Comparative electro-Fenton and UVA photoelectro-Fenton degradation of the antibiotic sulfanilamide using a stirred BDD/air-diffusion tank reactor

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HIGHLIGHTS

- Total mineralization of sulfanilamide by photoelectro-Fenton with a BDD/air-diffusion cell.
- Large, but slower, mineralization by comparative electro-Fenton.
- Oxalic and oxamic acids as the most persistent final carboxylic acids.
- Release of sulfate and ammonium ions, as well as nitrate ion in much lesser extent.

ABSTRACT

Here, the degradation of 100 mL of sulfanilamide solutions of pH 3.0 has been comparatively studied by electro-Fenton (EF) and photoelectro-Fenton (PEF) using a stirred tank reactor equipped with a 3 cm^2 boron-doped diamond (BDD) anode and a 3 cm^2 air-diffusion cathode. In both treatments, organics are destroyed by hydroxyl radicals formed at the BDD surface and in the solution bulk from Fenton's reaction between cathodically generated H_2O_2 and initially added Fe^{2+}, whereas in PEF, additional photolysis of intermediates under UVA radiation is also feasible. The influence of applied current density and substrate concentration on antibiotic decay, degradation rate and mineralization degree was examined. The sulfanilamide decay always followed a pseudo-first-order reaction, as found by reversed-phase liquid chromatographic monitoring, being faster for PEF. The EF process led to large mineralization of sulfanilamide concentrations up to 2390 mg L^{-1}. Nevertheless, the PEF process was much more potent and allowed achieving total mineralization (>99% of dissolved organic carbon removal) of all the solutions tested. Results showed that the application of this treatment is preferable at low current densities and high substrate concentrations to obtain the best mineralization current efficiencies. Ion-exclusion liquid chromatography revealed that oxalic and oxamic acids were the most persistent generated carboxylic acids. Their Fe(III) complexes were slowly removed by hydroxyl radical in EF and much more quickly photolyzed by UVA light in PEF. Ion chromatography confirmed the main release of NH_4^+ and SO_4^{2-} ions, and NO_3^- ion in relatively smaller extent, during all the mineralization processes.

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1. Introduction

Recently, our groups have studied the treatment of several antibiotics in waters from electrochemical advanced oxidation processes (EAOPs) based on Fenton's reaction chemistry like electro-Fenton (EF) and photoelectro-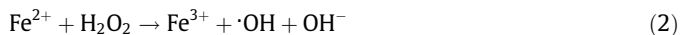Fenton (PEF) [1–7]. Our interest in this research is to develop powerful oxidation processes with ability to remove these compounds from the aquatic environment in order to avoid their potential adverse health effects on humans and animals [8–10]. The detection of a large number of antibiotics at relatively high concentrations in soils, surface waters, ground waters and drinking waters has been well documented [11–13]. Due to their antimicrobial nature, they are not effectively removed in sewage treatment plants [14,15] and accumulate progressively in natural water body. For this reason, the occurrence and fate of antibiotics in water streams is recognized as one of the emerging

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issues in environmental chemistry [12,16]. Despite their very low concentration in natural waters, antibiotics can be dangerous for living beings since they can originate multi-resistant strains of microorganisms, can affect the endocrine systems of fishes and invertebrates, and can be toxic on algae and small invertebrates [16–20].

The EF process consists in the addition of a catalytic amount of Fe^{2+} to an acidic solution contained in an electrolytic cell in which H_2O_2 is continuously produced from the two-electron reduction of injected O_2 at a carbonaceous cathode by reaction (1) [3]. Fe^{2+} reacts with electrogenerated H_2O_2 yielding Fe^{3+} and hydroxyl radical ($\cdot$OH) from the well known Fenton's reaction (2). $\cdot$OH is the second strongest oxidant known after fluorine because it has so high standard reduction potential ($E°(\cdot OH/H_2O) = 2.80$ V/SHE) that can non-selectively react with organics up to their mineralization to carbon dioxide, water and inorganic ions [5,8,21,22]. The best operating pH for EF is 3, near the optimum pH of 2.8 for Fenton's reaction (2) [3,10]. An advantage of EF over the classical chemical Fenton is that reaction (2) can be largely propagated from the regeneration of Fe^{2+} by Fe^{3+} reduction at the cathode via reaction (3) [3,5].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

Carbonaceous cathodes like carbon sponge [21], carbon nanotubes on graphite [23], carbon nanotubes-polytetrafluoroethylene (PTFE) [24,25], carbon-felt [1,2,5,7,21,26,27], graphite-felt [28], boron-doped diamond (BDD) [29] and carbon-PTFE gas (O_2 or air) diffusion electrodes [1,2,6,8,22,30,31] have shown good efficiencies for generating H_2O_2 from reaction (1).

In PEF, the solution under EF conditions is simultaneously irradiated with an artificial UVA lamp [3,8,22,24,31]. This radiation can then produce different effects: (a) the photolysis of $Fe(OH)^{2+}$, the pre-eminent Fe^{3+} species near pH 3, regenerating Fe^{2+} and producing more $\cdot$OH from reaction (4) and (b) the photodecarboxylation of some generated Fe(III)-carboxylate complexes according to the general reaction (5) [6,32,33].

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \tag{4}$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R\cdot \tag{5}$$
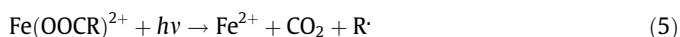
When an undivided cell is used in EF and PEF, organic pollutants can also be attacked by heterogeneous physisorbed $\cdot$OH, designed as M($\cdot$OH), produced from water oxidation at a high O_2-overvoltage anode M as follows [3,34]:

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \tag{6}$$

The most potent anodes known for water remediation in anodic oxidation (AO) are the boron-doped diamond (BDD) thin-film electrodes. They possess technologically important characteristics like an inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media and extremely high O_2-evolution overvoltage, enhancing the organic removal with reactive BDD($\cdot$OH) [34,35]. BDD anodes are thus potent enough to mineralize aromatic pollutants from waters [36–41] and their generated carboxylic acids [32] and have much higher oxidation power than other common anodes such as Pt [42–44] and PbO_2 [45].

The combined action of $\cdot$OH at the anode surface and in the bulk in EF, along with that of UVA light in PEF, are key parameters that need to be clarified to understand their oxidation role on organic pollutants. In previous work [41], one of our groups reported that

the AO degradation of the antibiotic sulfanilamide in divided and undivided BDD/stainless steel cells cannot yield its total mineralization, then being necessary to assess more potent EAOPs to try to destroy sulfanilamide and its oxidation products. Sulfanilamide is the parent molecule of sulfonamides, an antimicrobials family widely used in aquaculture and animal husbandry, as well as in human medicine. Sulfonamides are polar amphoteric compounds that have been detected in many surface waters [12,46] proceeding from waste dump leachates [47], animal manure effluents [48] and manure waste lagoons from swine farms [49]. They are resistant to biological degradation [50], exhibiting a potential toxicity to some aquatic organisms and promoting the emergence of antibiotic resistant strains [51].

This paper presents a careful study on the comparative degradation of sulfanilamide by EF and PEF using a BDD/air-diffusion cell under similar conditions to those applied to its AO treatment in order to clarify the role of BDD($\cdot$OH), $\cdot$OH in the bulk and UVA radiation in the oxidation processes. The effect of current density (j) and sulfanilamide concentration on its decay kinetics, degradation rate and mineralization degree for each EAOP was examined. Much higher substrate concentrations, between 239 and 2511 mg L^{-1}, than those found in the aquatic environment were used to better explain the action of the oxidizing species. The evolution of generated carboxylic acids and released inorganic ions was also followed by chromatographic techniques.

2. Methods and materials

2.1. Chemicals

Sulfanilamide (purity $\geqslant 98\%$) was of reagent grade purchased from Sigma–Aldrich. Oxalic and oxamic acids were of analytical grade supplied by Panreac. Anhydride sodium sulfate, used as background electrolyte, and heptahydrated ferrous sulfate, used as catalyst, were of analytical grade purchased from Fluka. All solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C. The initial solution pH was adjusted to 3.0 with analytical grade sulfuric acid supplied by Merck. Organic solvents and other chemicals used were either of HPLC or analytical grade from Merck, Fluka and Avocado.

2.2. Electrolytic system

All electrolytic experiments were performed with an open, undivided and cylindrical cell containing a 100 mL solution. It was surrounded with a double jacket for circulation of external thermostated water to regulate the solution temperature at 35 °C with a Thermo Electron Corporation HAAKE DC 10 thermostat. This is the maximum temperature that can be used in the cell without significant water evaporation [31]. The cell was equipped with a 3 cm^2 BDD thin-film anode purchased from Adamant Technologies and a 3 cm^2 carbon-PTFE air-diffusion cathode supplied by E-TEK, separated by a distance of about 1 cm. The cathode was mounted as described elsewhere [22] and was fed with air pumped at 300 mL min^{-1} for continuous H_2O_2 generation. All the assays were made at constant j using an Amel 2053 potentiostat–galvanostat. The solution was stirred with a magnetic bar at 800 rpm to ensure mixing and the transport of reactants towards/from the electrodes. In the PEF trials, a Philips TL/6W/08 fluorescent black light blue tube was placed at 7 cm above the solution. This tube emitted UVA light in the wavelength region 320–400 nm with $\lambda_{max} = 360$ nm, supplying a photoionization energy of 5 W m^{-2} determined with a Kipp & Zonen CUV 5 radiometer. Before use, the electrodes