Photoelectrocatalytic degradation of fungicide using titanium-tungsten oxide in a pilot-scale flow reactor

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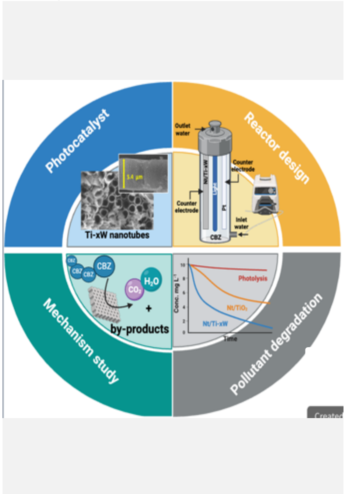

Pesticides are commercially distributed to consumers in plastic packages. After using the pesticide, these packages need to be decontaminated, before being entrained in a recycling process. In general, the decontamination process includes a triple-rinsing protocol with appropriate substances, with which the pesticides are solubilized. The effluents generated are rich in toxic compounds and need to be treated before being discarded into the environment. In the quest to find a suitable technique for removing these toxic compounds from washing water, the photoelectrocatalytic (PEC) oxidation method has attracted a lot of attention, as it is a compact and easy-to-handle system. This work describes the use of a Ti-O-W mixed oxide nanotube photoanode synthesized from Ti-xW (wt%) alloy (x =0.5, 2.5, 5.0 %) in the oxidation of carbendazim fungicide (CBZ) via PEC in a pilot-scale reactor. Oxide nanotubes grown on Ti-5.0W (% wt.) (NT/Ti-5W) exhibited a mixture of binary oxides (TiO_2 and WOx) in their composition which promoted an increase in absorbance under UV and visible light spectra, achieving the generation of a biodegradable effluent and removal of 90% of CBZ in a mere 1 h.

Introduction

CBZ is a fungicide highly employed by industries worldwide, being considered a hazardous substance. On the other hand, PEC is a promising process for pollutants removal from water. This process combined with semiconductors could reach remarkable results on CBZ mineralization. Titanium dioxide (TiO_2), an n-type semiconductor, has considerable attention because of its outstanding properties, such as higher photoactivity under UV radiation and chemical stability[1]. Tungsten oxides are one of the most widely investigated materials for many catalytic applications and exist in different phases: being more stable phases WO_2 and WO_3 [2]. Overall, tungsten trioxide is a promising semiconductor to combine with TiO_2 due to its small band gap (2.3–2.8 eV), which is advantageous for the absorption of visible light. In addition, the position of the valence band (2.7 eV) and conduction band (0.25 eV) may permit the charge transfer between the oxide bands and the inhabitation of charge carrier recombination[2].

These modified materials may contribute to the ongoing search for an efficient decrease of the band gap energy and to reduce the electron-hole recombination rate. Then, we prepared a Ti-O-W mixed oxide nanotubular electrode grown on a Ti-xW alloy (wt%) (x =0.5, 2.5, 5.0 %) by electrochemical anodization and verified its efficiency in the CBZ removal from real sample wastewater in a pilot-scale reactor.

Material and Methods

Synthesis and characterization of Ti-O-W mixed oxide nanotubular electrode

The nanotube layer was synthesized from Ti-xW (wt.%) alloys (x =0.5, 2.5, 5.0 %) prepared using an arc-voltaic furnace followed by sliced and lamination to obtain foils with dimensions compatible with the reactor. Ti and Ti-W foils were anodized in an organic electrolyte containing HF + 5.0% H_2O. After, the oxide layers were submitted in a heat treated at 550 °C in air atmosphere for crystallization. The morphology, structure, and photocatalytic properties of this electrode were investigated by Field Emission Gun – Scanning Electron Microscope (FEG-SEM), X-ray diffraction (XRD), Diffuse Reflectance Spectroscopy (DRS), and linear sweep voltammetry under irradiation (photocurrent curves).

Photoelectrocatalytic Oxidation experiments

In PEC experiments, the light source was a 125 W Hg vapor lamp emitting UV-Vis irradiation. The degradation of CBZ in a standard solution was monitored by High-performance liquid chromatography (HPLC) for experiments carried out on a bench-scale. Then, an electrochemical cell with two electrodes setup was loaded with 100 ml of effluent containing 10 mg CBZ + dimethylformamide (DMF), in aqueous solution pH 7.2, applying a potential of -0.4 V on the system. While the washing water containing CBZ, the degradation efficiency was carried out on a pilot-scale reactor. The compact flow reactor was constructed to treat 1 L of real effluent (CBZ concentration ~50 mg L^{-1}) and optimized in relation to the flow rate. In this study, the optimized conditions in a bench-scale configuration (electrode composition and potential) were used on the washing water containing CBZ carried out in the pilot-scale reactor. The degradation and CBZ inactivation were controlled by toxicity tests using *Aspergillus* species.

Results and Discussion

Characteristics of the Materials

SEM-FEG images exhibited the formation of nanotubular structures from the Ti pure and Ti-xW alloy After the anodization process in both geometric areas of the electrodes (1 cm^2 and 54 cm^2), as illustrated in Figure 1a. The nanotubular matrix showed an inner diameter of around ~40 nm and a thick layer of 4.0 and 6.0 µm, respectively. Figure 1b shows XRD analysis carried out after heat treatment, Titanium crystalline phases (anatase and rutile) for TiO_2 nanotubes are revealed. While nanotubes grown alloy, tungsten oxides (WO_3 and non- stoichiometric oxide) are also observed. The presence of tungsten oxide is derived from the intermetallic, an equilibrium phase that is present on the Ti-W substrate.

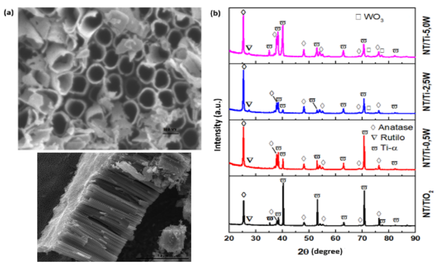

Figure 1. (a) Microscope images of Ti-W nanotubes array (b) XRD analyses.

In addition, the presence of tungsten may provide new properties to the electrode, such as an increase in absorbance in the length of the visible light and more photocatalytic activity compared to that of TiO_2. These characteristics can be attributed to oxygen sharing between Ti and W species due to the insertion of tungsten into the TiO_2 crystal lattice or the creation an intermediate level between valence and conduction band of TiO_2. These phenomena increase the efficient of photogenerated charges separation and decrease the recombination rate.

CBZ degradation by PEC using a pilot-scale reactor. After CBZ degradation experiments in an photoelectrochemical bench-cell, which showed that the Nt/Ti-5W applying a potential of -0.4V under UV-Vis irradiation was able to remove the CBZ from standard water after 2h by PEC, according to Figure 2a. After optimization of the parameters by bench-scale, we defined the range of the flow of pilot-scale reactor using the identical condition defined in bench-scale for CBZ removal in standard solution (PEC, Nt/Ti-5.0W and potential at -0.4V) (Figure 2b). The degradation of the CBZ in different was more efficient at a flow rate of 30 L h^{-1}, indicating that the photoelectrode was stable under in that continuous flow. The same electrode was used for more than 10 experiments and remains stable. The Nt/Ti-5.0W photoelectrode reached high performance, removing almost 90 % of CBZ after 60 min when the PEC was carried out in pilot-scale under a flow reactor under rate of 30 L h^{-1}.

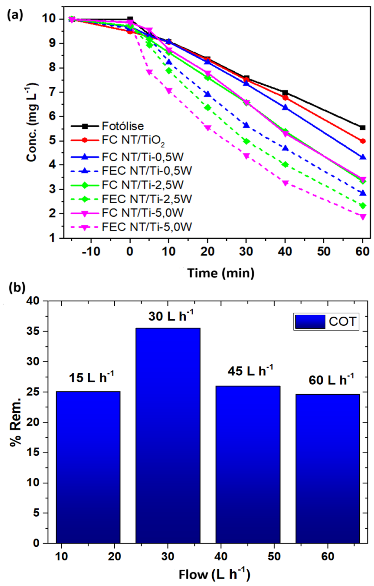

Figure 2. (a) Degradation and mineralization of carbendazim standard solution on bench-scale and (b) flow rate optimization on pilot-scale reactor.

Conclusions

At the first time, the Nt/Ti-5W (wt%) were prepared and applied for CBZ degradation by PEC, decaying almost totally from standard wastewater in less than 2h in bench-scale and 1 h in pilot -scale after mere 1h under a flow reactor under rate of 30 L h^{-1}. In addition, as the Nt/Ti-5.0W is very stable to be used in a continuous flow. Currently our experiments are focusing on the evaluation this photoanode in large pilot-scale reactor for CBZ commercial removal from washing water controlled by toxicological analyses using *Aspergillus* species control grown.

Acknowledgments

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