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Electrochemical degradation of chlortetracycline using N-doped Ti/TiO_2 photoanode under sunlight irradiations

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ABSTRACT

The appearance and the persistence of pharmaceutical products in the aquatic environment urgently call for the development of an innovative and practical water treatment technology. This study deals with the development of nanostructured nitrogen-doped TiO_2 photoanodes and their subsequent use for chlortetracycline (CTC) photoelectrocatalytic oxidation under visible light. The N-doped TiO_2 photoanodes with different nitrogen contents were prepared by means of a radiofrequency magnetron sputtering (RF-MS) process, with the objective to tune shift their optical absorption from the UV towards the visible. The N-doped TiO_2 consist of nanostructured anatase phase with average TiO_2 nanocrystallite size of 29 nm. The nitrogen doping is clearly shown to produce the desired red shift of the absorption onset of the TiO_2 coatings (from ~380 nm to ~550 nm). Likewise, the N-doped TiO_2 are found to be highly photo-electroactive not only under the UV light but most interestingly under the visible light as well. Using the optimal N-doped photoanodes, 99.6% of CTC (100 μg/L) was successfully degraded after 180 min of treatment time with a current intensity of 0.6 A. Under these conditions, a relatively high mineralization of CTC (92.5% ± 0.26% of TOC removal and 90.3% ± 1.1% of TN removal) was achieved.

1. Introduction

The occurrence and the fate of endocrine disrupting compounds (EDC) in aqueous environment have received considerable interest over the past several years due to their adverse effects on aquatic organisms (Daskalaki et al., 2013). Antibiotics are extensively used in human and veterinary medicine for preventing or treating diseases, increasing feed

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efficiency and improving growth rate for livestock (Sarmah et al., 2006; Kummerer, 2009; Homem and Santos, 2011; Gao et al., 2012). After consumption by humans and animals, antibiotics are thrown out via urine or feces in both unchanged and/or metabolized forms. These contaminants are soluble in water and are detected in soils, sediments, surface water, drinking water, and wastewater at concentrations ranging from ng/L to μg/L (Gao et al., 2012; Chenxi et al., 2008).

Chlortetracycline hydrochloride (CTC) belongs to the tetracycline (TCs) antibiotic groups. TCs are bacteriostatic agents used in both human and animal medicine for treating infections caused by strains of Gram negative and Gram positive bacilli streptococci, Rickettsia bacteria and spirochetes, among others. Besides, TCs are extensively administered as an additive in avian, cattle and pig feed to promote growth. Due to its widespread usage, the introduction of these residual compounds into environment through different sources will lead to serious environmental problems including ecological risk and human health damage. Few previous studies have examined the CTC toxicity to a variety of species. Wang et al. (2011) showed that CTC has negative effect on the growth of freshwater algae, whereas Guo and Chen (2012) have reported that CTC had significantly toxic effects on freshwater phytoplankton species. Accordingly, the removal of CTC from aquatic matrix is become as important for environmental protection.

Generally, the wastewater treatment plants (WWTPs) using conventional activated sludge treatment process are not designed to effectively remove this micropollutant. For instance, the removal efficiency of TCs varied significantly from 12% (Spongberg and Witter, 2008) to 80% (Karthikeyan and Meyer, 2006). Physicochemical methods such as adsorption using activated carbon have been applied by Choi et al. (2008) to remove more than 68% of TCs (tetracycline, doxycycline-hyclate, and chlortetracycline-HCl). The main disadvantage of such methods is that they do not destroy the pollutants but transfer the pollutant from one phase to another (Tahir and Rauf, 2006; Ozcan et al., 2004). Likewise, chemical oxidation processes using UV/H_2O_2 and O_3 have been successfully applied to degrade CTC (Lopez-Penalver et al., 2010; Kim et al., 2012). However, the high chemical consumption, the complexity of these methods and the relatively high treatment cost represent the major drawbacks that limit their implementation at large scale (Daghrir et al., 2012a,b; Martinez-Huitle and Ferro, 2006).

Photoelectrocatalytic oxidation (PECO) processes combining both photocatalytic and electrolytic processes have been evolved as an efficient technique for the removal of organic contaminants and pathogens in aqueous matrices (Daghrir et al., 2012a,b; Wang et al., 2010; Frontistis et al., 2011; Hou et al., 2012; Daghrir et al., 2013). Owing to the external potential applied, the PECO process is able to retard the recombination of the electron/hole pairs (e^-_{CB}/h^+_{VB}) photogenerated on the surface of the catalyst and consequently to ensure higher efficiency in the degradation of pollutants (Frontistis et al., 2011; Daghrir et al., 2012a,b; Liu et al., 2009).

Among the various semiconductors, titanium dioxide (TiO_2) is the prime photocatalytic candidate owing to its promising physical and chemical properties such as: high oxidation efficiency, non-toxicity, low cost, high photostability, chemical inertness and environmentally friendly nature (Ouyang et al., 2012; Valentin et al., 2007; Peng et al., 2012; Kuo et al., 2010). However, TiO_2 can only be activated under UV irradiation using a wavelength lower than 387 nm, this is due to its large optical band gap (~3.2 eV). Thus, only a small fraction of solar light (less than 5% of solar energy is emitted as UV irradiation) is actually photoconverted by pure TiO_2 (Ren et al., 2007). This drawback limits the use of TiO_2 at large scale application. For the sake of efficient utilization of sunlight, great deals of efforts have been made to extend the absorption of TiO_2 into the visible light region (Wu et al., 2010; Yap et al., 2010; Cheng et al., 2013). Impurity doping of TiO_2 (either cations or anions) is one of the typical approaches that has been applied by several research works to extend the spectral response to visible light region (Valentin et al., 2007; Wang and Lewis, 2005; Chen et al., 2007; Park et al., 2006). Doping pure TiO_2 with anions such as nitrogen has been shown to create an effective red shift in the absorption spectra of the TiO_2 well into the visible spectrum (Asahi et al., 2001; Ananapattarachai et al., 2009; Kang et al., 2008; Choi et al., 2007). The usage of a higher portion of the solar energy spectrum will promote exciton generation to be used in photo-electro-catalytic reactions (Daghrir et al., 2013).

The aim of the present work is to evaluate the potential of a PECO process using N-doped TiO_2 photoanodes deposited by means of a magnetron sputtering process for the treatment of waters contaminated by CTC under solar irradiation (1.5 AM). Thus, after optimizing the nanostructure and the optoelectronic properties (namely bandgap narrowing) of N-doped TiO_2 photoanodes, the latter were successfully used to investigate their degradation efficiency and mineralization rate for CTC under sun irradiation conditions. By carrying out systematic studies of the effect of different operating parameters (such as current intensity, treatment time and type of photoanode), we were able to identify the optimal processing conditions that lead not only to a full degradation of CTC (of up to 99,6%), but also to its mineralization (of up to 92.5%) into CO_2 and H_2O. Possible CTC degradation pathways under visible light irradiation are discussed.

2. Material and methods

2.1. *N-doped TiO_2 photoanodes preparation*

The photoanodes were prepared by depositing N-doped TiO_2 coatings onto Ti metallic grids by means of a radiofrequency magnetron sputtering (MS) process, which permits their *in-situ* doping through the incorporation of nitrogen (N) gas with the argon (Ar) during the sputtering process. The nitrogen content of the N-doped TiO_2 coatings was controlled by adjusting the $[N_2]/([Ar] + [N_2])$ gas flow ratio during the sputter-deposition process, while keeping the total pressure at 1.4 mTorr in the deposition chamber. The background chamber pressure prior to deposition between each deposit was kept at an ultra-high vacuum value as low as $\sim 2 \times 10^{-8}$ Torr. The deposition temperature of the N-doped coatings was maintained at 650 °C, while the RF power for the magnetron sputtering was set at 350 W. More experimental details on our MS system can be found elsewhere (Brassard