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Mineralization of the antibiotic chloramphenicol by solar photoelectro-Fenton. From stirred tank reactor to solar pre-pilot plant

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ABSTRACT

Chloramphenicol is a widely used broad-spectrum antibiotic, which has been detected as emerging pollutant in natural waters. The mineralization of this drug in a synthetic sulfate solution of pH 3.0 has been studied by anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2), electro-Fenton (EF), UVA photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF). Comparative electrolyses carried out with 100 mL stirred tank reactors equipped with a boron-doped diamond (BDD) or Pt anode and an air-diffusion cathode at constant current density showed the superiority of the processes with BDD because of the higher oxidation ability of $^{\bullet}$OH formed from water oxidation at the BDD surface. Total mineralization was rapidly reached for the most potent treatment of SPEF with BDD due to the additional oxidation by $^{\bullet}$OH produced from Fenton's reaction between added Fe^{2+} (0.5 mM) and H_2O_2 generated at the cathode, together the synergistic photolytic action of sunlight, much more intense than the 6 W UVA lamp used in PEF. Chloramphenicol decay always followed a pseudo-first-order kinetics. The influence of current density and substrate concentration on SPEF with BDD was examined. Nine aromatic products, thirteen hydroxylated derivatives and seven carboxylic acids were identified by different chromatographic techniques. While the initial Cl of the drug was released as chloride ion, its initial N was lost as nitrate ion and, in smaller proportion, as ammonium ion. From the detected products, a general reaction pathway for chloramphenicol mineralization is proposed. The viability of SPEF was confirmed in a 10 L pre-pilot plant with a Pt/air-diffusion filter-press reactor coupled to a solar CPCs photoreactor. After 180 min of electrolysis at 100 mA cm^{-2}, a 245 mg L^{-1} chloramphenicol solution in 0.05 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 underwent 89% mineralization with 36% current efficiency and 30.8 kWh m^{-3} energy cost.

1. Introduction

Recently, there exists an increasing attention on pharmaceuticals as potential bioactive chemicals in the aquatic environment. Many pharmaceutical drugs have been detected at relatively low contents up to μg L^{-1} level in soils, surface waters, ground waters and even drinking waters [1–3]. Antibiotics are the most commonly drugs found in the aquatic environment because their antimicrobial nature prevents effective removal in sewage treatment plants [4–6]. The occurrence and fate of antibiotics as well as their metabolites in water streams is recognized as one of the emerging issues in environmental chemistry [1,3,7,8]. Several authors reported that these pollutants can produce multi-resistant strains of microorganisms, can affect the endocrine systems of fishes and invertebrates, and are toxic on small invertebrates and algae [9–12]. Powerful oxidation treatments then need to be developed for the removal of antibiotics from waters and wastewaters to avoid their potential adverse health effects on humans and animals.

Several electrochemical advanced oxidation processes (EAOPs) are being currently developed for water prevention [12–17]. EAOPs are based on the *in situ* generation of hydroxyl radical ($^{\bullet}$OH), which is the second strongest oxidant known after fluorine since it has so high standard reduction potential ($E^{\circ}(^{\bullet}OH/H_2O) = 2.80$ V/SHE) that can non-selectively react with organic pollutants up to their mineralization to CO_2, water and inorganic ions. The most potent EAOPs use both, heterogeneous and homogeneous $^{\bullet}$OH formed at the anode and in the solution bulk, respectively, as oxidizing agents. Mediated electro-oxidation with homogeneous $^{\bullet}$OH is usually achieved by decomposition of H_2O_2 generated from the two-electron cathodic reduction of injected O_2 [12,16]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

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Good efficiencies for H_2O_2 generation from reaction (1) have been reported for carbonaceous cathodes such as carbon sponge [18], carbon nanotubes-polytetrafluoroethylene (PTFE) [19,20], carbon-felt [18,21–25], graphite-felt [26], boron-doped diamond (BDD) [27] and carbon-PTFE gas (O_2 or air) diffusion electrodes [21,22,28–32].

In our laboratory, we have checked the good oxidation ability of EAOPs like anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2) [28,32], electro-Fenton (EF) [21,22,28–31], UVA photoelectro-Fenton (PEF) [28–30] and solar photoelectro-Fenton (SPEF) [29,31] to destroy several antibiotics and other drugs in acidic solutions using small stirred tank reactors equipped with either a BDD or Pt anode and a gas-diffusion cathode. Our interest is to show that these EAOPs can be useful for the treatment of wastewaters contaminated with antibiotics. To do this and in view of the large variety of these drugs, it is necessary to know the degradative characteristics of more compounds. In this way, the scaling-up of EAOPs to a pre-pilot plant also needs to be assessed in order to demonstrate their possible viability at industrial level.

This paper aims to investigate the mineralization of the antibiotic chloramphenicol (2,2-dicloro-*N*-[1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl] acetamide) in acidic medium by AO-H_2O_2, EF, PEF and SPEF in order to clarify: (i) the role of generated $^{\bullet}OH$ in the degradative processes using stirred Pt/air-diffusion and BDD/air-diffusion tank reactors of 100 mL under comparable conditions, (ii) the photolytic action of UVA and solar radiation in these systems, (iii) the effect of experimental parameters on substrate decay and mineralization rate, (iv) the products formed and their evolution to propose a general reaction pathway for chloramphenicol mineralization and (v) the viability of SPEF in a 10 L pre-pilot plant with a Pt/air-diffusion filter-press reactor coupled to a solar compound parabolic collectors (CPCs) photoreactor. Note that chloramphenicol is a broad-spectrum antibiotic, which is effective against a wide variety of Gram-positive and Gram-negative bacteria, including most anaerobic organisms. While in the developed countries it is currently prescribed only to treat bacterial conjunctivitis, chloramphenicol is widely used in developing countries. For this reason, it has been detected worldwide in ground waters, lakes, rivers and influents and effluents of sewage treatment plants [3,6–8,33–36]. However, less is known about the degradation of chloramphenicol from waters and its oxidation products formed from $^{\bullet}OH$ attack have not been identified yet. It has been reported that it can be removed by UVC radiation [37], TiO_2/UV photocatalysis [38] and ozonation [39]. The electrochemical reduction of its nitro group to hydroxylamine or amine at a graphite cathode has also been described by means of cyclic voltammetry [40].

2. Experimental

2.1. Chemicals

Chloramphenicol (98% purity) was of reagent grade from Sigma–Aldrich. Carboxylic acids were of reagent grade from Panreac and Avocado. Anhydrous sodium sulfate and heptahydrated ferrous sulfate were of analytical grade from Fluka. Solutions treated in the stirred tank reactor were prepared with ultrapure water obtained from a Millipore Milli-Q system (resistivity > 18 MΩ cm at 25 °C). Solutions of 10 L to be degraded in the solar pre-pilot plant were prepared with deionized water. All solutions were adjusted to pH 3.0 with analytical grade sulfuric acid purchased from Merck. Other chemicals employed were of LC–MS, HPLC or analytical grade from Merck, Panreac and Sigma–Aldrich.

2.2. Electrochemical and photoelectrochemical systems

Experiments with 100 mL solutions were conducted in an undivided and cylindrical stirred tank reactor, with a double jacket in which external water circulated to maintain the solution temperature at 35 °C. The anode was either a BDD thin film electrode provided by Adamant Technologies or a Pt sheet of 99.99% purity supplied by SEMPSA. The cathode was a carbon-PTFE air-diffusion electrode purchased from E-TEK. The preparation of this cathode was described elsewhere [41] and was fed with air pumped at 300 mL min^{-1} for H_2O_2 generation from reaction (1). The area of both electrodes was 3 cm^2 and the interelectrode gap was ca. 1 cm. To remove the impurities of the BDD surface and activate the air-diffusion cathode prior use, they were polarized in 0.05 M Na_2SO_4 at 100 mA cm^{-2} for 60 min. All trials were carried out under vigorous stirring with a magnetic bar at 800 rpm to ensure homogenization and the transport of reactants toward/from the electrodes. For the PEF assays, a Philips 6-W black light blue tube was placed at 7 cm above the solution. This lamp emitted UVA light between 320 and 400 nm with λ_{max} = 360 nm, yielding a photoionization energy of 5 W m^{-2} as detected with a Kipp & Zonen CUV 5 global UV radiometer. In the SPEF assays, the tank reactor was directly exposed to solar radiation with a mirror placed at its bottom to better collect the sun rays.

A scheme of the solar pre-pilot plant operating in batch circulation mode was presented elsewhere [42]. For each EF or SPEF trial, the solution was introduced in the reservoir and continuously recirculated by a peristaltic pump at a flow rate of 200 L h^{-1} adjusted by a rotameter. The temperature was maintained at 35 °C by two heat exchangers. The electrolytic cell was an undivided filter-press reactor equipped with a Pt sheet anode from SEMPSA and a carbon-PTFE air-diffusion cathode from E-TEK. A PVC liquid compartment with a central window of 9.5 cm × 9.5 cm (90.2 cm^2) was used to contact the effluent with the outer faces of both electrodes, separated 1.2 cm. The inner face of the cathode was pressed to a Ni mesh as electrical connector in contact with a PVC gas chamber where circulated compressed air at a flow rate of 4.5 L min^{-1} regulated with a back-pressure gauge. The solar CPCs photoreactor with an area of 0.4 m^2 and concentration factor of 1 was composed of twelve borosilicate-glass tubes of 50.5 cm length × 1.82 cm inner diameter (irradiated volume 1.57 L), with connecting tubing and valves mounted in an aluminum frame on a platform tilted 41° to better collect the direct sun rays in our laboratory of Barcelona (latitude: 41°21′N, longitude: 2°10′E). In EF, the solar CPCs photoreactor was coated with a black plastic.

All solar trials were made for 240 min as maximal in sunny and clear days during summer 2012. The average solar UV radiation intensity (between 300 and 400 nm) was 30–32 W m^{-2}, as measured with a Kipp & Zonen CUV 5 global UV radiometer.

2.3. Apparatus and analytical procedures

The solution pH was measured with a Crison GLP 22 pH-meter. Galvanostatic electrolyses were performed with an Amel 2051 potentiostat–galvanostat for the tank reactor experiences and a Grelco GDL3020 power supply for the assays with the solar pre-pilot plant. Aliquots of 1 mL were withdrawn from electrolyzed solutions and filtered with 0.45 μm PTFE filters from Whatman before analysis. The mineralization of chloramphenicol solutions was monitored from their dissolved organic carbon (DOC) abatement, determined on a Shimadzu TOC-VCSN analyzer. Reproducible DOC values with an accuracy of ±1% were obtained by injecting 50 μL aliquots to the analyzer. Total nitrogen (TN) was determined with a Shimadzu TNM-1 unit coupled with the TOC analyzer.