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Advances in solar photoelectro-Fenton: Decolorization and mineralization of the Direct Yellow 4 diazo dye using an autonomous solar pre-pilot plant

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ABSTRACT

Here, an overview on the advances in solar photoelectro-Fenton (SPEF) is initially presented to show that it is the more potent electrochemical advanced oxidation process based on Fenton's reaction chemistry to remove organic pollutants from waters, due to the synergistic action of generated hydroxyl radicals and solar irradiation. As a novel advance for SPEF, an autonomous solar pre-pilot plant is proposed to make an energetically inexpensive process that can be viable at industrial level. The plant of 10 dm^3 capacity contained a Pt/air-diffusion cell with 90.2 cm^2 electrode area, coupled to a solar compound parabolic collectors (CPCs) photoreactor of 1.57 dm^3 irradiation volume and to a solar photovoltaic panel that provides a maximum average current of 5.0 A. The oxidation ability of this plant was assessed by studying the degradation of Direct Yellow 4 (DY4) diazo dye, which involved the predominant destruction of organics by $^{\bullet}OH$ formed from Fenton's reaction between H_2O_2 generated at the cathode and added Fe^{2+}, along with the photolysis of Fe(III)-carboxylate complexes with sunlight in the CPCs photoreactor. The effect of Fe^{2+} and dye contents as well as current on decolorization rate, substrate decay and mineralization rate was examined. About 96-97% mineralization was rapidly attained using 0.50 mmol dm^{-3} Fe^{2+} and up to 0.32 mmol dm^{-3} DY4 at 5.0 A. The DY4 decay always obeyed a pseudo-first-order kinetics. Eleven aromatic products, twenty two hydroxylated derivatives and nine short-linear carboxylic acids were identified as intermediates. The Fe(III) complexes of most acids were rapidly removed, pre-eminently photolyzed by sunlight, except those of acetic and oxamic acids that were slowly destroyed. The initial N of the dye was mainly released as NH_4^+ ion and its initial S was lost as SO_4^{2-} ion. A plausible reaction sequence for DY4 mineralization involving all the detected products was finally proposed.

1. Introduction

Over the past fifteen years, electrochemical advanced oxidation processes (EAOPs) have received increasing attention for the removal of toxic and non-biodegradable organic contaminants from waters [1–6]. These treatments are based on the in situ generation of hydroxyl radical ($^{\bullet}OH$), which has so high standard redox potential (E° = 2.80 V/SHE) that reacts with most organics yielding dehydrogenated or hydroxylated derivatives, which can be in turn mineralized. The most typical EAOP is anodic oxidation (AO), where pollutants are oxidized by electron transfer to the anode M and/or mediated oxidation with heterogeneous M($^{\bullet}OH$) formed from water discharge at the anode surface at high current [2,4,7]:

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

Boron-doped diamond (BDD) electrodes are the best anodes for AO because they interact very weakly with physisorbed BDD($^{\bullet}OH$) produced from reaction (1) and promote a much greater O_2-overpotential than other conventional anodes like Pt, enhancing the removal of organics [8–10].

Other EAOPs based on Fenton's reaction chemistry are electro-Fenton (EF) and photoelectro-Fenton (PEF), in which H_2O_2 is supplied to an acidic contaminated solution from the two-electron reduction of injected O_2, for example, at a carbon-PTFE gas (O_2 or air) diffusion cathode [5,6,11]:

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

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In Fenton based EAOPs, Fe^{2+} ion is added as catalyst to react with H_2O_2 to give Fe^{3+} ion and $^{\bullet}OH$ from Fenton's reaction with optimum pH 2.8 [5,12–17]:

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

Reaction (3) is catalytic and can be mainly propagated from Fe^{3+} reduction to Fe^{2+} at the cathode. When an undivided cell is used in EF, organics can be attacked by heterogeneous M($^{\bullet}OH$) formed from reaction (1) and by $^{\bullet}OH$ produced in the bulk from Fenton's reaction (3). In PEF, the degradation rate is enhanced under the simultaneous irradiation of the solution with UV light due to: (i) the greater Fe^{2+} regeneration and $^{\bullet}OH$ production by photolysis of $Fe(OH)^{2+}$, the pre-eminent Fe^{3+} species in solution at pH near 3, by reaction (4) and (ii) the photodecarboxylation of complexes of Fe(III) with generated carboxylic acids, which are hardly attacked by $^{\bullet}OH$, by the global reaction (5) [15,16,18–23].

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (4)$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (5)$$

An important drawback of PEF is the high electrical cost of the UV lamps used. To solve this problem, we have proposed the alternative use of the SPEF method in which the solution is directly irradiated with sunlight as an inexpensive and renewable energy source with $\lambda > 300$ nm [24,25]. The higher intensity of UV radiation supplied by sunlight and the additional absorption at $\lambda > 400$ nm, e.g. for the photolysis of Fe(III)-carboxylate complexes, enhance the mineralization process of SPEF compared with PEF.

Despite the more cost-effective treatment by SPEF, the electrolytic systems used spend energy from a power supply that provides the electric current to the electrolytic cell and this still represents an economical problem for its possible application to water remediation at industrial level. For this reason, we have designed a novel autonomous solar pre-pilot plant in which the electrical energy needed for the electrolytic cell is supplied by a solar photovoltaic panel, making thereby an energetically inexpensive SPEF process. The ability of such autonomous plant for organic removal has been assessed by studying the decolorization and mineralization of a typical diazo dye such as Direct Yellow 4 (DY4), whose chemical structure and characteristics are collected in Table 1.

This paper presents, in the first place, a brief overview over the advances in SPEF to show more clearly the interest of using the designed autonomous solar pre-pilot plant of 10 dm^3 capacity containing a Pt/air-diffusion cell coupled to a compound parabolic collectors (CPCs) photoreactor and controlled by a 50 W photovoltaic panel. The degradation of synthetic DY4 solutions in 0.05 mol dm^{-3} Na_2SO_4 at pH 3.0 by SPEF using such a plant is later reported to check the high effectiveness of this EAOP. The effects of Fe^{2+} content, applied current and DY4 concentration on the decolorization rate, substrate decay and mineralization rate and degree were examined. The decay kinetics for DY4 was followed by high-performance liquid chromatography (HPLC). Aromatic intermediates were detected by liquid chromatography-mass spectrometry (LC-MS) and generated short-linear carboxylic acids and released inorganic ions were quantified by different chromatographic techniques. From these results, a plausible reaction pathway for DY4 mineralization is finally proposed.

1.1. Advances in the solar photoelectro-Fenton process

The degradation of the drugs salicylic acid [26], ibuprofen [27], enrofloxacin [28] and chloramphenicol [29], as well as of the pharmaceutical precursor α-methylphenylglycine [30] and the dye Sunset Yellow CFC (SY) [31], has been comparatively studied by SPEF and other EAOPs using a 100 cm^3 stirred and thermostated tank reactor with a BDD or Pt anode and a gas (O_2 or air) diffusion cathode, all with 3 cm^2 area. In EF, PEF and SPEF, 0.05 or 0.10 mol dm^{-3} Na_2SO_4 was used as background electrolyte and 0.5 mol dm^{-3} Fe^{2+} was usually added as catalyst. The PEF trials were made with a 6 W UVA lamp of $\lambda_{max} = 360$ nm and the SPEF ones under direct solar irradiation with an average UV intensity of ca. 31 W m^{-2}. The performance of each EAOP increased using a BDD anode instead of Pt, indicating the higher oxidizing power of BDD($^{\bullet}OH$) than Pt($^{\bullet}OH$) formed from reaction (1) to remove the contaminants. Although UV light enhanced the degradation, almost total mineralization was more rapidly achieved in SPEF due to the higher intensity of sunlight. It was found an optimum pH of 3.0 for EF, PEF and SPEF treatments, near the optimum pH of 2.8 for Fenton's reaction (3), as expected if $^{\bullet}OH$ was the main oxidant of organics. Moreover, a Fe^{2+} content of 0.5-1.0 mmol dm^{-3} was found optimal for all processes. The amount of total organic carbon (TOC) removed always increased at higher current density and greater pollutant concentration, and so, the efficiency of SPEF rose when current decreased and more contaminant was present in the solution. The decay kinetics for pollutants always followed a pseudo-first-order reaction, with rate constants much higher for SPEF than for EF and PEF, due to the additional production of $^{\bullet}OH$ induced by reaction (4). GC-MS and HPLC analysis of treated solutions allowed the detection of aromatic intermediates like 2,3-, 2,5- and 2,6-dihidroxy-benzoic acids for salicylic acid, 34 products for chloramphenicol and 48 products for SY. Oxalic acid was always the ultimate generated carboxylic more largely accumulated which was not removed in EF but rapidly destroyed in PEF and much more quickly in SPEF by the fast photolysis of its Fe(III) complexes by reaction (5). This phenomenon explained the higher mineralization ability of the SPEF process. For enrofloxacin and α-methylphenylglycine, the initial N was mainly converted into NH_4^+ ion and in smaller proportion into NO_3^- ion. However, the opposite trend was found for chloramphenicol.

The SPEF treatment of organics has been scaled-up to a recirculation pre-pilot plant of 2.5 dm^3 with a BDD/O_2-diffusion cell coupled to a flat solar photoreactor composed of a polycarbonate box of 600 dm^3 of irradiated volume. The electrodes of 20 cm^2 area were separated about 1.2 cm. Solutions with 50-200 mg dm^{-3} of TOC in 0.05-0.10 mol dm^{-3} Na_2SO_4 with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0, 50 mA cm^{-2} and flow rate of 180-200 L h^{-1} were tested. SPEF was much more potent to mineralize organics than AO and EF, as found for the herbicide mecoprop [24], *o*-, *m*- and *p*-cresol [25] and the dyes Acid Yellow 36 (AY36) [15], Acid Red 88 (AR88) [32], Acid Yellow 9 (AY9) [32], Disperse Red 1 (DR1) [33] and Disperse Red 3 (DR3) [33]. For all these compounds, the SPEF efficiency rose at lower current density and higher pollutant content, being much more cost-effective than the EF process. The performance of SPEF was slightly enhanced from the combined use of Fe^{2+} and Cu^{2+} as co-catalysts as found for Disperse Blue 3 (DB3) [34] since mineralization was accelerated by the attack of $^{\bullet}OH$ on Cu(II)-carboxylate species, competitively formed with Fe(III)-carboxylate ones. A drawback of this plant, however, was the high energy consumption of the BDD/air-diffusion cell as a result of its great potential difference between electrodes. For this reason, more recent studies with the 2.5 dm^3 solar pre-pilot plant were focused to the degradation of sulfanilic acid [35] and sulfanilamide [36] using a more economic Pt/air-diffusion reactor since this cell possesses a lower potential difference compared with the BDD/air-diffusion one. For the SPEF process of sulfanilic acid, the application of response surface methodology allowed obtaining 100 mA cm^{-2}, 0.5 mmol dm^{-3} Fe^{2+} and pH 4.0 as optimum variables, yielding 76% mineralization with 275 kWh kg^{-1} TOC energy cost and 52% current efficiency at 120 min. For the SPEF treatment of 239-1195 mg dm^{-3} sulfanilamide solutions of pH 3.0, 91-94% mineralization was achieved after 240 min at 100 mA cm^{-2} with consumption < 470 kWh kg^{-1} TOC. All the initial compounds