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Effect of anions on electrochemical degradation of azo dye Carmoisine (Acid Red 14) using a BDD anode and air-diffusion cathode

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ABSTRACT

Solutions of 2.5 L with 209.3 mg L^{-1} of the azo dye Carmoisine in 0.050 M SO_4^{2-}, ClO_4^- or Cl^- have been comparatively treated by electrochemical oxidation with electrogenerated H_2O_2 (EO-H_2O_2) and electro-Fenton (EF) with 0.5 mM Fe^{2+} as catalyst at constant current density. Experiments were made using a recirculation flow plant containing a reactor with a boron-doped diamond (BDD) anode and an air-diffusion cathode to allow H_2O_2 generation. The dye and its oxidation products were oxidized by hydroxyl radical and/or HClO formed at the anode from water or Cl^- oxidation, respectively, in EO-H_2O_2, as well as by hydroxyl radical produced in the bulk from Fenton's reaction between added Fe^{2+} and generated H_2O_2 in EF. In both methods, the decolorization process was always much faster in Cl^- medium because of the quick oxidation of colored compounds by HClO, being enhanced by increasing current density and Cl^- concentration. The solutions with SO_4^{2-} or ClO_4^- were more rapidly decolorized in EF due to the higher oxidation power of hydroxyl radicals in the bulk. Regarding the overall decontamination, a poor and similar mineralization of about 50% was obtained by EO-H_2O_2 at 480 min in all the supporting electrolytes at 100 mA cm^{-2}. The comparative EF treatments were always much more powerful, being SO_4^{2-} the most favorable medium leading to 76% mineralization with the lowest energy consumption. Up to 15 aromatic products were detected by GC–MS and short-linear carboxylic acids like tartronic, oxalic, oxamic and formic were quantified by ion-exclusion HPLC. The large persistence of Fe(III)-oxalate complexes accounted for the partial mineralization of the Carmoisine solution in EF. Nitrate and sulfate were the major ions released during the mineralization process.

1. Introduction

The recent United Nations World Water Development Report has given prominence to the growing concern on dyeing industrial effluents [1]. Large volumes of these wastewaters with high dye contents are daily discharged into water bodies, thus causing not only aesthetic problems but also toxic effects on aquatic organisms and humans [2,3], including proven carcinogenic, mutagenic and bactericide activity [1]. Synthetic dyes with one or various azo groups (—N=N—) as chromophore bound to benzene or naphthalene rings containing —OH and —SO_3H groups are largely produced [4]. They account for over 70% of the world dyestuff production, being widely used in textile, cosmetic, pulp and paper, food and pharmaceutical industries owing to their unique properties such as brilliant shades, relative low cost and simple manufacture [4,5]. Among them, food azo dyes are suspected to be dangerous according to the European Food Safety Authority (EFSA) due to their possible connection to hyperactivity in children, like in the case of Carmoisine (disodium 4-hydroxy-3-[(4-sulfo-1-naphthalenyl)azo]-1-naphthalenesulfonate, $C_{20}H_{12}N_2O_7S_2Na_2$, also known as Acid Red 14 or additive E122, see its chemical structure in Fig. 1) [6]. Azo dyes are highly recalcitrant, being only hardly removed by conventional biological and physicochemical methods. As a result, they are largely persistent in the aquatic environment [5]. Aiming to prevent the adverse environmental and health impact of these pollutants and their by-products, research efforts are needed to develop powerful and effective degradation methods.

The electrochemical advanced oxidation processes (EAOPs) like electrochemical oxidation (EO) and electro-Fenton (EF) have received increasing interest in the last years for water remediation [4,7–9]. In EO, the organic pollutants are destroyed by physisorbed hydroxyl radical M($^{\cdot}$OH) generated from water discharge at an anode (M) with high O_2-overpotential via reaction (1) upon application of a high current [7,10–13].

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$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \tag{1}$$

Although the standard redox potential of $^{\bullet}OH$ ($E^{\circ} = 2.8$ V/SHE) is so high that it can non-selectively react with most organics up to their mineralization, the effectiveness of EO dramatically depends on the anode material. While the $M(^{\bullet}OH)$ radical formed from reaction (1) on active anodes such as Pt, IrO_2 and RuO_2 is easily oxidized to a chemisorbed MO species with weaker oxidizing ability, only allowing the electrochemical conversion of organics into carboxylic acids [7,12,14], it becomes more stable on non-active anodes like SnO_2, PbO_2 and boron-doped diamond (BDD) eventually yielding the electrochemical incineration of organics [7,15,16]. Among the latter anodes, BDD is preferred for EO since it generates very high amounts of reactive physisorbed $BDD(^{\bullet}OH)$ due to the very weak BDD–$^{\bullet}OH$ interaction resulting in a greater O_2-overpotential and an enhanced destruction of organics [7,11].

The electrolyte composition can also modify the effectiveness of EO. Thus, in chloride medium, the oxidation of organics by $M(^{\bullet}OH)$ competes with that mediated by active chlorine species like Cl_2, HClO and/or ClO^-, which are electrogenerated as follows [7,17,18]:

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \tag{2}$$

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+ \tag{3}$$

$$HClO \leftrightarrows ClO^- + H^+ \tag{4}$$

The use of a carbonaceous cathode such as graphite [19], carbon nanotubes [20], activated carbon fiber (ACF) [21,22], carbon sponge [23], graphite felt [24,25], carbon felt [23,26–30] and carbon-polytetrafluoroethylene (PTFE) gas (O_2 or air) diffusion [17,18,31–34] allows the electrogeneration of H_2O_2 from the two-electron reduction of injected O_2 via reaction (5):

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{5}$$

When an undivided cell is used, the EO process with electrogenerated H_2O_2 (EO-H_2O_2) then involves the destruction of organics pre-eminently by $M(^{\bullet}OH)$, along with other weaker reactive oxygen species (ROS) like H_2O_2 and hydroperoxyl radical $M(HO_2^{\bullet})$ formed from reaction (6) [8,9]:

$$M + H_2O_2 \rightarrow M(HO_2^{\bullet}) + H^+ + e^- \tag{6}$$

A more effective EAOP based on H_2O_2 electrogeneration is EF [4,9,18–31,35,36], in which organics can undergo additional attack by $^{\bullet}OH$ produced in the bulk by Fenton's reaction (7), which occurs by reaction between generated H_2O_2 and low quantities of Fe^{2+} ion at optimum pH 2.8. This event is catalytic and can be propagated from Fe^{2+} regeneration [23,28].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \tag{7}$$

The generation of oxidants in the above EAOPs depends not only on the electrode materials, but it is also affected by the operating parameters. However, the information on the influence of supporting electrolytes on the EF treatment of dyestuff solutions using an air-diffusion cathode for H_2O_2 generation is scarce. This electrode is advantageous in such treatment because it minimizes the possible cathodic reduction of organic pollutants [9]. To gain a better understanding on the ability of EAOPs to oxidize synthetic dyes, a comparative study on the degradation of Carmoisine solutions in sulfate, chloride and perchlorate media by EO-H_2O_2 and EF using a batch recirculation plant with an electrochemical reactor equipped with a BDD anode and an air-diffusion cathode has been undertaken. All the trials were made at the optimum pH ~ 3.0 [4,9,29–34]. Carmoisine has been chosen by many authors as a model molecule to test the removal of azo dyes by ozonation [37], photocatalysis [38–41], sonochemistry [42] and chemical Fenton [42,43]. Solutions of Carmoisine have also been treated by electrocoagulation with an iron anode in the presence of chloride [44] and by several EAOPs in sulfate medium, such as EO with a Ti/SnO_2 anode and a Ni cathode [45] as well as EF [21] and photoelectro-Fenton [22] with a Ti/RuO_2 anode and an ACF cathode. Worth highlighting, key issues regarding the viability of processes like current efficiency, specific energy consumption and reaction intermediates formed were not addressed in those works.

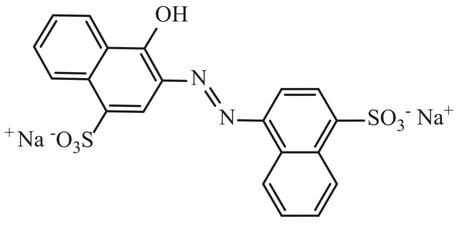

Fig. 1. Chemical structure of Carmoisine (Acid Red 14, additive E122).

This paper reports the degradation of 2.5 L of 209.3 mg L^{-1} Carmoisine solutions of pH 3.0 by EO-H_2O_2 and EF using a BDD/air-diffusion reactor. The role of the oxidants formed in Na_2SO_4, NaCl or $LiClO_4$ medium was clarified. The influence of applied current density (j) and NaCl and dye contents on the decolorization efficiency, mineralization rate, mineralization current efficiency (MCE) and specific energy consumption was examined. Primary aromatic intermediates were identified by gas chromatography-mass spectrometry (GC–MS) and final carboxylic acids and generated inorganic ions were quantified by chromatographic techniques.

2. Materials and methods

2.1. Chemicals

Commercial Carmoisine dye (60% purity and 40% of inorganic ions for stabilization) was provided by Sigma–Aldrich and used as received. Anhydrous sodium sulfate, sodium chloride and lithium perchlorate used as supporting electrolytes and iron(II) sulfate heptahydrate used as catalyst in EF were of analytical grade purchased from Fluka and Sigma–Aldrich. The corresponding sulfuric, hydrochloric and perchloric acids used to regulate the initial pH to 3.0 were of analytic grade supplied by Merck, Panreac and Acros Organics, respectively. Solutions were prepared with deionized water. Organic solvents and other chemicals used were of HPLC or analytical grade supplied by Sigma–Aldrich, Merck and Panreac.

2.2. Recirculation flow plant

A scheme of the batch recirculation flow plant used in this work can be found elsewhere [46]. In each assay, 2.5 L of a Carmoisine solution were introduced into the reservoir and recirculated through the plant using a centrifugal pump. The flow rate was kept at 200 L h^{-1} with a flowmeter and the solution temperature was regulated at 35 °C by means of two heat exchangers connected to a water bath. The electrochemical cell was an undivided filter-press reactor equipped with a 20 cm^2 BDD thin-film anode from Adamant Technologies and a 20 cm^2 carbon-PTFE air-diffusion cathode from E-TEK, with an interelectrode gap of 1.2 cm. The cathode was in contact with a PVC gas chamber fed with atmospheric air at an overpressure of about 8.6 kPa regulated with a back-pressure gauge to continuously produce H_2O_2 from reaction (5). All the trials were performed at constant j provided by an Agilent 6552A DC power supply.