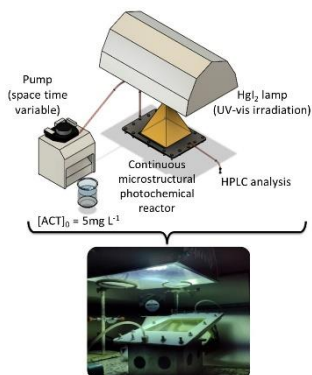


# Immobilized WO<sub>3</sub>-Ag-AgCl photocatalyst for the degradation of pharmaceutical contaminants in a continuous flat plate photochemical reactor

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WO<sub>3</sub> coupled with Ag/AgCl is a material with enhanced photocatalytic activity, standing out as a promising alternative photocatalyst for the removal of contaminants of emerging concern using the heterogeneous photocatalytic process. This work aimed to synthesize immobilized the WO<sub>3</sub>-Ag-AgCl photocatalyst by the ultrasonic spray-pyrolysis/photoreduction method for application in a continuous microstructured flat plate photochemical reactor. The material shows exceptional morphological uniformity and high crystallinity. Acetaminophen (ACT) was used as a model contaminant in the photodegradation experiments, conducted with a HgI<sub>2</sub> lamp, which covers the same wavelength range of the solar spectrum. The fabricated reactor showed behavior similar to a plug flow reactor, while maximum ACT removal of 93.1% was obtained under 120 min of space time. The results suggest the successful synthesis of a good alternative material for solar photocatalysis.

## Introduction

Conventional wastewater treatment processes are generally unable to effectively remove pollutants of emerging concern, which can cause significant harm to aquatic ecosystems and human health. In this context, advanced oxidation processes, such as heterogeneous photocatalysis, have shown promising results in addressing this issue. Among the various photocatalysts explored, WO<sub>3</sub> is a semiconductor with a band gap of 2.5-2.8 eV, which allows it to be active in a broad UV-visible spectrum. Combining WO<sub>3</sub> with silver-based materials, such as Ag<sub>2</sub>S, Ag<sub>2</sub>WO<sub>4</sub> or AgCl, can enhance its photocatalytic performance by broadening its absorption properties into the visible range and reducing charge recombination [1,2].

The type of reactor is key to assessing the performance of the materials. Although batch reactors are common in laboratory settings, continuous microreactors are preferred for their ability to screen different photocatalysts on a smaller scale and facilitate scale-up studies [3].

Immobilization of photocatalysts can increase photocatalytic efficiency and minimize the use of materials. Among the methods for synthesizing immobilized materials, the ultrasonic spray-pyrolysis technique is preferred for its cost-effectiveness, versatility, speed and reproducibility [4].

Thus, this project aims to synthesize WO<sub>3</sub>-Ag-AgCl photocatalysts immobilized on glass substrates by ultrasonic spray-pyrolysis/photoreduction for application in a continuous microstructured flat plate photochemical reactor. The system was evaluated for the degradation of the model emerging contaminant acetaminophen (ACT). In addition, the effects of parameters such as material stability and irradiation sources were also evaluated.

## Material and Methods

The reactor was fabricated using two 20 × 30 cm and one 20 × 20 cm aluminum plates. The plates were machined and assembled to form a continuous microstructured flat plate photochemical reactor. The immobilized materials were synthesized using the ultrasonic spray-pyrolysis/photoreduction method. Briefly, metallic tungsten (W) was dissolved in 35% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), forming the precursor peroxotungstic acid (WO<sub>3</sub>·nH<sub>2</sub>O<sub>2</sub>·mH<sub>2</sub>O). The solution was then heated at 90 °C for around 3 h until the color changed from transparent to yellow. The final solution was diluted in pure ethanol to reach 0.05 mol L<sup>-1</sup>. For the deposition process, the aforementioned solution was nebulized onto a borosilicate glass substrate (14 × 14 cm) with two nebulizers positioned on opposite sides of the substrate, which was placed horizontally on a hotplate. The resulting film was then calcined at 450 °C for 3 h, to allow the formation of WO<sub>3</sub>. For AgCl deposition, 0.086 mol L<sup>-1</sup>-aqueous solutions of NaCl and AgNO<sub>3</sub> were simultaneously nebulized onto the WO<sub>3</sub>-coated substrate. Finally, the material was photoreduced under UV-C radiation (254 nm), resulting in the WO<sub>3</sub>-Ag-AgCl material.

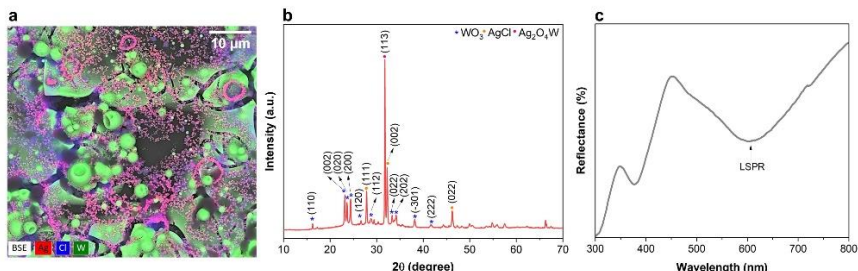
For the photocatalytic tests, a 5-mg L<sup>-1</sup> solution of ACT was fed into the reactor, operated in continuous mode, and samples were collected over time until steady-state, and analyzed by HPLC using a C18 column and a UV-vis detector. The reactor was irradiated with a HgI<sub>2</sub> lamp (UV-vis irradiation) from its top window or with UV-A LEDs from its bottom.

## Results and Discussion

SEM images revealed that the WO<sub>3</sub>-Ag-AgCl film was composed of flat plates and deformed, nearly-

spherical particles of  $\text{WO}_3$  (green), covered by small clustered spherical AgCl particles (pink), with an average thickness of  $2.8 \pm 1.3 \mu\text{m}$  (Fig. 1a). XRD analyses indicated the presence of monoclinic  $\text{WO}_3$  and cubic AgCl phases (Fig. 1b). The UV-vis DRS spectrum showed an additional peak around 600 nm, related to localized surface plasmon resonance

(LSPR) (Fig. 1c), which allows both  $\text{WO}_3$  and AgCl efficiently absorb visible light. The Tauc plot and calculated bandgap energies indicated the occurrence of two transitions, i.e., 2.76 and 3.58 eV, associated with the bandgap energies of  $\text{WO}_3$  and AgCl, respectively.

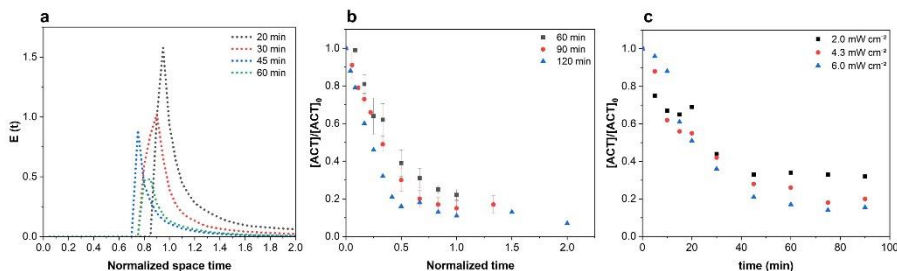


**Figure 1.** a) SEM image of the immobilized photocatalyst; b) XRD spectrum; c) UV-vis DRS diffuse reflectance spectrum.

Residence time distribution (RTD) studies indicated that the reactor behaved similarly to a plug flow reactor (PFR) (Fig. 2a). The residence time represented 80% of the space time, with a linear relationship. When space times were varied during the photocatalytic experiments, 77.9%, 86.8% and 93.1% ACT removal were obtained for space times of 60, 90 and 120 min, respectively (Fig. 2b). Thus,

in order to reduce operating costs and obtain high photocatalytic performance, the 90-min space time was selected to be used in the following experiments.

Subsequently, the UV-vis irradiance was varied at values of 2.0, 4.3 and  $6.0 \text{ mW cm}^{-2}$  on the reactor surface, achieving 67.7, 79.9 and 84.5% of ACT removal, respectively (Fig. 2c).



**Figure 2.** a) Study of residence space time distribution (RTD); b) ACT removal for different space times; c) ACT removal for different irradiances.

## Conclusions

In this project, immobilized  $\text{WO}_3\text{-Ag-AgCl}$  photocatalysts were successfully synthesized using the cost-effective ultrasonic spray-pyrolysis/photoreduction method. These materials exhibited high morphological homogeneity and crystallographic properties suitable for the photodegradation of organic pollutants. The reactor was designed and fabricated to enable scalable heterogeneous photocatalysis. Initial photodegradation tests, carried out at different space times and irradiance levels, showed high acetaminophen removal. Thus, the scenarios tested and the application of the concept are very promising for the removal of acetaminophen from water. Ongoing progress is now being made to understand the effects of irradiation sources (UV-Vis and UV-A LEDs) on the degradation process.

## Acknowledgments

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