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Electro-Fenton degradation of the food dye amaranth using a gas diffusion electrode modified with cobalt (II) phthalocyanine

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ABSTRACT

Electrodegradation of the azo dye amaranth using a modified gas diffusion electrode (MGDE), prepared with Printex 6L carbon black and 5.0% cobalt (II) phthalocyanine, has been investigated with the aim of developing an efficient method of treating contaminated effluent derived from the food and beverage processing industries. Hydrogen peroxide was electrogenerated at a potential of −0.7 V (*vs*. Ag/AgCl) under a constant flow of O_2, and electrodegradations were performed in the absence or presence of Fe^{2+} or Fe^{3+} (electro-Fenton conditions). The removal of color and total organic carbon (TOC) from the dye solution was observed under all reaction conditions, although process efficiency was improved markedly by the addition of Fe ions. Following 90 min of electrolysis, maximal values for decolorization (79.3%) and mineralization (67.3%) were achieved in the presence of 0.15 mM Fe^{2+}, and energy consumption (370.0 kW h kg^{-1} per kg of TOC removed) was minimal under these conditions. Concentrations of residual Fe in treated electrolytes were either below the permissible limit or could be rendered so by conventional treatment. It is concluded that the electro-Fenton reaction with Fe^{2+} and a MGDE represents a viable process for the degradation of amaranth in aqueous medium.

1. Introduction

The continuous increase in the production and consumption of food materials has been accompanied by a significant rise in the level of environmental contamination. Such pollutants derive from the entire production chain, commencing with the run-off of fertilizers and pesticides during the cultivation stages and terminating with the wastewaters and effluents generated during the industrial processing of the final product. With regard to the production of commercially prepared foodstuffs, a number of studies have focused on the use of additives, particularly food colorings [1–6], and their influence on humans [7–9] and the environment [10–12].

Artificial dyes comprise one of the largest groups of additives employed in the food industry. These substances not only impart color to food and beverages without adding nutritional value, but they are also likely to be present as contaminants in process effluents. Many synthetic dyes and their by-products, mainly aromatic amines and phenolics, are toxic to aquatic biota and, by virtue of the potential carcinogenic and mutagenic nature of these compounds [13–15], can be harmful to human consumers of polluted waters. Moreover, artificial dyes generally contain organic and inorganic groups that are recalcitrant, thus promoting bioaccumulation in the various food chains of the biota. Additionally, the color imparted by these dyes can interfere with the transmission of light in the contaminated water, possibly reducing the photosynthetic activity of aquatic organisms and increasing biochemical oxygen demand. These factors may give rise to an increase in anaerobic activity and the consequential formation of sulfides and mercaptans resulting in the emission of unpleasant odors [12,16,17].

Various techniques for the treatment of dye-contaminated wastewaters have been described, the most straight for ward of which involve biosorption [18] or adsorption [19] onto inorganic materials, including zero-valent metals [20] and zeolite encapsulated with Fe–TiO_2 [21] among others [22], generally coupled with the application of ultrasound. Alternatively, direct degradation of the contaminant may be achieved through the use of microorganisms [17,23] or by the application of ultraviolet (UV) light in combination with metal oxides [24], mainly TiO_2 [25], or oxidizing species such as H_2O_2 [26]. Considerable research interest has targeted the use of H_2O_2 in effluent treatment either in isolation [27] or in association with oxidizing species [28], photo-assisted systems [29] or catalysts [30].

In this context, the *in situ* generation of H_2O_2 has been employed in numerous electro-Fenton degradation reactions [31–33] carried out under diverse experimental conditions [34–38], in which H_2O_2 can to produce hydroxyl radicals ($^{\bullet}OH$) in

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the process, using ion Fe^{2+} ion in acid medium as well as the decomposition of H_2O_2 is also catalyzed by Fe^{3+} ion. In this process, the H_2O_2 is decomposed to water molecules and oxygen and a Fe^{2+} stationary concentration is maintained during decomposition. However, the formation of H_2O_2 is limited by the low solubility of O_2, the main reagent in H_2O_2 synthesis, in aqueous medium [39], and careful selection of electrodes is essential in order to increase the efficiency of the process. Gas diffusion electrodes (GDEs) offer a number of advantages for this application, since they possess porous structures with hydrophobic characteristics that allow unlimited supplies of O_2 to be delivered to the electrode/electrolyte interface. Under these conditions, the limitation of the mass transport in the generation of H_2O_2 is eliminated [40–44]. Various reports are available concerning the use of GDEs for the electrogeneration of H_2O_2 with the purpose of treating various types of wastewater in the presence of iron ions [45–47]. Additionally, the specific construction of GDEs allows the efficient anchoring of different modifiers [40,41,43], a number of which have been investigated with regard to the oxygen reduction reaction (ORR) with the purpose of achieving higher currents at less negative potentials. In this context, the use of metal phthalocyanine as modifier reportedly promotes greater selectivity for the ORR by supporting H_2O_2 production through a two-electron transfer mechanism [48].

Amaranth (AM) is a dark red, water-soluble monoazo dye ($C_{20}H_{11}N_2Na_3O_{10}S_3$, molecular weight 604.47 g mol^{-1}) used as a coloring agent for food, beverages and cosmetics. Studies conducted prior to 1976 had indicated that AM possessed carcinogenic activity, and the additive was subsequently banned in the United States. More recent investigations have, however, failed to confirm these findings and AM is currently authorized (albeit with various restrictions) as an additive for beverages and foods in various countries, including some members of the European Union [49]. Given the need for novel methods of treatment of wastewater contaminated with industrial dyes, the aim of the present study was to determine the efficiency of degradation of AM using H_2O_2 electrochemically generated at a GDE, modified with 5.0% cobalt (II) phthalocyanine (CoPc), in isolation or in the presence of different concentrations of Fe^{2+} or Fe^{3+}.

2. Experimental

2.1. Electrochemical characteristics of AM

In order to characterize the oxidation and reduction reactions of AM, cyclic voltammetry (CV) was performed in a single-compartment electrochemical cell equipped with a glassy carbon (GC) working electrode, a Ag/AgCl reference electrode and a platinum counter electrode. The test solution was prepared using ultrapure water (Millipore Milli-Q) and contained AM (0.01 mg L^{-1}; 85–95% purity; Sigma–Aldrich) in H_2SO_4 (0.1 mol L^{-1}) and K_2SO_4 (0.1 mol L^{-1}) as supporting electrolyte. Solutions were bubbled with N_2 for 10 min prior to each experiment, and CVs were recorded in the potential range −0.5 to +1.0 V (*vs.* Ag/AgCl) at a scan rate of 50 mV s^{-1} using an Autolab PGSTAT-30 potentiostat/galvanostat system with a BSTR-10A current booster.

2.2. Electrochemical degradation of AM

The solutions employed in the electro-Fenton experiments were prepared with ultrapure water (Millipore Milli-Q) and adjusted to pH 2.5 prior to use. Test solutions contained AM (100 mg L^{-1}) in H_2SO_4 (0.1 mol L^{-1}) and K_2SO_4 (0.1 mol L^{-1}), as supporting electrolyte, together with different concentrations (0.05, 0.1 or 0.15 mM) of $FeSO_4{\cdot}7H_2O$ (Sigma–Aldrich) or Fe $(NO_3)_3{\cdot}9H_2O$ (Sigma–Aldrich). *In situ* generation of H_2O_2 was accomplished using a modified gas diffusion electrode (MGDE) prepared with Printex 6L carbon black and 5.0% CoPc (Sigma–Aldrich), according to the method described previously by our group [48]. The working electrode used was MGDE, an Ag/AgCl reference electrode and a 30.0 mm diameter screen fabricated from platinum (99.95% pure) wire (diameter 0.25 mm; space between wires 4.0 mm) as counter electrode. Experiments were performed in an electrochemical cell containing 400 mL of test solution maintained at 20 °C being pressurized with N_2 (anodic oxidation) and O_2 insufflation at 0.2 bar, and electrolysis was continued for 90 min at a constant applied potential of −0.7 V (*vs.* Ag/AgCl. An Autolab PGSTAT-30 potentiostat/galvanostat system and a BSTR-10A current booster were employed in these experiments, and the cell potential (E_{cell}) was measured using a high impedance digital multimeter connected in parallel to the MGDE and the counter electrode.

Samples of the electrolyte were collected at appropriate time periods following the commencement of electrolysis and immediately treated with $NaHSO_3$ to convert residual H_2O_2 into H_2O and SO_4^{2-}, thereby preventing any further oxidation of AM. The absorbances of samples at 521 nm were measured in a Varian Cary-50 UV–Vis spectrophotometer in order to determine the progress of decolorization of the dye. The decay in the concentration of AM was monitored by high performance liquid chromatography (HPLC) using a Shimadzu model LC-20AT solvent delivery unit coupled with a model SPD-20A UV detector and a Phenomenex Luna C_{18} column (250 × 4.6 mm i.d.). Elution was isocratic with a 30:70 v/v mixture of methanol (Merck; HPLC grade reagent) and ammonium acetate 0.08 mol L^{-1} aqueous solution (Synth; analytical grade reagent) at a flow rate of 0.5 mL min^{-1} and a column temperature of 25 °C. The detection wavelength was set at 260 nm and the amount of AM present was determined by reference to a calibration curve constructed using analytical standard AM (Sigma Aldrich).

With the aim of identifying intermediates or by-products formed during the degradation of AM, selected samples were subjected to HPLC analysis under the conditions indicated above but with a Shimadzu model SPD-M20A photodiode array detector (PAD) incorporated into the chromatographic system.

The rate of mineralization during electrochemical degradation was determined from the total organic carbon (TOC) content of the samples monitored using a Shimadzu model TOC-VCPN PC-controlled TOC analyzer.

The concentrations of Fe^{2+} and Fe^{3+} remaining in the electrolyte at the end of electrolysis were determined spectrophotometrically using the Phenanthroline Colorimetric method recommended by the American Public Health Association [50]. Levels of residual H_2O_2 in electrolyte samples could not be determined spectrophotometrically owing to interference by the Fe ions present.

3. Results and discussion

3.1. Electrochemical characteristics of AM

In order to investigate the electrochemical behavior of AM on the surface of a GC electrode, CV traces of supporting electrolyte [H_2SO_4 (0.1 mol L^{-1}) and K_2SO_4 (0.1 mol L^{-1})] in the presence and absence of dye (0.01 mg L^{-1}) were recorded in the potential range −0.5 to +1.0 V (*vs.* Ag/AgCl) at a scan rate of 50 mV s^{-1} (Fig. 1). In contrast to the supporting electrolyte, for which no peaks associated with oxidation or reduction could be observed, the CV of AM showed two oxidation peaks (located at approximately +0.38 and +0.8 V) and one reduction peak (at around −0.15 V). The oxidation peak +0.38 V is probably associated with polymerization processes on the surface of the GC electrode. According to the literature [51], the redox couple +0.8 V and −0.15 V refers,