Photoelectrochemical Oxidation Activity Of CN-TiO_2 In The Removal Of Cefadroxil In Wastewater

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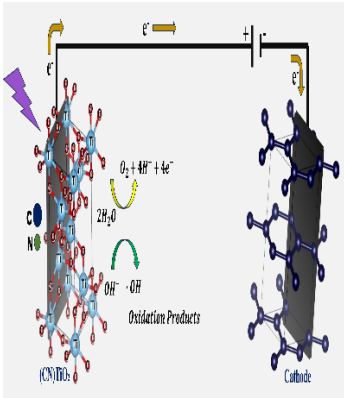

This study aims the development of photoelectrodes to be incorporated in a photoelectrocatalytic and ozonation (PECO) process for tertiary treatment of urban wastewaters, targeting the removal of contaminants of emerging concern (CEC). PECO tests were performed using an urban wastewater after secondary treatment fortified with Cefadroxil (CFX). Three (CN-TiO_2) electrodes were synthesized by anodizing at 50, 70, and 90 V. All abatement processes were followed by high-performance liquid chromatography. At neutral and alkaline conditions, CFX is eliminated to levels below the analytical detection limit after 90 min of treatment (TOC removals of 87 and 91 %, respectively), indicating that the coupling between the CN-TiO_2-70 PEC process is effective in eliminating the contaminant due to parallel routes forming •OH species.

Introduction

The pharmaceutical drugs are discarded after consumption, they enter the sewer system until arriving at the urban wastewater treatment plant (WWTP) as the original compound or metabolized. [1]. Likewise, those types of compounds can be associated with the proliferation of antibiotic resistant organisms, thus, generating toxic effects even at low concentrations due to the fact that their degradation is affected by multiple factors [3]. Among the various techniques used for hydrogen production by water splitting [2]. The photoelectrocatalysis (PECO) has emerged as a promising option and a potential clean and renewable route for energy production [3]. This method is bases on *in situ* generation of reactive oxygen species (•OH, O_2^-•, H_2O_2). The photo-generated electrons (e^-) could react with the electron acceptors, such as dissolved O_2 in aqueous solution generated the superoxide radical anion O_2^-•and holes (h^+) could oxide OH^- and H_2O_2 into •OH radicals [4]. To understand these issues, the degradation of cefadroxil (CFX) [4], fortified in a secondary urban wastewater collected from the San Juan Ixhuatepec WWTP, municipality of Tlalnepantla, State of Mexico is herein evaluated at different modified pH values. Three different photoelectrodes anodized at 50, 70, and 90 V in ethylene glycol, ethylenediamine and NH_4F were evaluated as PECO process; and subsequently characterized using different techniques.

Material and Methods

Three photoanodes of 4 cm^2 of area were prepared at different potential conditions (50, 70 and 90 volts) by anodization in order to find the highest current produced able to carry out the pollutant degradation study. The structural and textural characterization by XRD, (SEM) and elemental analysis (EDS). Tauc plots (UV-Vis Diffuse Reflectance) were collected for all the photoelectrodes employing a UV–Vis spectrophotometer. The electrochemical characterization techniques, including electrochemical impedance spectroscopy and chronoamperometry, were applied for the three synthesized CN-TiO_2 electrodes using a three-electrode electrochemical cell (Ag/AgCl as reference and a graphite cathode as counter electrode in an electrolytic solution of 0.05 mol L^{-1} Na_2SO_4). The electrochemical techniques were applied under dark and light conditions, applying 1V of potential. The wastewater was enriched with 20 mg L^{-1} of CFX, and the pH was adjusted at 3.2, 7.2 and 9.0. CFX degradation tests using real wastewater samples at different pH values were performed using a three-electrode reactor applying 1.2 V, considering the most active CN-TiO_2 photoanode selected from its characterization. As reference electrode and

cathode, an Ag/AgCl electrode saturated with 3 mol L^{-1} NaCl and a carbon paper electrode were used. All tests were performed employing a 150 W Xe lamp simulating the solar spectrum. A 18 W O_3 generator was employed to produce ozone. The ozone gas stream (Q_{O_3} = 0.8 g h^{-1}) was introduced.

Results and Discussion

Fig. 1 describes the Rietveld refinement curves resulting from the XRD studies for the CN-TiO_2 obtanied at different voltages. This refinement reveals the presence of metallic Ti ($P6_3/mmc$, COD 1532765), while the detection of anatase TiO_2 ($I4_1/amd$, COD 1010942) confirms the successful synthesis of the active phase. The presence of rutile ($P4_2/mnm$, COD 1532819) is caused by the heat treatment at 450 °C after anodization. Nevertheless, the rutile contents are lower compared to the anatase phase, and it does not exist in CN-TiO_2-90, presumably due to the high oxidation potential imposed during anodization.

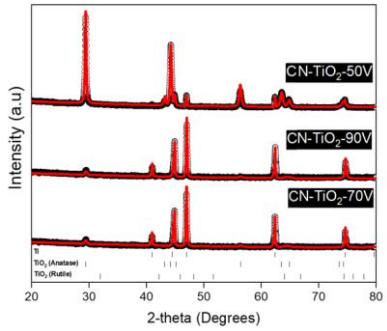

Figure 1. XRD studies for the CN-TiO_2 doped at different voltages.

Fig. 2 shows that CN-TiO_2 modified the main bandgap of anatase to generate a significant reduction of this value between ~2.8 and 2.9 eV.

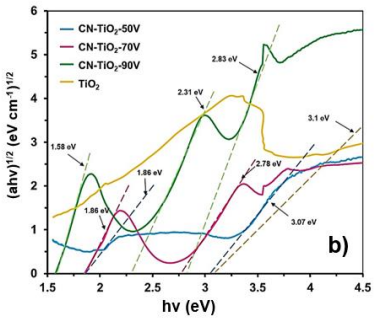

Figure 2. Tauc plot calculated for the CN-TiO_2 photoelectrodes

Fig. 3 shows the CFX concentration profile as a function of time for the PECO using the wastewater at different pH values. The intention was not to identify the exact chemical composition of each WWTP component but to analyze the effects of a real wastewater matrix upon the CFX degradation evaluated at different pH values. Under acidic conditions, the CFX is decomposed after 60 min, compared to neutral and basic conditions where removals were around 90 % during the first 30 min

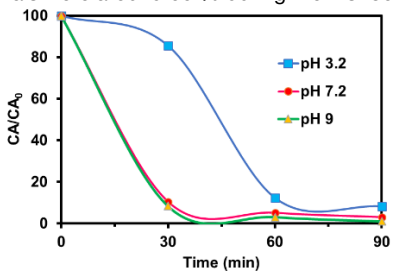

Figure 2. Percentage of normalized CFX concentration ([CFX]/[CFX_0]) as a function of time as detected by HPLC analysis

Conclusions

CN-TiO_2 presents exceptional properties as photoelectrode, but it needs to be subjected to UV irradiation for tractable applications. In the present study. The CN-TiO_2-70 showed interesting results in the degradation of CFX spiked in a real urban wastewater after secondary treatment, mainly working at neutral and basic pH conditions, associated with the direct oxidation by ozone and indirect oxidation with •OH generated in parallel routes.

Acknowledgments

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