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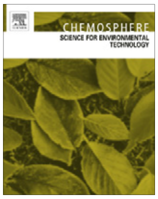

Electrochemical mineralization of the azo dye Acid Red 29 (Chromotrope 2R) by photoelectro-Fenton process

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HIGHLIGHTS

- ▶ Quick decolorization of Acid Red 29 solution by photoelectro-Fenton.
- ▶ Almost total mineralization at optimum values of 0.5–1.0 mM Fe^{2+} and pH 3.0.
- ▶ More rapid pseudo-first-order kinetics for dye decay than solution decolorization.
- ▶ Tetrahydroxy-*p*-benzoquinone and short-linear carboxylic acids detected by HPLC.
- ▶ Mineralization of initial N as ammonium ion and in lesser proportion as nitrate ion.

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ABSTRACT

The degradation of 100 mL of 244 mg L^{-1} of the azo dye Acid Red 29 (AR29) has been studied by photoelectro-Fenton (PEF) using an undivided cell containing a boron-doped diamond (BDD) anode and an air-diffusion cathode under UVA irradiation. The effect of current density, concentration of catalytic Fe^{2+} and pH on the process was examined. Quick decolorization and almost total mineralization were achieved due to the synergistic action of UVA light and oxidant hydroxyl radicals formed in the bulk from Fenton's reaction between electrogenerated H_2O_2 at the cathode and added Fe^{2+}, as well as in the BDD surface from water oxidation. Optimum PEF conditions were found for 0.5–1.0 mM Fe^{2+} and pH 3.0. Comparable electro-Fenton (EF) degradations in the dark yielded much poorer mineralization. The decay kinetics of AR29 followed a pseudo-first-order reaction with similar rate for EF and PEF. The azo dye disappeared much more rapidly than solution color, suggesting the formation of colored conjugated products with λ_{max} similar to that of AR29. Ion-exclusion HPLC allowed the detection and quantification of tetrahydroxy-*p*-benzoquinone, oxalic, oxalacetic, tartronic, tartaric, oxamic, malonic and fumaric acids as intermediates in the PEF process. Oxalic acid, accumulated in large extent, was quickly destroyed by the efficient photolysis of Fe(III)–oxalate complexes with UVA light, whereas tartronic and oxamic acids were the most persistent byproducts because of the larger stability of their Fe(III) complexes. The mineralization of the initial N of the azo dye yielded NH_4^+ ion and NO_3^- ion in smaller proportion.

1. Introduction

Over the last decade, electrochemical advanced oxidation processes (EAOPs) based on Fenton's reaction chemistry such as electro-Fenton (EF) and photoelectro-Fenton (PEF) have received increasing attention for the degradation of toxic and/or biorefractory organics in waters (Brillas et al., 2009; Martínez-Huitle and Brillas, 2009; Peralta-Hernández et al., 2009). This interest is due to their environmental compatibility, versatility, high efficiency, amenability of automation and safety because they operate at mild conditions. These EAOPs are characterized by the continuous supply of hydrogen peroxide to a contaminated acidic solution by the two-electron cathodic reduction of injected O_2 from the following reaction:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

Efficient carbonaceous cathodes for H_2O_2 electrogeneration from reaction (1) are carbon nanotubes on graphite (Khataee et al., 2012), carbon nanotubes–polytetrafluoroethylene (PTFE) (Khataee et al., 2009; Zarei et al., 2010), carbon felt (Guivarch et al., 2003; Hammami et al., 2008; Özcan et al., 2009), carbon

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sponge (Özcan et al., 2008), graphite felt (Panizza and Oturan, 2011), graphite cloth (Peralta-Hernández et al., 2008), activated carbon fiber (Wang et al., 2008, 2010) and carbon-PTFE gas (O_2 or air) diffusion electrodes (Boye et al., 2003; Panizza and Cerisola, 2009; Borràs et al., 2011).

In EF, the oxidation ability of electrogenerated H_2O_2 is strongly enhanced by adding small quantities of Fe^{2+} ion as catalyst to yield homogeneous $^{\cdot}OH$ and Fe^{3+} ion from Fenton's reaction (2) (Brillas et al., 2009; Özcan et al., 2009):

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-} \qquad (2)$$

$^{\cdot}OH$ is a strong oxidant with so high standard reduction potential ($E°(^{\cdot}OH/H_2O) = 2.80$ V/SHE) that non-selectively reacts with most organics giving rise to dehydrogenated or hydroxylated derivatives, which can be in turn totally mineralized. An advantage of EF in front of the classical chemical Fenton process is that reaction (2) is propagated by the cathodic reduction of Fe^{3+} to Fe^{2+} from the following reaction (Özcan et al., 2008; Sirés et al., 2008):

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

When an undivided cell with a boron-doped diamond (BDD) anode is used in EF, organics can also be attacked by heterogeneous $^{\cdot}OH$, designed as BDD($^{\cdot}OH$), produced from water oxidation at the anode by the following reaction (Marselli et al., 2003; Brillas et al., 2009):

$$\mathrm{BDD + H_2O \rightarrow BDD({}^{\cdot}OH) + H^+ + e^-} \qquad (4)$$

BDD thin-film electrodes are the most potent anodes known for water remediation (Martínez-Huitle and Brillas, 2008; Panizza and Cerisola, 2008). This is due to the very weak BDD–$^{\cdot}OH$ interaction giving a higher O_2-overpotential than other anodes like Pt (Hammami et al., 2008; Hamza et al., 2009) and PbO_2 (Flox et al., 2009) and the formation of higher amounts of heterogeneous $^{\cdot}OH$ from reaction (4), which destroy more rapidly the organic pollutants.

In PEF, the mineralization of the contaminated solution under EF conditions is enhanced by simultaneous irradiation with either artificial UVA light (Wang et al., 2008; Anotai et al., 2011; Borràs et al., 2011; Zhang et al., 2011; De Luna et al., 2012) or sunlight (Flox et al., 2007; Almeida et al., 2011; Salazar et al., 2011). The irradiation causes: (i) the photolysis of $Fe(OH)^{2+}$, the predominant species of Fe^{3+} in the pH range 2.5–4.0, yielding more Fe^{2+} and $^{\cdot}OH$ from reaction (5) and (ii) the photolysis of Fe(III)–carboxylate complexes, as the Fe(III)–oxalate complexes given by the following reaction for $n = 1–3$ (Garcia-Segura and Brillas, 2011).

$$\mathrm{Fe(OH)^{2+}} + h\nu \rightarrow \mathrm{Fe^{2+} + {}^{\cdot}OH} \qquad (5)$$

$$2\mathrm{Fe(C_2O_4)}_n^{(3-2n)} + h\nu \rightarrow 2\mathrm{Fe^{2+}} + (2n-1)\mathrm{C_2O_4^{2-}} + 2\mathrm{CO_2} \qquad (6)$$

Recent work has reported an enhancement of PEF treatment when it is combined with TiO_2 (Khataee et al., 2010; Zarei et al., 2010) or ZnO (Iranifam et al., 2011) photocatalysis.

More than 10000 dyes and pigments with Mt quantity are consumed every year in the world. About 70% of these products correspond to azo dyes, characterized by one or more azo bonds (—N═N—) as chromophore group associated with aromatic structures containing functional groups such as —OH and —SO_3H (Martínez-Huitle and Brillas, 2009). Azo dyes cause not only esthetic problems in waters, but also potential health and environmental risks due to their toxic, carcinogenic and mutagenic properties (Robinson et al., 2001; Kunz et al., 2002; Umbuzeiro et al., 2005; Sharma et al., 2007; Ulson de Souza et al., 2007). Only a limited number of papers have been published dealing with the degradation of azo dyes by the PEF process (Wang et al., 2008; Ruiz et al., 2011; Zhang et al., 2011). To gain a better knowledge of the viability of this treatment, we have studied the decolorization and mineralization of the azo dye Acid Red 29 or Chromotrope 2R (AR29) by means of PEF with UVA light of $\lambda_{max} = 360$ nm. AR29 is widely used in the textile industry and its characteristics are collected in Table 1. Previous work showed that low contents of AR29 can be removed by photocatalysis using nanocrystalline TiO_2/activated-carbon composite catalysts (Wang et al., 2007).

This paper reports the results obtained for the degradation of 244 mg L^{-1} AR29 solutions by PEF using a BDD/air diffusion cell exposed to UVA light. The influence of current density, Fe^{2+} concentration and pH on the decolorization and mineralization processes was examined. Comparative EF trials were also made to clarify the oxidation role of generated hydroxyl radicals and UVA irradiation. The kinetics of the azo dye decay and the evolution of oxidation products were followed by chromatographic techniques.

2. Experimental

2.1. Chemicals

Reagent grade azo dye AR29 (98.2% purity) was supplied by Carbone Scientific and used for the electrochemical experiments as received. Tetrahydroxy-*p*-benzoquinone was of reagent grade from Merck. Heptahydrated ferrous sulfate, used as catalyst, was of analytical grade from Fluka. Anhydrous sodium sulfate, used as background electrolyte, and sulfuric acid and sodium hydroxide, used to regulate the solution pH, were of analytical grade from Merck. Carboxylic acids were of analytical grade from Panreac and Avocado. Solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C. Organic solvents and other chemicals used were either of HPLC or analytical grade from Aldrich, Merck and Panreac.

2.2. Electrolytic system

All electrolytic experiments were conducted in an open and undivided cylindrical cell of 150 mL capacity with a double jacket where external thermostated water recirculated to maintain the solution temperature at 35 °C using a Thermo Electron Corporation HAAKE DC 10 thermostat. This temperature was chosen because it is the maximum value allowed in the cell with insignificant water evaporation during prolonged electrolysis. The anode was a BDD electrode purchased from Adamant Technologies, synthesized by the hot filament chemical vapor deposition technique on single-crystal *p*-type Si(100) wafers (0.1 Ω cm, Siltronix). The cathode was a carbon–PTFE air-diffusion electrode supplied by E-TEK and mounted as described elsewhere (Brillas et al., 2004). This cathode was fed with air pumped at 300 mL min^{-1} to generate H_2O_2 from reaction (1). The geometric area of both electrodes was 3 cm^2 and the interelectrode gap was ca. 1 cm. All the assays were performed at constant current density provided with an Amel 2053 potentiostat–galvanostat. To remove the impurities of the BDD surface and activate the air-diffusion cathode, they were previously polarized in 0.05 M Na_2SO_4 at 100 mA cm^{-2} for 60 min.

Comparative EF and PEF treatments of 100 mL of 244 mg L^{-1} AR29 (corresponding to 100 mg L^{-1} TOC) in 0.05 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 were made at current densities in the range 16.6–100 mA cm^{-2}. The influence of Fe^{2+} concentration between 0.2 and 5 mM and pH between 2.0 and 6.0 on the PEF process was also examined. In PEF, a Philips TL/6W/08 fluorescent black light blue tube of 320–400 nm with $\lambda_{max} = 360$ nm was placed at 7 cm above the solution for UVA illumination. This lamp supplied a photoionization energy input of 5 W m^{-2}, as detected with a Kipp&Zonen CUV5 radiometer. All electrolyses were carried out under vigorous stirring with a magnetic bar at 800 rpm to ensure