



Original research article

Synergism between anodic oxidation with diamond anodes and heterogeneous catalytic photolysis for the treatment of pharmaceutical pollutants



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ABSTRACT

The mineralization of diclofenac and acetaminophen has been studied by single anodic oxidation with boron-doped diamond (AO-BDD) using an undivided electrolysis cell, by single heterogeneous catalytic photolysis with titanium dioxide (HCP-TiO₂) and by the combination of both advanced oxidation processes. The results show that mineralization can be obtained with either single technology. The type of functional groups of the pollutant does not influence the results of the single AO-BDD process, but it has a significant influence on the results obtained with HCP-TiO₂. A clear synergistic effect appears when both processes are combined showing improvements in the oxidation rate of more than 50% for diclofenac and nearly 200% for acetaminophen at the highest current exerted. Results obtained are explained in terms of the production of oxidants on the surface of BDD (primarily peroxodisulfate) and the later homogeneous catalytic light decomposition of these oxidants in the bulk. This mechanism is consistent with the larger improvement observed at higher current densities, for which the production of oxidants is promoted.

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1. Introduction

In recent years, a large number of research groups around the world have conducted investigations on the detection and removal of pharmaceutical compounds, such as analgesics, anti-inflammatories, anti-microbials, antiepileptics, beta-blockers, estrogens and lipid regulators, typically found as emerging pollutants in surface water, ground water (including drinking water) and industrial wastewaters at concentrations ranging from a few $\mu\text{g L}^{-1}$ to several mg L^{-1} [1–3]. In developing countries, such as Mexico, the management of these pollutants is not regulated and, therefore, they are continuously discharged into the environment without any treatment. Consequently, they do not undergo any significant

degradation in industrial wastewater treatment facilities or in conventional urban wastewater treatment plants.

Diclofenac and acetaminophen are two common drugs used to treat various diseases in human beings. Diclofenac (sodium salt (2-[2-(2,6-dichlorophenyl) aminophenyl] acetate ion)), is one of the most common non-steroidal anti-inflammatory drugs. It is widely used for controlling renal colic and protecting against recurrent urinary calculi, and it is also present in numerous pharmaceutical preparations to treat other various diseases. As a result of its resistance to biodegradation, it is one of the pollutants most frequently detected in groundwater, rivers and lakes around the world with concentrations in the environment as high as $4.4 \mu\text{g L}^{-1}$ [4–6]. Acetaminophen (paracetamol), N-(4-hydroxyphenyl) acetamide is a drug with analgesic properties. It inhibits the synthesis of prostaglandins, cellular mediators responsible for the onset of pain. It also has antipyretic effects. It is usually presented in the form of capsules, tablets, suppositories or oral drops.

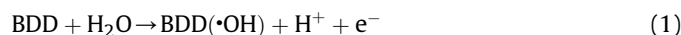
In the search for efficient ways to remove these pollutants, several technologies have been used, highlighting the electrochemical processes, such as electro-oxidation, also known as

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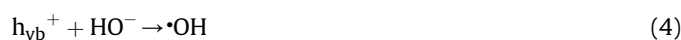
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anodic oxidation (AO), a method for the treatment of wastewaters containing anthropogenic organic pollutants [7]. When using a proper anode material, this process acts as an advanced oxidation process (AOP) that permits the electrochemical degradation of pollutants with free hydroxyl radicals ($\cdot\text{OH}$) generated on the surface of high O_2 -overtoltage anodes [8]. The best anodes for this procedure are non-active boron-doped diamond (BDD) thin-film electrodes because they interact very weakly with the physorbed $\cdot\text{OH}$ produced by Eq. (1) [9].



AO with BDD (AO-BDD) presents advantages with respect to other electrochemical technologies from the point of view of efficiency, stability and performance [10–13]. The production of powerful oxidants during the treatment of wastewater can expand the oxidation from the electrode surface to the bulk and thereby enlarge the efficiency of the electrolysis. However, the main drawback is the loss of efficiency when applied to lowly concentrated waste because of mass transfer limitations commonly associated with electrochemical technologies, in which the main processes do not occur in the bulk but on the electrode surfaces. For this reason, this technology is commonly recommended for a pollutant concentration range between 1500 and 20,000 ppm of Chemical Oxygen Demand (coarse removal of pollutants from an industrial wastewater), for which the current efficiency is usually close to 100% [14]. For lower concentrations, combination with other AOP is suggested in order to increase the efficiency by activating oxidants or producing new oxidants in the bulk.

One of these technologies is heterogeneous catalytic photolysis with titanium dioxide (HCP-TiO₂). This process is developed when semiconductor materials, such as TiO₂, are irradiated with light with energy higher than their band-gap energy [15]. The catalyst is suspended (slurry) directly in the solution to be treated, and this irradiation produces excited high-energy states of electron and hole pairs (Eqs. (2)–(5)). Technological interest in TiO₂ (band-gap energy = 3.2 eV) has focused on its photocatalytic and hydrophilic properties because it is highly reactive, nontoxic, relatively inexpensive and chemically stable [16,17].



A current hot topic in the electrolysis of organics is the combination with other effective treatments, looking for synergistic interactions [18,19]. However, to the knowledge of the authors, very few of these works have focused on combining AO-BDD with TiO₂ photocatalytic processes. This paper aims to be a comparative study of the mineralization of diclofenac and acetaminophen by single AO-BDD, single HCP-TiO₂ and the combination of both technologies. Special attention has been paid to the assessment of synergistic interactions between both technologies.

2. Materials and methods

In Fig. 1 is shown the chemical structure for diclofenac and acetaminophen. Both reagents (of reactive grade from Sigma–Aldrich) were used in the experiments as received. The anhydrous sodium sulfate used to prepare the electrolyte and/or the buffer medium of pH 6.5 was of analytical grade from J.T. Baker and

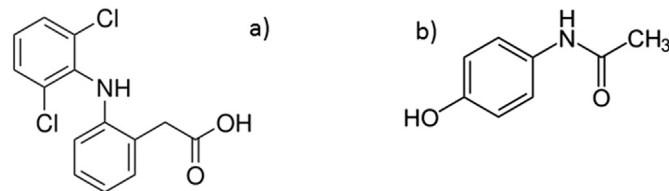


Fig. 1. Diclofenac (a) and acetaminophen (b).

Panreac. Solutions were prepared with high-purity water from a Millipore-Elixsystem, with resistivity $\geq 18 \text{ M}\Omega \text{ cm}$ at 25 °C. Titanium dioxide (P25) was purchased from Degussa.

The solution pH was measured with a Crison 2000 pH meter. Samples extracted from treated solutions were filtered with 0.45 μm PTFE filters from Whatman prior to analysis. The degradation of drug solutions was monitored by the removal of total organic carbon (TOC), measured on a Shimadzu TOC-L analyzer.

Assays were conducted in a one-compartment, thermostated cylindrical glass cell containing a 1 L solution vigorously stirred with a magnetic bar. The anode was a 5 cm^2 BDD thin film deposited on a conductive niobium plate, and the cathode was a 5 cm^2 stainless steel (AISI 304) sheet. The interelectrode gap was 0.5 cm. Solutions containing up to 170 mg L^{-1} diclofenac and 190 mg L^{-1} acetaminophen and 0.05 M Na_2SO_4 at pH 6.5 were treated at constant currents of 0.5, 1.0, and 1.5 A at 35 °C. A BK Precision DC Regulated power supply was used to supply electricity. Photocatalytic tests were performed by adding 100 mg L^{-1} TiO₂ catalyst, and the solution was irradiated with a Philips TL/6W/08 fluorescent black light blue tube of $\lambda = 360 \text{ nm}$ and intensity = 75 mW cm^{-2} .

3. Results and discussion

3.1. AO-BDD

The degradation of the two drug solutions was performed by AO-BDD at three different current densities (100, 200 and 300 mA cm^{-2}). The results in terms of mineralization are shown in Fig. 2. Both pollutants are efficiently mineralized during the electrolysis, as can be observed in Fig. 2a for diclofenac and in Fig. 2b for acetaminophen.

Initially, the pollutants are expected to be destroyed by the direct or mediated action of the adsorbed $\cdot\text{OH}$ formed as an intermediate during the oxidation of water to oxygen on the surface of the conductive diamond coatings, according to Eq. (1). This production was demonstrated a decade ago [20] with several specific reactions, i.e., with 5,5-dimethyl-1-pyrroline-N-oxide using spin trapping for the detection of hydroxyl radicals and with salicylic acid using electron spin resonance and liquid chromatography measurements. These results were significant because they allowed electrolysis to be considered as an AOP. Free radical $\cdot\text{OH}$ is a non-selective, strong oxidizing reagent that can react with most organic compounds in an efficient way. However, according to the results obtained in various AOPs, such as Fenton oxidation, in which $\cdot\text{OH}$ is the main oxidant participating in the oxidation of pollutants; this oxidation is not effective for the mineralization because there are some carboxylic acids remaining. This is not the case with AO-BDD because, in this particular case, the total mineralization [21] of the organic species is demonstrated, regardless of their functional groups. To explain this better performance, in addition to the direct oxidation of organics by hydroxyl radicals, it should be considered that alternatively to the attack on organic molecules, hydroxyl radicals can combine with other species, such as sulfate, to form more stable oxidants, such as peroxosulfates, which can expand the

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