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Combined process for removal of tetracycline antibiotic – Coupling pre-treatment with a nickel-modified graphite felt electrode and a biological treatment

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ABSTRACT

Biodegradability improvement of tetracycline-containing solutions after an electrochemical pre-treatment was examined. Cyclic voltammetry with a nickel electrode revealed a significant electrochemical activity of tetracycline, in both oxidation and reduction. Electrochemical treatment was therefore performed in a home-made flow cell using a nickel-modified graphite felt electrode as the working electrode. Optimal conditions, namely 100 mg l^{-1} initial tetracycline, above 0.45 V potential, and between 1 and 6 ml min^{-1} flow rate, led to a more than 99% conversion yield of tetracycline in oxidation in alkaline conditions, after only a single pass through the percolation cell. However, total organic carbon (TOC) analyses revealed a low mineralization level, i.e., always below 31%, underscoring the importance of a combined electrochemical and biological treatment. This was confirmed by the favorable trends of the COD/TOC ratio, decreasing from 2.7 to 1.9, and the average oxidation state, increasing from 0.044 to 1.15, before and after oxidation pretreatment at 0.7 V and 3 ml min^{-1} flow rate. Electrolyzed solutions appeared biodegradable, since BOD_5/COD increased from 0 to 0.46 for untreated and pretreated TC at 0.7 V/SCE. Biological treatment showed only biosorption for non-pretreated tetracycline, while after 11.5 days of culture, the mineralization of solutions electrolyzed in oxidation was 54%, leading to a 69% overall TOC decrease during the combined process.

Introduction

Tetracycline (TC) represents an important group of polyketide antibiotics. It is commonly used in human and veterinary medicine, in aquaculture, and as an additive to animal feeds, and it can also inhibit fungal growth in fruit trees. It is active against a wide range of Gram-positive and Gram-negative bacteria (Chopra and Roberts, 2001). It is widely used in European countries; in Germany, for instance, in 2007, over 17,000 kg of tetracycline were consumed by livestock as antimicrobial substances applied to pigs (Merle et al., 2012).

Only small portions of antibiotics administered to treated species are metabolized or absorbed in the body; most of the unchanged form of the drug is eliminated in faeces and urine (Arikan et al., 2006). Between 30 and 90% is excreted unchanged into the waste system (Hirsch et al., 1999). The presence of low levels of antibiotics and their transformation products in the environment could have adverse effects, such as bacterial resistance and disruption of key cycles critical to aquatic ecology or crop and animal production (Kummerer, 2004; Costanzo et al., 2005; Crane et al., 2006).

Due to their refractory characteristics as well as their antibacterial effects, biological methods are not efficient for antibiotic removal (Reyes et al., 2006). Indeed, biological removal using activated sludge showed only adsorption onto the solid phase without degradation (Prado et al., 2009).

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Chemical oxidation could efficiently destroy antibiotics and overcome most of the limitations encountered during other conventional processes; especially the advanced oxidation processes (AOP), which constitute the most important and widely documented group (Chiron et al., 2000; Oppenländer, 2003; Badawy et al., 2006). The AOP can be divided into three categories: photochemical processes, ozonation combined with UV irradiation and/or hydrogen peroxide (H_2O_2), and in-situ generation of free radicals •OH by other technologies. They are efficient but can be costly (Mohajerani et al., 2009).

Electrochemical processes also showed a remarkable ability to remove recalcitrant organic contaminants such as antibiotics (Walsh and Mills, 1993). An electrochemical reaction is based on a heterogeneous electronic transfer, and the mean reactants are electrons. Weichgrebe et al. (2004) studied the biocide effect during electrochemical oxidation of tetracycline in water at an initial concentration of 1 g l^{-1}. Zhang et al. (2009) investigated the effect of various operating conditions on the electro-oxidation of tetracycline with a Ti/RuO_2 anode; similar studies used gold diamond and platinum anodes (Weichgrebe et al., 2004; Kraft, 2007; Masawat and Slater, 2007; Zhang et al., 2009). Electro-oxidation has appeared efficient for tetracycline degradation but has been carried out mostly on expensive anode materials.

For electroactive target compounds, oxidation or reduction can be carried out for their removal. Direct electrochemical processes are relevant in the case of a specific pollutant owing to the targeted selectivity, and therefore would be appropriate to treat low volumes of highly concentrated pollutants.

Reducing the antibacterial activity of a tetracycline solution does not necessarily require its complete mineralization. All that is needed is to break down the initial tetracycline molecules (Vedenyapina et al., 2008). Effluent mineralization can subsequently be completed during biological treatment; the potential advantages of the strategy of combining physicochemical and biological processes to treat contaminants in wastewater have previously been described (Scott and Ollis, 1995, 1997; Pulgarin et al., 1999; Farré et al., 2007).

Biodegradability improvement of solutions of 2,4-dichlorophenoxyacetic acid after a direct electrochemical oxidation in a homemade flow-cell involving a bare graphite felt electrode has been shown (Fontmorin et al., 2012), and complete mineralization (97%) of a pesticide, phosmet, was obtained by coupling an electrochemical reduction by means of the same electrolysis system and an activated sludge culture (Alonso-Salles et al., 2010).

Regarding the target compound, tetracycline, a significant electrochemical activity was shown by cyclic voltammetry with a vitreous carbon electrode, and hence electrochemical treatment was performed in a home-made flow cell with a bare graphite felt electrode. Biodegradability, based on the BOD_5 (five-day biochemical oxygen demand) to COD (chemical oxygen demand) ratio, increased with the oxidation potential until reaching 0.39, namely a biodegradable solution for 1.6 V/SCE, while no biodegradability improvement was observed after electrolysis in reduction, even though the resulting solution was not toxic for activated sludge. In addition, TOC analyses of the electrolyzed solution revealed that the level of mineralization remained low indicating the potential of a combined electrochemical and biological treatment (Belkheiri et al., 2011).

In order to improve the efficiency of the electrolysis pretreatment, especially through attempts to reduce the working potential, modification of the graphite felt electrode by nickel electrodeposition has been considered (Chamoulaud et al., 2001). Indeed, nickel oxidation on the electrode leads to the formation of a nickel oxyhydroxide, NiOOH, known to catalyze the oxidation of some organic molecules (Fleischmann et al., 1971; Vértes and Horányi, 1974). The purpose of this study was therefore to examine the electrochemical behavior of tetracycline with an electrode modified by nickel electrodeposition and to determine if this improved the biodegradability of the tetracycline.

Materials and methods

Chemicals and reagents

Tetracycline hydrochloride (<96% HPLC-grade) is displayed in Fig. 1 and was obtained from Sigma Aldrich (Saint-Quentin Fallavier, France). Acetonitrile (ACN) was HPLC grade from Fisher Scientific (Illkirch, France), and formic acid (LC-MS grade, 98%) was purchased from J.T. Baker (Deventer, Holland). Standards were prepared with ultra-pure water (Purelab Options- Q7/15, Elga, 18.2 MΩ cm^{-1}). All other reagents were of analytical grade.

Materials for the electrochemical pre-treatment

Electrochemical pre-treatment, in a continuous system, was performed in a home-made flow cell (Fig. 2a). The working electrode was obtained by nickel electrodeposition on the surface of the carbon felt. The electrode was made in the laboratory (by Floner and co-workers) at room temperature in an electrochemical cell formed by an open rectangular tank containing 1 L of the electrolyte solution (sodium sulfate and boric acid, 0.25 M each). The mechanism of nickel electrodeposition in acidic medium can be summarized in its simplest form by the reaction: $Ni^{2+}_{aq} + 2e^- \rightarrow Ni$ (Floner and Moinet, 2004; Floner and Geneste, 2007). The electrode was uniformly covered by nickel (around 1 µm thickness). There were no obvious defects and cracks of the coating layer found on the electrode surface and it had a smooth surface, as shown in the SEM micrograph obtained with a JEOL 6301F (9 kV) microscope (Fig. 2b). Its specific area, measured by the BET method, was 1 m^2 g^{-1} and its density was about 0.37 g cm^{-3}, with a specific surface area related to the volume of 3700 cm^2 cm^{-3}. The working electrode was 0.3 cm high and 4 cm in diameter, leading to a volume of 3.768 cm^3, with a total surface of 1.39 m^2. The electrode was separated from the two interconnected stainless steel counter-electrode compartments by cationic exchange membranes (Ionac 3470 – Lanxess SAS, Courbevoie, France). A good homogeneity of the potential distribution in the three-dimensional working electrode was obtained when the felt was located between two counter-electrodes (Moinet, 1994). The reference electrode (SCE) was positioned in the middle of the felt. The potential control was performed using an e-daq potentiostat linked to an e-corder 401 converter (AD Instruments Pty Ltd., Castle Hill, Australia). The tetracycline concentration (TC) was 100 mg l^{-1}. The supporting

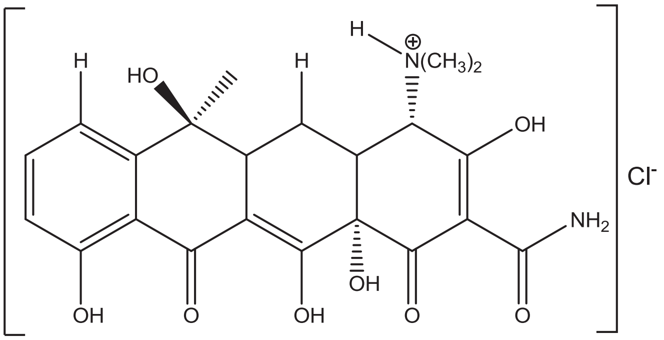

Fig. 1. Chemical structure of hydrochlorated tetracycline.