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Electrochemical and sonoelectrochemical processes applied to amaranth dye degradation

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HIGHLIGHTS

- Application of the hybrid method (sonoelectrochemistry) to degrade amaranth dye.
- Amaranth mineralization occurs after 90 min of sonoelectrochemical treatment with overall mineralization of the compound.
- Degradation mechanism for amaranth was proposed based on HPLC–MS analyses.

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ABSTRACT

Amaranth dye is an organic compound largely used in the food and beverage industries with potential toxicity effects on humans. It can be found as a pollutant species in aquatic environments and has been classified as an endocrine disruptor. This study describes amaranth degradation upon ultrasonication associated with an electrochemical system that uses a boron-doped diamond anode BDD, defined as a sonoelectrochemical process. Ninety-minute electrolyses were performed using current densities in the 10–50 mA cm^{-2} range, and the concentration decay, pH, energy and current efficiencies, as well as the discoloration rate were evaluated. The amaranth concentration decayed as a function of electrolysis time and the reactions obeyed pseudo first-order kinetics, with an apparent constant rate between 10^{-1} and 10^{-3} min^{-1}. The electrochemical and sonoelectrochemical processes at 35 mA cm^{-2} yielded TOC removal values between 92.1% and 95.1% respectively, after 90 min. Current efficiency values obtained for both processes were 18.2% and 23.6%. Exhaustive 5 h electrolysis was performed and the degradation products were identified by HPLC–MS. A mechanism for the degradation of amaranth was proposed based on an analysis of the aromatic and aliphatic intermediates.

1. Introduction

Awareness regarding the need to avoid contamination of the environment has considerably increased, although large amounts of synthetic or natural pollutants, including industrial chemicals, agrotoxics, hormones, dyes, pharmaceuticals and personal care products (PPCP) are released in wastewaters on a daily basis and accumulate in the aquatic environment. Many of these substances have adverse properties as carcinogenic, mutagenic and potential toxicity, which affect the health of living species, including human beings (von Sperling, 1996; Halling-Sorensen et al., 1998; Cisneros et al., 2002; Filale-Mekanassi et al., 2004).

Among these compounds, dyes greatly contribute to this contamination process, and their presence in the aquatic environment can cause problems such as color changes, odor alteration, eutrophication, underoxygenation and bioaccumulation (Kapdan et al., 2000a,b; Crini, 2006). Most dye industries use a specific class of synthetic or natural azo compounds (—N=N—), which are resistant to the chemical and biological degradation processes and have mutagenic and carcinogenic features (Chung and Cerniglia, 1992).

Amaranth ($C_{20}H_{11}N_2Na_3O_{10}S_3$) is a very common azo dye used in the beverage and food industries. However, it can be found in the aquatic environment as a potential pollutant and has been classified as an endocrine disruptor (Collins and McLaughlin, 1972; Catino et al., 1978; Brown and Dietrich, 1983; Reid et al., 1984; Filale-Mekanassi et al., 2004).

Viable technologies for the overall removal of these contaminants are required and involve the search for innovative materials and effective methods. Alternative technologies, as advanced oxidation processes (AOPs), have been applied for the remediation of many types of effluents and have contributed to environmental

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pollution control; these methods show good performance in terms of discoloration and dye degradation (Cisneros et al., 2002). The most commonly used AOPs includes heterogeneous photocatalytic oxidation (Pérez et al., 2002), treatment with ozone combined with H_2O_2 (Arslan and Balcioglu, 2001), H_2O_2/UV systems (Georgiou et al., 2002; Neamtu et al., 2002), along with Fenton (Kuo, 1992; Pignatello, 1992; Pérez et al., 2002) and photo-Fenton reactions (Neamtu et al., 2002; Torrades et al., 2004; Martínez-Huitle and Brillas, 2009).

There are also electrochemical methods, which are quite feasible and apply a potential capable of either oxidizing or reducing the substrates of interest (Motheo et al., 2000; Panizza and Cerisola, 2004; Malpass et al., 2006a,b; Oturan et al., 2008; Brillas et al., 2009; Alves et al., 2012; Oturan and Aaron, 2012; Sirés and Brillas, 2012; Alves et al., 2013; Assumpção et al., 2013; Barros et al., 2013, 2014; Pipi et al., 2014; Steter et al., 2014; Thiam et al., 2014). The electro-oxidation of organic compounds often occurs by applying high potential; oxygen evolution is a competitive pathway to the degradation process. However, these removal methods often generate sub-products, which are not eliminated, completely, by the processes or can be even more toxic than the original compound.

Recently, studies have focused on the development of combined techniques to potentiate the elimination of organic pollutants present in water (Abdelsalam and Birkin, 2002; Gogate and Pandit, 2004; Minero et al., 2005; Catanho et al., 2006; Gogate, 2008; Souza et al., 2014; Thiam et al., 2014).

Ultrasound is a technique that has been applied in several research fields, like cell disruption, degassing, polymerization processes, nanotechnology, chemical reactions, food preservation, ultrasonic imaging, sonar detection and others (Adewuyi, 2005). It has also been used as AOPs in wastewater treatment (Thompson and Doraiswamy, 1999; Adewuyi, 2001). The sonochemical process applied to the oxidation of organic compounds consists of $^{\cdot}OH$ radical production by water decomposition, under ultrasonic action, represented by))), according to the following equations (Weiss, 1944; Makino et al., 1982; Wu et al., 2001):

$$H_2O +))) \rightarrow H^{\cdot} + {}^{\cdot}OH \tag{1}$$

$$H^{\cdot} + O_2 +))) \rightarrow HOO^{\cdot} \tag{2}$$

$$\text{Pollutants} + {}^{\cdot}OH +))) \rightarrow \text{degradation products} \tag{3}$$

$$\text{Pollutants} + HOO^{\cdot} +))) \rightarrow \text{degradation products} \tag{4}$$

The formation of hydrogen peroxide, a secondary oxidant species, occurs by the recombination of the $^{\cdot}OH$ radical species and can help in the degradation process (Suslick, 1988).

$$2{}^{\cdot}OH \rightarrow H_2O_2 \tag{5}$$

$$\text{Pollutants} + H_2O_2 +))) \rightarrow \text{degradation products} \tag{6}$$

Sonolysis or sonochemistry is a complex process that employs sound waves at frequencies between 20 kHz and 10 MHz for the generation of the cavitation phenomenon. The cavitation process involves the formation, expansion and collapse of microscopic bubbles in aqueous systems, causing turbulent motion. Some areas, localized in specific regions such as inside the cavitation bubble and at the interface, encounter high temperatures and pressure which can enhance chemical reactivity, because of the association between the degradation of the organic compound and free radical generation (Suslick, 1990; Crum, 1995; Goel et al., 2004; Gogate and Pandit, 2004; Mason and Pétrier, 2004).

The degradation process consists of a complex mechanism than can occur by: (i) pyrolysis inside the cavity of the bubble, (ii) in the interfacial region due to thermolysis or oxidation mediated via radical species ($^{\cdot}OH$) and (iii) in the bulk solution and near the interface, due to reactions with radical species ($^{\cdot}OH$). Ultrasonic action can be affected by several factors, including the power and frequency applied, the nature of the electrolyte, the presence of dissolved gas, and the volatility of the compounds formed (Berlan et al., 1994; Pétrier et al., 1994; Mason and Pétrier, 2004).

As present previously, many studies have focused on oxidative degradation of organic compounds by coupled techniques as sonoelectrochemical (Wu et al., 2012; Cheng and Huang, 2014; Souza et al., 2014). The present study reports on amaranth dye degradation in aqueous solution (0.05 M K_2SO_4, pH 5.45) under electrochemical and sonoelectrochemical conditions, by applying a BDD electrode as the anode. It is important to notice that the sonoelectrochemical method applied, in this study, is differentiated from those described in the literature, because the cavitation process occurs on the electrode surface and not in the bulk solution. A coupling effect of these processes was demonstrated and after 90 min of electrolysis, overall mineralization of the amaranth dye occurred. A mechanism for the degradation process of amaranth dye was also proposed based on HPLC–MS analyses of the aromatic and aliphatic intermediates.

2. Experimental

2.1. Materials

Amaranth dye was obtained from Aldrich (reagent grade 85–95%); potassium sulfate (Vetec) and ammonium acetate (Synth) analytical grade reagents were used as received. Chromatographically pure methanol was purchased from Merck. All solutions were prepared with ultrapure water (> 18 MΩ, Milli-Q, Millipore Inc.).

2.2. Electrochemical and sonoelectrochemical set up

The sonochemical studies were performed using an XL-2020 Sonicator Programmable Ultrasonic Liquid Processor® in which the ultrasound waves are produced by a titanium probe (11 mm) operating at 20 kHz. Calorimetric analyses were performed to quantify the energy dissipation of the system using a thermocouple Type J 42 1OP therm (Fe–CuNi) IOPE. The ultrasonic frequency was set at 30%, which corresponds to intensity of 523 W cm^{-2}.

The electrochemical cell coupled to the ultrasound system consisted of a one-compartment Pyrex cell (400 mL) with temperature control at 25 ± 1 °C in batch mode. A BDD thin-film electrode with a geometric area of 9.68 cm^{-2} deposited on a single-crystal p-type Si (100) wafer provided by Adamant Technologies (La-Chaux-de-Founds, Switzerland) and used as the anode. The BDD electrode activation was performed by anodic polarization at 50 mA cm^{-2} during 30 min in 0.05 M K_2SO_4 aqueous solution. The characterization of the BDD electrode in amaranth dye solution (100 mg L^{-1} in 0.05 M K_2SO_4) was realized by cyclic voltammetry, applying the potential range of −1.0 to +2.5 V *vs.* saturated calomel electrode (SCE) and scan rate of 50 mV s^{-1}. A platinum wire, with a geometric area of 10.24 cm^{-2}, was employed as the cathode and the reference electrode was a SCE. Amaranth degradation processes (100 mg L^{-1} amaranth in 0.05 M K_2SO_4 aqueous solution at pH 5.45) were investigated by 90-min electrolyses using current densities of 10, 25, 35 and 50 mA cm^{-2} using a PGSTAT-30 potentiostat/galvanostat (AUTOLAB) with a high current (BSTR-10A) module.

2.3. Procedures and analysis

The concentration decay was determined by HPLC (Shimadzu, model LC-20AT) coupled to a SPD-20A UV module and