Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: Effect of electrode materials

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ABSTRACT

This paper presents the removal of the antibiotic tetracycline (TeC) from water using electrochemical advanced oxidation processes (EAOPs); namely electrochemical oxidation (EO) and electro-Fenton (EF). The effect of different cathode materials (carbon-felt and stainless steel) on the direct/indirect electro-oxidation of tetracycline, and that of different anode materials (Ti/RuO_2–IrO_2, Pt and BDD) on both processes was systematically investigated for the first time. The EO process was found to be more efficient in using the carbon-felt cathode than the stainless steel cathode. The EO and the EF processes using BDD anode demonstrated superior oxidation/mineralization power. Almost total mineralization (TOC removal up to 98%) of $100\,mg\,L^{-1}$ TeC solutions was achieved after 6 h treatment either by EO and/or EF treatment with BDD anode. The oxidative degradation of TeC followed pseudo-first-order-reaction kinetics in using all tested electrodes and anode/cathode configurations. Apparent rate constants of different anode/cathode configurations increased in the following sequence: Ti/RuO_2–IrO_2/stainless steel < Ti/RuO_2–IrO_2/carbon-felt < BDD/carbon-felt (EO) < BDD/carbon-felt (EF). The electrical energy consumed per gram of TOC removal was calculated for different electrode configurations to assess the cost effectiveness of the EO and the EF processes to mineralize TeC in water.

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1. Introduction

In recent years, occurrence of pharmaceuticals in water is receiving increasing attention as emerging contaminants. The presence of pharmaceuticals in wastewater not only affects the water quality, but also causes long term potential adverse impacts on the ecosystems and the human health [1,2]. Among various pharmaceuticals, antibiotics are widely used in human and veterinary medicines to treat diseases and to promote growth [3]. Tetracycline (TeC) is one of the most commonly applied antibiotics and its production and usage rank second worldwide after antimicrobial sulfonamides [4–6]. Additionally, TeC merits attention because it has been extensively used to treat humans and account for more than 60% of total antibiotics used in animals for therapeutics [7]. TeC has been frequently detected in soil and water samples [8,9]. In soil samples, concentration of TeC ranged from 86 to 199 $\mu g\,kg^{-1}$ whereas detected concentrations of TeC residues in surface water were at 0.07–1.34 $\mu g\,L^{-1}$. TeC in water may cause the spread of antibiotic resistant bacteria and antibiotic resistant genes in aquatic environment and thus constitutes a public health concern [10]. It is thus imperative to remove TeC from water adequately.
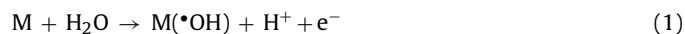
The physical removal methods such as adsorption, reverse osmosis or nanofiltration are able to separate TeC from water, but these methods only concentrate waste, without degradation, and induce another environmental problem [11]. Chemical oxidants like chlorine and chlorine dioxide have been applied to oxidize TeC [12], which form potential carcinogenic chlorinated byproducts. Ozonation, as advanced oxidation process (AOP), oxidizes TeC rapidly; however, incomplete mineralization was observed. Maximum removal of TOC was 40% after 2 h ozonation [4]. This weak mineralization degree was related to the relatively lower oxidation power of O_3 to mineralize reaction intermediates. Comparatively, electrochemical advanced oxidation processes (EAOPs) have shown much higher efficiency of mineralization and are the focus of the present study to mineralize TeC completely.

EOAPs have been widely investigated in recent years because of their low operating cost [13–17]. Electrochemical oxidation (EO) and electro-Fenton (EF) processes are two kinds of commonly used EAOPs based on in situ generation of highly oxidizing agent

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hydroxyl radicals ($^\bullet$OH) (E° = 2.72 V versus NHE). An EO process destroys the pollutant by the electro-generated $^\bullet$OH on a metallic (M) or metal oxide anode (reaction (1)) [18–20]. Heterogeneous $^\bullet$OH, formed at the anode surface, react efficiently with organics (reaction (2)) [21,22]. This process is highly potent in using a boron-doped diamond (BDD) anode, which has a high O_2 evolution overvoltage.

$$M + H_2O \rightarrow M(^\bullet OH) + H^+ + e^- \qquad (1)$$

$$M(^\bullet OH) + \text{organics} \rightarrow M + \text{oxidation products} \qquad (2)$$

In the EF process, homogeneous $^\bullet$OH are produced through the electrocatalytically generated Fenton's reagent ($H_2O_2 + Fe^{2+}$) in the bulk solution (reaction (3)) [14,23–25]. The regeneration of Fe^{2+} from Fe^{3+} takes place at the cathode (reaction (4)) [26–28], which subsequently regenerate $^\bullet$OH following the Fenton's reaction (reaction (3)).

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + {}^\bullet OH + H_2O \qquad (3)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$
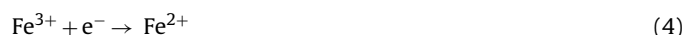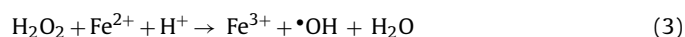
The oxidative degradation efficiency of the EF process depends on the nature of the cathode materials. For example, the carbon-felt (CF), which has large active surface and outstanding O_2 reduction performance, is an effective cathode material for electro-generating H_2O_2 in the reaction mixture (reaction (5)) [29].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (5)$$

This in situ production of H_2O_2 in combination with regeneration of Fe^{2+} allows continuous generation of $^\bullet$OH, based on reactions (3) and (4) [30].

Dimensionally stable anodes (DSA) [31,32], platinum (Pt) [33–36], and BDD [2,37,38,34,39] as anodes are commonly employed for treating organic pollutants [2,37,38,34,39]. Compared with DSA and Pt anodes, BDD is a relatively new anode material and has received greater attention since it has advantageous properties such as high oxygen overvoltage with extremely wide potential window, inert surface for adsorption, and strong oxidation power [40,41].

There are only handful studies reported on the application of AEOPs for the degradation of TeC [41–45]. To our knowledge, there has been no systematic study on the effect of different electrode materials on the electrochemical oxidation of TeC. Furthermore, no study on the degradation of TeC by the EF process has been reported previously.

Objectives of the present study are: (i) to investigate the effect of different cathode materials on the electrochemical oxidation of TeC, (ii) to learn the effect of different anode materials in both electrochemical oxidation and electro-Fenton processes on the oxidation of TeC, and (iii) to seek complete mineralization of TeC in water.

2. Materials and methods

2.1. Chemicals

Analytical grade (>98% purity) tetracycline hydrochloride, $C_{22}H_{24}N_2O_8 \cdot HCl$, was purchased from Fluka and was used in the electrolytic experiments without further purification. Sulfuric acid, anhydrous sodium sulfate, and ferrous sulfate heptahydrated of analytical grades, were purchased from Fluka and Acros Organics. All solutions were prepared with ultra-pure water obtained from a Millipore Mill-Q system with resistivity >18 MΩ cm at a room temperature.

2.2. Analytical procedures

The analysis of TeC was carried out by injecting 20 μL sample to the reversed-phase high performance liquid chromatography (HPLC) set-up, which had a Merck Lachrom liquid chromatograph, equipped with a L-7100 pump and was fitted with a Purospher RP-18, 5 μm, 25 cm × 4.6 mm (i.d.) column at 40 °C. Detection was done using a L-7455 photodiode array detector and a selected wavelength was 280 nm. The concentration of TeC was determined periodically using an isocratic solvent mixture of water/methanol/acetic acid 24.5:74.5:1 (v/v/v) as a mobile phase at a flow rate of 0.8 mL min^{-1}.

The electrolyses were performed with a Hameg HM8040 triple power supply at a constant current. This instrument displayed the cell voltage along the treatments as well. The solution pH was measured by using a CyberScan pH 1500 pH-meter (Eutech Instruments). The mineralization of treated solutions was assessed from the abatement of their dissolved organic carbon, which can be considered as the total organic carbon (TOC) in the case of highly water-soluble organic compounds such as TeC. A Shimadzu VCSH TOC analyzer was used to determine TOC. Samples withdrawn from the treated solution at different electrolysis times were microfiltered onto a hydrophilic membrane (Millex-GV Millipore, pore size 0.22 μm) before subjected to analysis. Reproducible TOC values, within ±1% accuracy, were found using the non-purgeable organic carbon method.

2.3. Electrolytic systems for the degradation of TeC

For all the EAOPs, the electrolyses were performed in an open, undivided and cylindrical electrochemical cell of 6 cm diameter and 250 mL capacity in which the aqueous solutions of TeC were placed. Three electrodes, all with 24 cm^2 (4 cm × 6 cm) area were used as anode: commercial pure Pt, boron-doped diamond (BDD, thin-film deposited on a niobium substrate (CONDIAS, Germany), and commercial DSA (mixed metal oxide T_i/RuO_2–IrO_2) from Baoji Xinyu GuangJiDian Limited Liability Company, China). A stainless steel plate of 24 cm^2 (4 cm × 6 cm) area and a tri-dimensional, large surface area carbon-felt (14 cm × 5 cm × 0.5 cm in width, Carbone-Lorraine, France) electrodes were used as cathode.

In EF experiments, the anode was centered in the electrochemical cell and was surrounded by the cathode (case of carbon-felt), which covered with the inner wall of the cell. H_2O_2 was produced in situ from the reduction of dissolved O_2 in the solution. The concentration of O_2 in the solution was maintained by continuously bubbling compressed air through a frit at about 1 L min^{-1}. A period of 10 min before electrolysis was sufficient to reach a stationary O_2 level. Initial concentration of 0.1 mM Fe^{2+} as a catalyst in the electrolysis experiments was obtained by adding solid $FeSO_4 \cdot 7H_2O$ into the solution. The use of 0.1 mM Fe^{2+} is recommended as the catalyst optimum amount in the EF process with a minimum contribution of parasitic reactions [14,15]. A pH of 3.0 was considered as the optimum pH for the EF process.

The EO experiments were conducted either at a natural pH 4.3 of TeC solution or at pH 3.0, adjusted by adding H_2SO_4. In all cases, 220 mL synthetic aqueous solutions of 100 mg L^{-1} TeC containing 0.05 M Na_2SO_4 as a supporting electrolyte were subjected to electrolysis at room temperature (23 ± 2 °C). A constant current of 200 mA was applied for kinetics studies while 500 mA current was applied for mineralization experiments. Solutions were vigorously stirred by a magnetic PTFE stirrer during the treatment to enhance the mass transport toward electrodes.