁺ concentration were chosen since they have been found optimal for similar treatments of other aromatics [11,15,33–36]. The solution was maintained at 35.0 °C, which is the maximum temperature that our system can be thermostated without significant water

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