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Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Degradation of antibiotic ampicillin on boron-doped diamond anode using the combined electrochemical oxidation - Sodium persulfate process

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ARTICLE INFO

Keywords:

BDD
Emerging contaminants
Ecotoxicity
Kinetics
Process coupling
Solar irradiation

ABSTRACT

In this work, the electrochemical oxidation of antibiotic ampicillin (AMP) on a boron-doped diamond anode in the presence of sodium persulfate (SPS) was investigated (EO/SPS process). Experiments were conducted at AMP concentrations between 0.8 and 3 mg/L, SPS concentrations between 100 and 500 mg/L, current densities between 5 and 110 mA/cm², in three water matrices (ultrapure water, bottled water and secondary treated wastewater), using 0.1 M Na₂SO₄ as the supporting electrolyte. AMP degradation follows a pseudo-first order kinetic expression with the apparent rate constant increasing with (i) increasing SPS concentration (from 0.08 min⁻¹ to 0.36 min⁻¹ at 0 and 500 mg/L SPS, respectively, 1.1 mg/L AMP, 25 mA/cm²), (ii) increasing current (from 0.08 min⁻¹ to 0.6 min⁻¹ at 5 and 110 mA/cm², respectively, 1.1 mg/L AMP, 250 mg/L SPS), and (iii) decreasing AMP concentration (from 0.16 min⁻¹ to 0.31 min⁻¹ at 3 and 0.8 mg/L, respectively, 250 mg/L SPS, 25 mA/cm²). The presence of various anions (mainly bicarbonates) in bottled water did not impact AMP degradation. The observed kinetic constant decreased by 40% in the presence of 10 mg/L humic acid. On the other hand, process efficiency was enhanced almost 3.5 times in secondary effluent due to the electrogeneration of active chlorine species that promote indirect oxidation reactions in the bulk solution. The efficacy of the EO/SPS process was compared to and found to be considerably greater than a process where SPS was activated by simulated solar irradiation at an intensity of 7.3×10^{-7} E/(L.s) (SLR/SPS process). Coupling the two processes (EO/SLR/SPS) resulted in a cumulative, in terms of AMP degradation, effect. The combined process was tested for AMP degradation, mineralization and inhibition to *Vibrio fischeri* in wastewater; fast AMP removal was accompanied by low mineralization and incomplete toxicity removal.

1. Introduction

In recent years, there is a growing concern in the scientific community about the increased misuse of antibiotics. Pharmaceutical drug abuse can lead to the inadequacy of the existing antibiotics to combat microbial populations due to the development of antibiotic resistance of bacteria (Richardson and Kimura, 2016; Michael et al., 2013; Rizzo et al., 2013; Ventola, 2015). Ampicillin (AMP) is a broad spectrum antibiotic, derived from penicillin. It can treat mainly respiratory, urinary and streptococcal infections (Sharma et al., 2013). In a recent work, Kulkarni et al. (2017) collected 72 samples from two mid-Atlantic and two Midwest conventional wastewater treatment plants. AMP was detected at concentrations up to 49.7 µg/L in the influents and in the range 2.21–42.2 µg/L in the effluents. It is, therefore, vital to develop new technologies that will be able to remove even traces of pharmaceutical compounds from water and wastewater (Karthikeyan and

Meyer, 2006).

Nowadays, a growing number of researchers have been studying the application of advanced oxidation processes (AOPs), a family of processes based on the *in situ* production of highly active oxidants (reactive oxygen species - ROS), mainly but not exclusively hydroxyl radicals (Comminellis et al., 2008; Klavarioti et al., 2009; Wang and Xu, 2012). Some researchers have studied the removal of AMP by heterogeneous photocatalysis (Elmolla and Chaudhuri, 2010a; Elmolla and Chaudhuri, 2010b; Ozkal et al., 2016), while others (He et al., 2014) have employed the UVC/sodium persulfate and UVC/H₂O₂ processes. The observed UV fluence-based pseudo-first-order rate constant for the decomposition of 50 µM ampicillin was 0.24, 2.10 and 4.23×10^{-3} cm²/mJ for UVC, UVC/H₂O₂ and UVC/sodium persulfate, respectively. However, the total organic carbon (TOC) removal was only 25.5% for UVC/H₂O₂ and 33% for UVC/sodium persulfate.

Among various AOPs electrochemical oxidation appears to be a

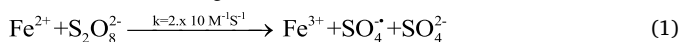
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promising technology for water purification (Sirés and Brillas, 2012), particularly after the development of a new generation of materials, such as the boron-doped diamond (BDD). This non active electrode exhibits great activity and stability (Moreira et al., 2017; Chaplin, 2014). Wirzal et al. (2013) reported that Ru-Ir-TiO₂ could completely eliminate ampicillin in less than 15 min with the addition of 500 mg/L NaCl at pH 4, 0.2 A and 10 V. Körbahti and Taşyürek (2015) reported that BDD could effectively degrade AMP. For example, 97.1% degradation of 618 mg/L AMP could be achieved at optimal conditions including 13.4 mA/cm², 3.6 g/L NaCl, 36 °C at the expense of 71.7 kWh/kg COD removed. A serious weakness of most of the aforementioned studies is that the initial AMP concentration is well beyond (i.e. up to 1 g/L) the concentrations that are typically found in municipal wastewater treatment plants. In addition, the majority of the experiments were conducted in ultrapure water.

A major disadvantage of electrolysis is the large surface area of the electrodes required. An interesting idea in order to enhance the efficiency is the addition of oxidants that can promote the production of extra ROS. Among different oxidants, persulfate has many advantages like long half-life, ease of storage and transportation. Moreover, it can be activated in different ways such as transition metals, ultraviolet irradiation and using electrochemistry (Matzek and Carter, 2016; Wacławek et al., 2017).

So far, most studies have focused on the use of iron electrodes (Govindan et al., 2014; Yu et al., 2016; Bu et al., 2017). In this case, the electrode acts as a sacrificial iron ion source. Thereafter, persulfate can be activated according to the reactions (Yu et al., 2016):



For example, Yu et al. (2016) studied the combined iron electrodes/persulfate system for the degradation of diuron. They found that the combined process have higher efficiency than electrocoagulation alone (i.e. in the absence of persulfate). In accordance with the classical Fenton reaction, the process is favored at acidic pH. Nevertheless, the yield is significantly reduced as the pH becomes alkaline due to iron precipitation.

On the other hand, electrochemical oxidation does not suffer from the aforementioned drawbacks associated with electrocoagulation. In principle, sulfate radicals can be electrogenerated at the cathode, while persulfate can be regenerated by the combination of sulfate ions in the anode (Bu et al., 2018; Matzek et al., 2018).

In their pioneering work, Chen et al. (2014) examined the mineralization of dinitrotoluenes by electroactivated persulfate with platinum electrodes. They found that the removal of TOC for the combined electrooxidation/persulfate process was significantly higher (70%) than the sum of individual removal values for the electrooxidation (45%) and oxidation due to persulfate (4%). Farhat et al. (2015) examined the electrochemical degradation of emerging contaminants using BDD in a two-compartment cell divided by an ion exchange membrane. They found that the rate constant for the electrooxidation of diatrizoate increased almost 10.5 times in the presence of 0.55 mM persulfate. The authors attributed this enhancement to the non-radical activation of persulfate. Recently, Song et al. (2018) demonstrated that the simultaneous use of BDD anodic oxidation and persulfates increased the apparent kinetic constant for the removal of carbamazepine from 0.058 min⁻¹ in the absence of persulfate to 0.114 min⁻¹ and 0.313 min⁻¹ in the presence of 5 mM of peroxydisulfate and peroxymonosulfate, respectively. However, the experiments were conducted in a two-chamber reactor, which did not allow the reduction of persulfate at the cathode. Liu et al. (2018) studied the electroactivated persulfate degradation of 50 mg/L tetracycline over platinum electrodes. After 240 min of treatment at 13.33 mA/cm² with the addition of 12.6 mM persulfate, the removal was > 80%, 43.8% and 19.8% for the combined process, electrooxidation only, and persulfate oxidation only,

respectively. Most recently, Matzek et al. (2018) studied the electrochemical decomposition of ciprofloxacin using BDD. The observed kinetic constant was 2.08, 1.39 and 0.24 × 10⁻⁴ M s⁻¹ when the electrolyte was persulfate, sulfate and nitrate, respectively.

The use of hybrid processes using UVA or solar radiation has started gaining ground in recent years (Sirés et al., 2014). Recently, Graça et al. (2017) demonstrated that UVA irradiation could partially activate persulfate for the production of sulfate radicals. According to Ioannidi et al. (2018) the combination of persulfate with UVA irradiation from light emitting diodes or simulated solar light can degrade endocrine disruptors like parabens in environmentally relevant concentrations.

This work studied the combined electrochemical oxidation on a BDD anode-sodium persulfate (EO/SPS) process for the degradation of AMP. Particular emphasis was given to the operating parameters in the presence of inorganic ions or organic matter and real water matrices. Finally, the effect of solar irradiation on the combined process was investigated, as well as the toxicity of the treated solution using *V. fischeri* as the indicator. To the best of our knowledge, the combination of the BDD/sodium persulfate system with solar light for the degradation of antibiotics is reported for the first time.

2. Materials and methods

2.1. Electrochemical experiments

Electrochemical experiments were conducted in a plexiglas, single-chamber reactor with a working volume of 200 mL. The reactor was open to the atmosphere, while stirring was provided by a magnetic stirrer. Unless otherwise stated, a BDD electrode with an active area of 8 cm² (Adamant Technologies SA, Switzerland; B/C 1000 ppm) was employed as the anode, while a platinum electrode (8 cm²) served as the cathode. Both electrodes were connected to a PeakTech 1885 power supply. In some preliminary experiments, an 8 cm² platinum anode was also tested. All the experiments were conducted under galvanostatic conditions (i.e. constant current) and ambient temperature; although the latter was left uncontrolled during the experiment, it never exceeded 33 °C. The reaction mixture always contained 0.1 M Na₂SO₄ serving as the electrolyte and, in most cases, Na₂S₂O₈ (typically 250 mg/L) serving as the source of sulfate radicals. In some experiments, the reactor was irradiated with the help of a solar simulator (Newport LCS-100 equipped with a 100 W xenon, ozone-free lamp). Irradiation was provided from the top at an incident intensity of 7.3 × 10⁻⁷ E/(L.s); more details can be found elsewhere (Kotzamanidi et al., 2018; Ioannidi et al., 2018).

2.2. Chemicals

Ampicillin (purity ≥ 98%, CAS number 69-53-4), humic acid (HA: technical grade) and sodium chloride (CAS number 7647-14-5) were purchased from Sigma Aldrich. Sodium persulfate (SPS: CAS number 7775-27-1) and sodium sulfate (CAS number 7757-82-6) were purchased from Scharlau. Most of the experiments were conducted in ultrapure water (UPW) taken from a Barnstead water purification system. Some experiments were conducted with bottled water and secondary treated municipal wastewater effluent. The physicochemical characteristics of different water matrices used in this work are summarized in Table 1.

2.3. Analytical methods

2.3.1. High-performance liquid chromatography and total organic carbon

High-performance liquid chromatography (HPLC: Alliance 2695, Waters) was used in order to monitor the residual concentration of AMP using the method developed by do Nascimento et al. (2009). The chromatographic column used was a Phenomenex Kinetex C18 100A column (2.6 μm, 2.1 mm × 150 mm) connected to a 0.5 μm inline filter

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