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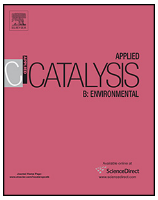

Evidence of Fenton-like reaction with active chlorine during the electrocatalytic oxidation of Acid Yellow 36 azo dye with Ir-Sn-Sb oxide anode in the presence of iron ion

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ABSTRACT

The degradation of 2.5 L of Acid Yellow 36 solutions at pH 3.0 by electro-oxidation (EO) has been studied in a flow plant with a reactor containing an Ir-Sn-Sb oxide anode and a stainless steel cathode. The anode was prepared onto Ti by the Pechini method and characterized by SEM-EDX and XRD. It showed a certain ability to electrocatalyze both, the generation of adsorbed $^{\bullet}$OH from water oxidation in sulfate medium and, more largely, the production of active chlorine in a mixed electrolyte containing Cl^- ion. The EO treatment of the dye solution in the latter medium led to a rapid decolorization because active chorine destroyed the colored by-products formed, but color removal was much slower in pure $NaClO_4$ or Na_2SO_4 due to the limited formation of $^{\bullet}$OH. In contrast, greater mineralization was obtained in both pure electrolytes since the by-products formed in the presence of Cl^- became largely persistent. The effect of liquid flow rate, current density and dye content on the EO performance in the mixed electrolyte was examined. The drop of absorbance and dye concentration obeyed a pseudo-first-order kinetics. Interestingly, the decolorization rate, dye concentration decay and TOC removal were enhanced upon catalysis with 1.0 mM Fe^{2+}. Such better performance can be accounted for by the formation of $^{\bullet}$OH in the bulk from the electro-Fenton-like process between electrogenerated HClO and added Fe^{2+}. Even larger mineralization was achieved by the photoelectro-Fenton-like process upon irradiation of the solution with UVA light due to photolysis of some refractory intermediates. Maleic and acetic acids were detected as final short-chain linear carboxylic acids. The loss of Cl^- and the formation of ClO_3^-, ClO_4^-, SO_4^{2-}, NO_3^- and NH_4^+ were evaluated as well.

1. Introduction

About 70% of the world dye production corresponds to azo compounds [1], which have a complex chemical structure containing one or various azo groups (—N=N—) as chromophore, linked to aromatic systems with lateral groups including —OH, —CH_3 and –SO_3^-, among others [2–4]. These dyes are extensively employed in textile industries, which are highly polluting in terms of the color, volume and complexity of their discharged effluents [5,6]. Dye wastewater contains dye concentrations up to 250 mg L^{-1}, along with other toxic components, thus causing aesthetic problems, scarce light penetration and health problems to aquatic organisms owing to their carcinogenic, toxic and mutagenic properties [7,8]. The resistance to biodegradation and poor destruction of these pollutants by conventional treatments in wastewater treatment plants explain their large persistence in the aquatic environment [4,9,10]. Research is thus focusing on the development of more powerful treatments to remove azo dyes from wastewater in order to avoid their hazardous effects on living beings.

Several electrochemical advanced oxidation processes (EAOPs), including electro-oxidation (EO, also called electrochemical oxidation or anodic oxidation) and processes based on Fenton's reaction like electro-Fenton (EF), have been recently utilized to efficiently destroy azo dyes [4,11–30]. EAOPs are easy to handle and very versatile, also presenting high energy efficiency, great effectiveness to oxidize organic pollutants and environmental compatibility. They

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show great ability for the in situ production of reactive oxygen species (ROS), like hydroxyl radical ($^{\bullet}$OH) with such a high oxidation power (E° = 2.80 V/SHE) that it can non-selectively attack most organic pollutants until their mineralization [4,21,23,30].

EO is the simplest EAOP applied to wastewater treatment. The most basic setup consists in an electrolytic cell containing the polluted wastewater in contact with a cathode and a large O_2-overvoltage anode (M) that catalyzes the generation of adsorbed M($^{\bullet}$OH) radical from water oxidation at high applied current density (j) as follows [31,32]:

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

The production of M($^{\bullet}$OH) radical depends on the kind of anode. At so-called active anodes such as Pt, IrO_2 and RuO_2, M($^{\bullet}$OH) is transformed into a less powerful oxidant like chemisorbed “superoxide” MO [19,33]. Such conversion can be minimized when using non-active anodes like PbO_2, SnO_2 and boron-doped diamond (BDD), which promote high contents of physisorbed M($^{\bullet}$OH) leading to the mediated electrochemical incineration of organic pollutants on the anode [11,12,18,34,35]. It has been found that several active mixed metal oxide (MMO) anodes yield larger degradation than pure metal oxides, as reported for phenol and Reactive Orange 4 using Ti/SnO_2-Sb_2O_3 and Ti/SnO_2-Sb-Pt, respectively [36].

This general description is valid when the EO treatment is performed in the presence of anions like ClO_4^-, NO_3^- and SO_4^{2-}, which remain stable during the electrolysis or become a source of weak oxidants, e.g., $S_2O_8^{2-}$ at the BDD surface [31,32]. In contrast, the EO process becomes much more complex in the presence of Cl^- because it can be oxidized to active chlorine (Cl_2, HClO and/or ClO^-) via Reactions (2)–(4), which competes with M($^{\bullet}$OH) to attack the organic molecules [1,4,21–23,26,37,38].

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \quad (2)$$

$$Cl_{2(aq)} + H_2O \rightleftarrows HClO + Cl^- + H^+ \quad (3)$$

$$HClO \rightleftarrows ClO^- + H^+ \quad (4)$$

The predominant active chlorine species is $Cl_{2(aq)}$ (E° = 1.36 V/SHE) up to pH 3.0, HClO (E° = 1.49 V/SHE) within the pH range 3–8 and ClO^- (E° = 0.89 V vs. SHE) at pH > 8.0. The mediated electrochemical oxidation of organics with these species is then expected to be more successful in acidic medium. On the other hand, Kishimoto et al. [39] recently suggested the enhanced decontamination of acidic wastewater containing Cl^- through the generation of $^{\bullet}$OH in the bulk using Fe^{2+} and HClO via Fenton-like Reaction (5) [40]. Note that, actually, this corresponds to an EF-like process in which Reaction (5) replaces the classical Fenton's reaction between H_2O_2 and Fe^{2+} catalyst to form Fe^{3+} and $^{\bullet}$OH [4,23]. Reaction (5) can thus be sustained from Fe^{2+} regeneration upon cathodic reduction of Fe^{3+} via Reaction (6). Additionally, one could envisage the production of larger amounts of $^{\bullet}$OH from the photolytic reduction of $Fe(OH)^{2+}$, the pre-eminent Fe^{3+} species at pH 3.0, by Reaction (7) upon use of UVA radiation [30,41]. The latter photoelectrocatalytic treatment, which is reported for the first time, can be so-called PEF-like process.

$$HClO + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + Cl^- \quad (5)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (6)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (7)$$

To give evidence of the upgrading of azo dye removal under EF-like and PEF-like conditions, we have undertaken a study on the degradation of Acid Yellow 36 in acidic chlorinated solutions using a purpose-made Ir-Sn-Sb oxide anode with ability to produce M($^{\bullet}$OH) radicals and active chlorine [38,42]. Acid Yellow 36 (also known as Metanil Yellow, see physicochemical properties in Table 1) has been chosen as model azo dye because it is present in wastewater from textile, tannery, paper and cosmetic industries, among others. This refractory dye is a toxic and carcinogenic pollutant that causes mortality and adverse health effects in fishes [43]. Its consumption by humans causes toxic methaemoglobinaemia and cyanosis, whereas its contact with skin produces allergic dermatitis [44]. Effective decolorization and/or mineralization of synthetic Acid Yellow 36 solutions upon the action of $^{\bullet}$OH has been described by several AOPs including photocatalysis with TiO_2 [45,46] and ZnO [47], Fenton [48] and photo-Fenton [49]. EAOPs such as EO [50], EF [14,51] and PEF [15] with BDD anode, as well as PEF combined with TiO_2 photocatalysis [46], have also been employed but only in sulfate medium.

This article presents the results obtained for the degradation of a 0.46 mM Acid Yellow 36 solution (100 mg L^{-1} of total organic carbon (TOC)) in a 35 mM NaCl + 25 mM Na_2SO_4 mixture at pH 3.0 by EO. The experiments were performed in a 2.5 L flow plant with a filter-press cell equipped with an Ir-Sn-Sb oxide anode and a stainless steel cathode. The anode was composed of an MMO film onto Ti plate prepared by the Pechini method [52]. It was characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray-diffraction (XRD), whereas its electrocatalytic ability to generate $^{\bullet}$OH and active chlorine was analyzed by electron paramagnetic resonance (EPR) and UV/vis spectroscopy, respectively. The effect of liquid flow rate, j and dye concentration on decolorization rate and mineralization degree was examined. Comparative trials using pure $NaClO_4$ or Na_2SO_4 as electrolyte were made to better assess the role of active chlorine in the mixed electrolyte. The influence of Fe^{2+} addition to the latter medium, either in the dark or under UVA irradiation, was studied to give strong evidence of the occurrence of a Fenton-like reaction. Intermediates and inorganic ions lost or released during the dye degradation were identified.

2. Materials and methods

2.1. Chemicals

Commercial Acid Yellow 36 (70% of dye content, the rest corresponding to inorganic products) was purchased from Sigma-Aldrich and used as received. The products for the MMO synthesis were $H_2IrCl_6{\cdot}xH_2O$, $SnCl_4$ and $SbCl_3$ of analytical grade supplied by Sigma-Aldrich. The electrolytic solutions were prepared with deionized water and contained $FeSO_4{\cdot}7H_2O$, Na_2SO_4, NaOH, NaCl and/or $HClO_4$ of analytical grade purchased from Fluka, Merck and Panreac. Analytical grade 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) used for $^{\bullet}$OH detection was supplied by Sigma-Aldrich. Other chemicals were of either HPLC or analytical grade purchased from Fluka, Merck, Panreac and Sigma-Aldrich.

2.2. Synthesis of the mixed metal oxide electrode

Titanium plates were initially pretreated by dipping them into concentrated HCl at 70 °C for 1 h, followed by immersion in concentrated HNO_3 at room temperature for 15 min, rinsing with distilled water and drying at room temperature. This pretreatment increased the material roughness to improve the adhesion of oxides. The precursor polymer solution to apply the Pechini method was prepared by mixing citric acid and ethylene glycol with molar proportion of 0.00750:1 at 60–70 °C. After this, $SbCl_3$, $SnCl_4$ and $H_2IrCl_6{\cdot}xH_2O$ were added with molar proportion of 0.00012:0.00925:0.00925 for Sb:Sn:Ir, maintaining the temperature at 60–70 °C for 30 min, as optimized in one of our previous works [19]. The resulting solution was applied to the Ti substrate using a brush and the electrode was then heated at 115 °C for 15 min