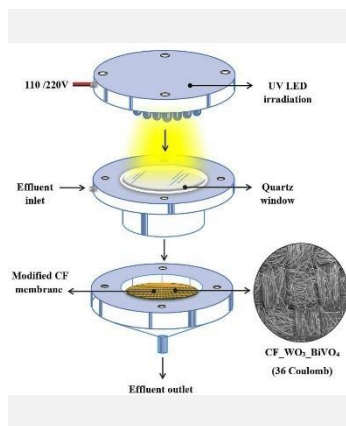


## Evaluation of Semiconductor-Modified Membranes Applied in the Simultaneous Filtration/Degradation of Emerging Contaminants.

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This study evaluated a carbon fiber (CF) modified by the chemical electrodeposition method through the anchoring of semiconductors  $\text{WO}_3$  and  $\text{BiVO}_4$  for use in a system capable of filtering and degrading the pharmaceuticals OTC and VEN simultaneously. X-ray diffraction patterns confirmed the formation of heterostructures from the representative peaks of the precursor oxides  $\text{WO}_3$  and  $\text{BiVO}_4$ . The developed heterostructure exhibited a monoclinic crystalline formation, with high absorption of irradiation in the range of 390 to 460 nm and a band gap ( $E_g$ ) of 2.6 eV. The study conditions: electrodeposition charge of 36 Coulombs and flow rate of  $170 \text{ mL min}^{-1}$  proved to be the most effective parameters, promoting adequate mass transfer and facilitating contact between the solid-liquid phases, enabling simultaneous degradation of (60%) VEN and (< DL) OTC, reducing issues such as membrane fouling, common in filtration processes.

### Introduction

Carbon fibers (CF) are interesting materials for applications in the filtration processes of contaminated water due to their remarkable properties. They exhibit high adsorption capacity, as well as both chemical and mechanical resistance, intumescent capability, and excellent chemical inertness<sup>[1]</sup>. However, they face challenges such as rapid fouling. An alternative to this problem involves the development of filter membranes with photocatalytic properties through surface modification with oxides such as  $\text{WO}_3$  and  $\text{BiVO}_4$ , as these semiconductors possess characteristics such as broad absorption in the UV-Vis region, narrow band gap (2.4 - 2.8 eV), and high thermal and chemical stability<sup>[2]</sup>. Their use as catalysts has shown promising results in degrading emerging contaminants. Therefore, this study aims to evaluate the use of photoactive membranes  $\text{CF\_WO}_3\text{-BiVO}_4$  to promote a continuous system that allows for the simultaneous retention and degradation of emerging contaminants oxytetracycline (OTC) and Venlafaxine (VEN).

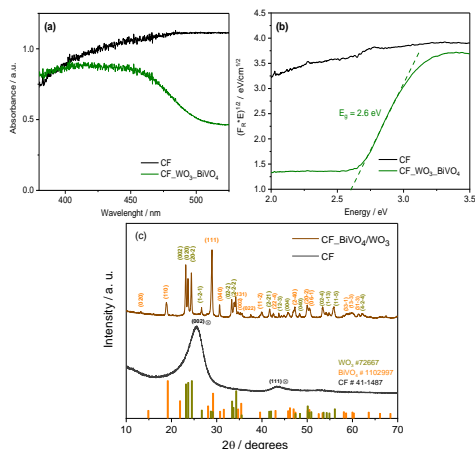
### Material and Methods

The CF modification was carried out by chemical electrodeposition. The  $\text{WO}_3$  electrodeposition was performed in an electrolytic solution (200 mL) containing  $5.0 \text{ mmol L}^{-1} \text{ Na}_2\text{WO}_4$ ,  $\text{H}_2\text{O}_2$  (0.075% v/v), and pH 1.4 ( $\text{HNO}_3$ ), applying a potential of  $-0.5 \text{ V}$  for 1 h<sup>[3]</sup>.  $\text{BiVO}_4$  particles were electrodeposited using a solution of vanadyl sulfate

( $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ ),  $\text{HNO}_3$  (65%), and bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), sodium acetate<sup>[4]</sup>. After modification of  $\text{CF\_WO}_3\text{-BiVO}_4$ , it was heat treated at  $450^\circ\text{C}/2\text{h}$  and evaluated using a filtration/photocatalysis system consisting of a continuous-flow photoreactor equipped with UV LED irradiation system (365 nm, 12W) and a peristaltic pump (13 Bar)<sup>[5]</sup>. The quantification of VEN-OTC was performed simultaneously by HPLC-DAD, and analytical conditions employed were  $2 \text{ mg L}^{-1}$  VEN-OTC, a flow rate of  $1 \text{ mL min}^{-1}$ , v.  $50 \mu\text{L}$ ,  $\lambda$ : 225 and 277 nm for VEN and OTC, with the mobile phase 0.1% formic acid/methanol in a gradient method (23-45% methanol over 7 min and 18 min of analyze).

### Results and Discussion

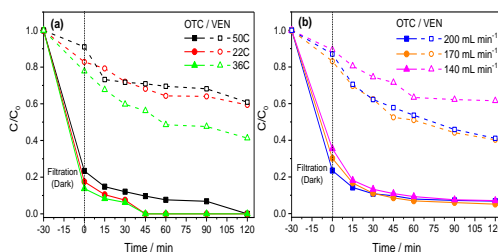
The  $\text{CF\_WO}_3\text{-BiVO}_4$  membrane exhibited high absorption in the 390 to 460 nm (Fig 1a). This broadened absorption of the heterostructures in the visible range is attributed to the presence of the semiconductor  $\text{BiVO}_4$ . Determination of the  $E_g$  showed the heterojunction of 2.6 eV, similar to  $\text{WO}_3$  (2.8 eV) and  $\text{BiVO}_4$  (2.4 eV) (Fig 1b). The X-ray diffraction patterns of the CF membrane showed peaks appearing at  $25.5^\circ$  (002) and  $43.8^\circ$  (111), characteristic of carbon-containing materials. The formation of the  $\text{WO}_3\text{-BiVO}_4$  heterostructure on the CF surface was confirmed by identifying the crystallographic planes of  $\text{WO}_3$  and  $\text{BiVO}_4$  oxides, both associated with a monoclinic crystal structure (Figure 1c).



**Fig 1.** (a) Absorption spectra. (b) Determination of bandgap energy ( $E_g$ ). (c) X-ray diffractograms.

During the dark filtration process, it was observed that OTC exhibited high removal rates ranging between 77-87%, whereas VEN showed lower removal rates ranging from 9-22%, with the 36C charge exerting the greatest influence on drug retention. In the filtration/photocatalysis process, OTC reached values  $< LD$  after 45 min using charges of 22C and 36C, respectively. In the case of VEN, maximum degradation percentages of 60% were achieved after 120 min (Fig. 2a) better membrane stability and greater degradation efficiency were observed in all cases when using electrodeposition charges of 36 C. When evaluating the flux variation between 140 and 200  $\text{mL min}^{-1}$  in the dark filtration process with a 36C electrodeposition charge, no significant differences were observed in OTC

removal (65-76%) after 30 min. For VEN, lower removal values between 11-17% were observed, indicating that the antidepressant does not readily adsorb onto the membrane (Fig. 2b). In the filtration/photocatalysis process for OTC, values close to 93% were achieved regardless of the flux used. However, VEN showed similar degradation percentages between 59% and 60% when applying 200 and 170  $\text{mL min}^{-1}$  flux, respectively, with the 140  $\text{mL min}^{-1}$  flux being the least effective, reaching a maximum degradation of 38%. The results demonstrated rapid retention and simultaneous degradation of OTC compared to VEN, which proved to be a compound of high recalcitrance with lower adsorption (Fig. 2b). The variation in flow rate showed that values both lower and higher than 170  $\text{mL min}^{-1}$  are not desirable, potentially resulting in respectively low retention/degradation or damage to the membrane surface.



**Fig 2.** Simultaneous degradation of OTC and VEN using  $\text{CF\_WO}_3\text{-BiVO}_4$  in filtration/photocatalysis process (a) heterostructure electrodeposition charge variation and flow 170  $\text{mL min}^{-1}$ . (b) flow variation. **Experimental conditions:**  $[\text{OTC/VEN}]_0$ : 2  $\text{mg L}^{-1}$ , flow: 140, 170 and 200  $\text{mL min}^{-1}$ , pH 7.0, volume 150 mL, electrodeposition charge: 22, 36 and 50 Coulombs.

## Conclusions

The determination of the operational parameters: electrodeposition charge of 36C and flow rate of 170  $\text{mL min}^{-1}$  demonstrated great potential for the application of the  $\text{CF\_WO}_3\text{-BiVO}_4$  membrane in filtration/photocatalysis systems, reducing issues such as membrane fouling and promoting rapid retention and simultaneous degradation of OTC-VEN in the treatment of contaminated water.

Different deposition charges (22, 36, and 50 Coulombs) showed variations in the curves  $\sim 12\%$  due to the increased amount of deposited material on the surface of CF, even when evaluated under the same flow.

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