Chemosphere 82 (2011) 495–501

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photoelectro-Fenton processes with a boron-doped diamond anode

Edgar J. Ruiz [a], Conchita Arias [b], Enric Brillas [b], Aracely Hernández-Ramírez [a], J.M. Peralta-Hernández [a,*]

[a] Laboratorio de Fotocatálisis y Electroquímica Ambiental, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Av. Guerrero y Progreso, Col. Treviño, 64570 Monterrey, Nuevo León, Mexico

[b] Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 3 September 2010
Received in revised form 1 November 2010
Accepted 3 November 2010
Available online 26 November 2010

Keywords:
Azo dyes
Boron-doped diamond
Electrochemical advanced oxidation processes
Electro-Fenton
Photoelectro-Fenton

ABSTRACT

The degradation of the Acid Yellow 36 (AY36) azo dye is studied by electro-Fenton (EF) and solar photoelectro-Fenton (SPEF) using a recirculation flow plant with an undivided cell containing a boron-doped diamond anode and an air-diffusion cathode for H_2O_2 electrogeneration, coupled with a solar photoreactor. A solution of 2.5 L with 108 mg L^{-1} of the dye and 0.5 mM Fe^{2+} at pH 3.0 was comparatively treated at constant current. Hydroxyl radicals formed from Fenton's reaction and at the anode surface are the main oxidants. Total mineralization is almost achieved in SPEF, while EF yields poor TOC removal. Both processes are accelerated with increasing current. AY36 decays with similar rate in EF and SPEF following a pseudo first-order reaction, but the solution is more slowly decolorized because of the formation of conjugated byproducts. NH_4^+ ion is released in SPEF, while NO_3^- ion is mainly lost in EF. Tartronic, maleic, fumaric, oxalic, formic and oxamic acids are detected as generated carboxylic acids. Fe(III)-oxalate complexes are largely accumulated in EF and their quick photodecomposition in SPEF explains its higher oxidation power. The SPEF method yields greater current efficiency and lower energy cost as current decreases, and then it is more viable at low currents.

1. Introduction

About 70% of the world dye production corresponds to azo dyes (Villanueva-Rodríguez et al., 2009). These compounds have a chemical structure characterized by the presence of the azo group (—N=N—) as chromophore, associated with aromatic systems and groups such as —OH and —SO_3H, among others (Augugliaro et al., 2002; Martínez-Huitle and Brillas, 2009). They are mainly used in the textile industry, which generates large volumes of wastewaters containing high concentrations of dyes, surfactants, suspended solids and organic matter. Azo dyes are very stable in the environment and persist under oxidation and reduction conditions, light exposure and biodegradation. They are toxic for aquatic organisms and humans (Martínez-Huitle and Brillas, 2009; Villanueva-Rodríguez et al., 2009), being difficultly removed by conventional biological and physicochemical methods (Méndez-Paz et al., 2005; Bahadir, 2007; Martínez-Huitle and Brillas, 2009; Melgoza et al., 2009). Research efforts are then needed to develop effective destruction methods for azo dyes to avoid their hazardous effects on living beings.

Promising technologies for dyes removal are the advanced oxidation processes (AOPs), involving the in situ production of $^{\bullet}OH$. This species is a strong oxidant with so high standard potential (E° = 2.80 V/SHE) that reacts with most organics giving mineralization to CO_2, H_2O and inorganic ions (Peralta-Hernández et al., 2005; Brillas et al., 2009; Martínez-Huitle and Brillas, 2009). Recently, electrochemical AOPs (EAOPs) based on H_2O_2 electrogeneration have received great attention for the remediation of acidic waters with synthetic dyes (Guivarch et al., 2003; Peralta-Hernández et al., 2006, 2008; Sirés et al., 2008b; Wang et al., 2008; Özcan et al., 2008, 2009; Villanueva-Rodríguez et al., 2009; Cruz-González et al., 2010), pesticides (Brillas et al., 2003; Diagne et al., 2007), drugs (Guinea et al., 2008; Skoumal et al., 2008, 2009) and chemicals (Brillas et al., 2004; Flox et al., 2007; Oturan et al., 2008). The most common EAOP is electro-Fenton (EF) in which H_2O_2 is formed by the two-electron reduction of O_2 at a carbonaceous cathode such as graphite, carbon felt, reticulated vitreous carbon and gas diffusion electrodes (Qiang et al., 2002; Friedrich et al., 2004; Brillas et al., 2009):

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

---

* Corresponding author. Tel.: +52 8183294000x3432.
E-mail address: juan.peraltahr@uanl.edu.mx (J.M. Peralta-Hernández).
URL: http://www.uanl.mx (J.M. Peralta-Hernández).

doi:10.1016/j.chemosphere.2010.11.013

The low oxidation ability of H_2O_2 is enhanced by adding Fe^{2+} ion as catalyst to the acidic solution to yield Fe^{3+} ion and $^{\cdot}OH$ from Fenton's reaction (Sun and Pignatello, 1993):

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

The optimum pH of reaction (2) is 2.8. An advantage of the EF process is the regeneration of Fe^{2+} by continuous Fe^{3+} reduction at the cathode from reaction (3) with $E^\circ = 0.77$ V/SHE (Vaghela et al., 2005), thus enhancing the destruction rate of organic pollutants:

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

when a one-compartment cell is employed in EF, the anode can also form heterogeneous $^{\cdot}OH$ that destroys the organic matter (Brillas et al., 2004, 2009; Diagne et al., 2007; Flox et al., 2007; Guinea et al., 2008; Skoumal et al., 2008; Cruz-González et al., 2010). This process is more effective using a boron-doped diamond (BDD) anode, since its high O_2 overpotential favors the large production of hydroxyl radical on its surface ($BDD(^{\cdot}OH)$), during water discharge (Marselli et al., 2003; Sirés et al., 2008a; Panizza and Cerisola, 2009):

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

The coupling of Fenton's reaction (2) and AO via reaction (4) improves the EF process.

In photoelectro-Fenton (PEF), the solution treated by EF is irradiated with an UVA lamp of $\lambda_{max} = 360$ nm (Brillas et al., 2003, 2004; Peralta-Hernández et al., 2006; Guinea et al., 2008; Skoumal et al., 2008, 2009; Wang et al., 2008). A variant of this EAOP is the solar PEF (SPEF) process that uses sunlight ($\lambda > 300$ nm) as renewable and inexpensive energy source (Flox et al., 2007; Skoumal et al., 2009). The UVA light enhances the mineralization process by the faster Fe^{2+} regeneration and $^{\cdot}OH$ production from $Fe(OH)^{2+}$ photoreduction, which is the predominant Fe^{3+} species at pH near 3 (Sun and Pignatello, 1993):

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

Moreover, carboxylic acids generated from aromatics destruction form complexes with Fe^{3+} ion that can be photodecarboxylated, as exemplified by reaction (6) proposed by Zuo and Hoigné (1992) for oxalic acid ($Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$):

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

The ability of SPEF to effectively destroy azo dyes solutions has not yet been explored. To check this, we have studied the degradation of the azo dye Acid Yellow 36 (AY36, 3-(4-anilinophenylazo) benzenesulfonic acid sodium salt) using a 2.5 L recirculation flow plant with an undivided BDD/air diffusion cell coupled with a solar photoreactor. In previous works, some of us tested its decolorization using a BDD anode to generate ferrate ion as oxidant (Villanueva-Rodríguez et al., 2009) and EF (Cruz-González et al., 2010). Its removal by electrocoagulation has been described by Kashefialasl et al. (2006).

This paper reports the EF and SPEF degradations of 2.5 L of 108 mg L^{-1} of AY36 (50 mg L^{-1} of TOC at pH 3.0, which is the optimum pH found for these EAOPs (Brillas et al., 2009). This solution simulates real effluents of many textile industries with 50–200 mg L^{-1} of AY36 (Villanueva-Rodríguez et al., 2009). The decay kinetics, decolorization rate and mineralization degree were compared to clarify the oxidation power of both methods. The influence of current on TOC decay and current efficiency was tested. Inorganic ions and generated carboxylic acids were determined to explain the action of hydroxyl radicals and UVA light during the mineralization processes.

2. Experimental

2.1. Chemicals

Reagent AY36 (80% content) was purchased from Aldrich. Anhydrous sodium sulfate and ferrous sulfate heptahydrate were analytical grade supplied by Merck and Fluka, respectively. Oxalic, oxamic, maleic, fumaric, tartronic and formic acids were analytical grade from Panreac, Merck and Avocado. The electrolytic solution was prepared with deionized water and its pH was adjusted to 3.0 with analytical grade sulfuric acid from Merck. Organic solvents and other chemicals used were either HPLC or analytical grade from Merck, Fluka, Panreac and Aldrich.

2.2. Electrolytic system

All electrolyses were performed in a 2.5 L flow plant designed to operate under EF and SPEF conditions. A schematic representation of the plant is shown in Fig. 1. The dye solution was introduced in the reservoir and recirculated through the plant using a centrifuge pump. The flow rate was kept at 200 L h^{-1} with a flowmeter and the solution temperature was regulated at 35 °C with two heat exchangers. The electrochemical cell was a one-compartment filter-press reactor with a BDD anode from Adamant Technologies (La Chaux-de-Fonds, Switzerland) and a carbon-polytetrafluoroethylene (PTFE) gas-diffusion cathode from E-TEK (Somerset, NJ, USA). This cathode was fed with atmospheric air at an overpressure of about 9 kPa to continuously produce H_2O_2 from reaction (1). The area of both electrodes in contact with the effluent was 20 cm^2 and their separation was 1.2 cm. The experiments were carried out at constant current using an Agilent 6552A DC power supply. Once passed the electrochemical cell and before returning to reservoir, the solution circulated through a solar photoreactor, which is a polycarbonate box of 24 cm × 24 cm × 2.5 cm (irradiated volume 600 mL) built-up with a mirror at the bottom and inclined 30° from the horizontal to collect better the direct sun rays. The PEF trials were performed during the summer of 2009 in Barcelona, Spain (latitude: 41°21′N, longitude: 2°10′E), with an average UV incident radiation of about 19 W m^{-2}, determined by the meteorological

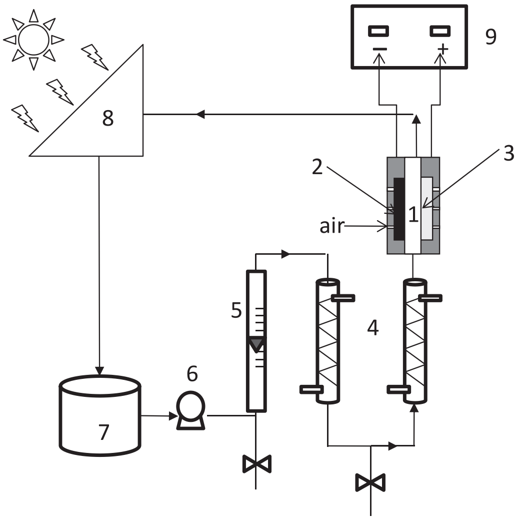

Fig. 1. Setup of the flow plant used for the EF and SPEF degradations of AY36. (1) One-compartment filter-press cell, (2) air-diffusion cathode, (3) BDD anode, (4) heat exchangers, (5) rotameter, (6) pump, (7) reservoir, (8) solar photoreactor and (9) power supply. Sampling was made in the reservoir. During the EF experiments the solar photoreactor was covered with a black cloth and the solution flow was maintained in the dark.