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Electrodegradation of tetracycline on BDD anode

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HIGHLIGHTS

- High degree of mineralization can be achieved in the electrooxidation of tetracycline at a BDD anode.
- During the anodic oxidation of tetracycline organic nitrogen is mainly converted to ammonium, nitrate and nitrite.
- Average mass transfer coefficients increase with recirculation flow rate.

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ABSTRACT

The anodic oxidation of tetracycline was performed in an up-flow reactor, operating in batch mode with recirculation, using as anode a boron-doped diamond electrode. The influence on the degradation rate of tetracycline initial concentration and recirculation flow rate were investigated. Assays were performed at constant current density, 300 A m^{-2}, using as electrolyte a sodium sulfate aqueous solution, 5 g L^{-1}. At the experimental conditions tested, HPLC results have shown an almost complete removal of tetracycline after 2 h assay. The removals of the organic load, measured as chemical oxygen demand (COD) and total organic carbon (TOC), increased with tetracycline initial concentration and recirculation flow rate. At the highest recirculation flow rate tested, 100 L h^{-1}, with an initial tetracycline concentration of 150 mg L^{-1}, after 4 h assay, the removals of COD, TOC and absorbance (measured at 276.5 and 360.0 nm) were 93%, 87%, 99% and 100%, respectively. Regarding the total Kjeldahl nitrogen elimination, it takes place mainly via transformation of organic nitrogen into ammonium, nitrate and nitrite. The total nitrogen removal increased with initial tetracycline concentration and showed also a tendency to increase with recirculation flow rate.

1. Introduction

Tetracyclines are a group of natural and semisynthetic products that are bacteriostatic agents with activity against a wide variety of organisms. In the middle of the twenty century, they were first developed from microorganisms present in soil samples (Streptomyces) collected worldwide, due to the need for more potent antibiotics [1].

Tetracyclines are characterized by a fused four-ring structure, with a carboxylamide functional group and several other ionizable functional groups, tricarbonyl methane, phenolic diketone, and dimethyl ammonium, as side chains, which are responsible for their pK_a and for the net anionic, cationic or zwitterionic charge [2].

Despite tetracyclines have been banned by the European Community for their use as animal growth promoters in the early 1970s and, more recently, added by US Food and Drugs Administration (FDA) to its Adverse Event Reporting System, this group of antibiotics was considered at the beginning of this century the second most common antimicrobial, with applications in human therapy, veterinary medicine and aquaculture [3–5].

Although tetracyclines are known to be highly adsorbed to clay materials, soils, and sediments, a reconnaissance study made by the United States Geological Survey (USGS) reported detectable levels of tetracyclines in several rivers and streams from many parts of the US [6], proving that their sorption in solids is not irreversible, thus favoring their mobility in the environment. Even at low levels, the presence of antibiotics like tetracycline and their by-products in the environment can spread the antibiotic resistance among microorganisms, which is an emerging issue in public health [7]. Tetracyclines can also generate the metabolite 4-epi-tetracycline, which is known to occur quite frequently in significant amounts during storage of manure and sludge [3].

Tetracycline (Fig. 1) is one of the most important tetracyclines and was synthesized for the first time in 1952. When administrated, only a small amount is metabolized or absorbed by the body, being most of the unchanged form of the drug eliminated in faeces and urine. Residues of tetracycline were already detected

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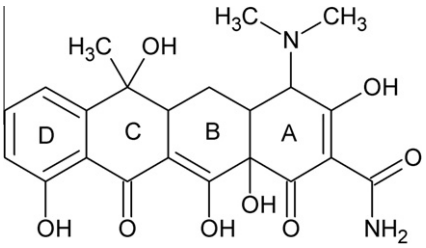

Fig. 1. Chemical structure of tetracycline.

in surface waters that received discharges from municipal wastewater treatment plants and agricultural drained [6,8]. For these reasons, the elimination of antibiotics from the terrestrial and aqueous resources is an emergent goal and, in the last years, several studies on the degradation of tetracycline, using different technologies, were conducted.

The elimination of tetracycline from aqueous solution was studied using activated sludge processes and the obtained results strongly suggest that tetracycline was mainly removed due to a sorption mechanism, being the biodegradation process of minor relevance [9]. Thus, due to tetracyclines' biorefractory nature there are a few studies reported in the literature using advanced oxidation processes, as an alternative to conventional biological treatment, for the degradation of these compounds. Liu and collaborators [10] studied the application of TiO_2 nanopore arrays electrode in the degradation of tetracycline, using three different processes: electrochemical, photochemical and photoelectrochemical. The best results were obtained for the photoelectrochemical combined process. TiO_2 and ZnO aqueous suspensions were also used in the photocatalytic oxidation of tetracycline, under simulated solar light [11]. The activity of both catalysts indicates that ZnO presents a slightly higher oxidation rate than TiO_2, under optimized conditions.

Tetracycline photocatalysis was performed using C–N–S tridoped TiO_2 material and it was found that photocatalytic degradation was more efficient under slightly alkaline pH condition and solar irradiation [12].

The degradation of tetracycline was also attained by electron pulse radiolysis [13]. The authors concluded that both oxidation and reduction contribute to the degradation. However, the variability in reaction efficiencies suggests that different degradation mechanisms can occur.

Anodic oxidation is another option for the degradation of tetracyclines [14–17]. Using Pt plates as anode, and applying low current densities, the electrochemical oxidation of tetracycline was performed and it was concluded that this treatment promote the cleavage of some aromatic rings of the tetracycline molecule, which may decrease its biological activity [14]. Similar results were obtained when a Ti/RuO_2 anode was used in the electrodegradation of an oxytetracycline hydrochloride, where a loss in anti-bacterial activity was achieved [15]. In this study, the electrochemical reactions followed pseudo-first order kinetics. This type of kinetics was again observed in the anodic oxidation of tetracycline at a Ti/RuO_2–IrO_2 anode [16], where the degradation rate increased with current density and decreased with the increasing in the initial antibiotic concentration. However, it was not significantly affected by solution pH. The influence of hydroxyl radicals' scavenger was also studied and the results indicated that anodic oxidation of tetracycline with this anode occurs mainly by direct electron transfer.

Recently, the results obtained by Miyata and co-workers [17] indicated that anodic oxidation using a Ti/IrO_2 and a Ti/PbO_2 anode was effective for the degradation of tetracyclines. These authors also evaluated the applicability of the electrooxidation using a Ti/IrO_2 anode on the treatment of a livestock wastewater spiked with oxytetracycline. The results were similar to the ones obtained in the oxytetracycline aqueous solutions, suggesting that this method may be suitable for the degradation of this compound in livestock wastewater.

However, in the majority of the studies previously referred no significant levels of mineralization were achieved with the active anodes used. In the last decade, boron-doped diamond (BDD) electrode, a non-active anode, is being widely used. This electrode material presents many advantages, namely, good chemical and electrochemical stability, extended lifetime and a wide potential window for water discharge, and it is known by its ability to promote the complete mineralization of a wide range of organic pollutants [18–20], due to the hydroxyl radicals formed from water discharged on the electrode's surface (Eq. (1)) that are the main species responsible for the oxidation of the pollutants.

$$BDD + H_2O \rightarrow BDD(^{\cdot}OH) + H^+ + e^- \quad (1)$$

In fact, these hydroxyl radicals being the most oxidizing species after fluorine (E° = 2.8 V vs. SHE) are capable of promoting unselectively the mineralization of different classes of organic compounds. However, it is well known that other strong oxidizing species can also be electrogenerated in the BDD surface, such as the peroxo-derivatives coming from the oxidation of the anion of the supporting electrolyte. For instance, the peroxodisulfate $\left(S_2O_8^{2-}\right)$ results from the sulfate oxidation [19,21].

Thus, in the present study, it is proposed the degradation of tetracycline using BDD anode. The influence of the initial concentration and the hydrodynamics inside the electrochemical cell on the rate of electrodegradation and mineralization of tetracycline will also be assessed.

2. Materials and methods

Tetracycline used in this study was the alkali form, with the chemical formula $C_{22}H_{24}N_2O_8{\cdot}xH_2O$, purchased from Sigma Aldrich (purity 99%) and used without further purification.

The cyclic voltammetric measurements were performed in a potentiostat/galvanostat VoltaLab PGZ 301, in a one compartment cell, with a 3 mm^2 BDD electrode as working electrode, a platinum plate, with identical area, as counter electrode and a commercial Ag/AgCl (KCl sat) as reference electrode. Cyclic voltammetries were recorded with 5 g L^{-1} Na_2SO_4 aqueous solutions and tetracycline concentration of 200 mg L^{-1}, at a scan rate of 10 mV s^{-1}.

Tetracycline degradation experiments were conducted in batch mode, with recirculation, in an up-flow electrochemical cell, composed by a BDD anode (Diachem®) of 4 × 5 cm^2 geometric area, obtained from Adamant Technologies, and a stainless steel cathode, with identical area. The distance between electrodes was 1 cm and the volume of the cell was 20 cm^3. The recirculation of the solution was enabled by a pump, Concessus, little giant, 2md, that allowed the use of different flow rates: FR1 = 37 L h^{-1}; FR2 = 75 L h^{-1}; FR3 = 100 L h^{-1}. A GW, Lab DC, model GPS-3030D (0 – 30 V, 0 – 3 A), was used as power supply. The assays were conducted at room temperature (25 ± 2 °C), adding as support electrolyte anhydrous sodium sulfate (Merck, 99.5%), with a concentration of 5 g L^{-1}. The imposed current density was 300 A m^{-2} and a volume of solution of 200 mL was used. Two different initial concentrations of tetracycline were studied: 100 and 150 mg L^{-1}.

Degradation tests were monitored by the following determinations: total organic carbon (TOC) and total nitrogen (TN), measured in a Shimadzu TOC-V CPH analyser combined with a TNM-1 unit; chemical oxygen demand (COD), performed using closed reflux and titrimetric method [22]; total Kjeldahl (TKN) and ammonia nitrogen (N–NH_3), determined according to standard procedures [22], using a Kjeldatherm block-digestion-system and a Vapodest