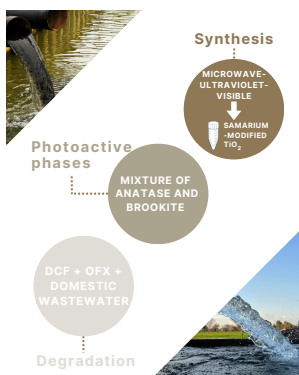


# Photoactivity of samarium-modified TiO<sub>2</sub> under UV-A radiation for the degradation of emerging contaminants in wastewater

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By applying the microwave-ultraviolet-visible radiation-assisted synthesis method, samarium-modified TiO<sub>2</sub> samples were successfully produced. A mixture of rutile, anatase, and brookite polymorphs was observed, with the photoactive phases being responsible for at least 93% of the crystalline composition. These materials were applied to degrade a mixture of diclofenac sodium (DCF) and ofloxacin (OFX) in a complex domestic wastewater matrix. The concentration of TOC = 253.0 mg L<sup>-1</sup> in the original domestic wastewater did not limit the photocatalytic activity of the materials, which achieved a DCF and OFX removal > 81% in 2h under UV-A light (365 nm). The removal of DCF was very effective by the adsorption mechanism, while OFX was removed by the photocatalytic mechanism. The results show that the materials were effective for removing pharmaceuticals from domestic wastewater.

## Introduction

Emerging contaminants are substances resistant to conventional treatment processes because they are resistant to degradation and end up remaining in water bodies, causing an impact on the health of organisms and the environment [1]. Heterogeneous photocatalysis has been used as an effective technique for the degradation of these compounds. However, the most faced challenges include the degradation of these compounds in real effluents. These challenges include achieving good performance. These challenges are due to the complexity of matrices, the presence of multiple contaminants, and other interferents that can hinder the effectiveness of photocatalysis [1,2].

The co-catalysts modified TiO<sub>2</sub> have a high potential to improve photocatalytic activity for the elimination of organic substances. The modifications on TiO<sub>2</sub> improve due to several properties, high oxidation rate, non-toxicity, low cost, and chemical stability compared to other metal oxides [3]. Its catalytic activity when present in the anatase phase is widely known, however, its performance for contaminants degradation when formed by a mixture of anatase and brookite can still be better explored.

## Material and Methods

**Synthesis of nanomaterials:** In a 50 mL beaker, 20 mL of the 20% (v v<sup>-1</sup>) isopropanol solution followed by 5 mL of the titanium isopropoxide (Sigma Aldrich, 98%) were added under constant stirring. For the doped samples, 50 mg of SmCl<sub>3</sub>·6H<sub>2</sub>O, was added to the mixture and kept stirring for 1 h. The whole mixture was then transferred to a Teflon vessel, added to the microwave discharge electrodeless lamp (MDEL) when necessary, and subjected to microwave treatment by time of 40 min. The synthesis variables investigated were microwave

power (400 or 500 W), dopant, MDEL, and heat treatment (400 or 600 °C). The samples were identified by DTiL\_P\_T, where D = presence of Samarium, L = presence of MDEL, P = microwave power, and T = heat treatment temperature. In the photodegradation studies, a mixture of diclofenac sodium (DCF) and Ofloxacin (OFX) at a concentration of 1 mg L<sup>-1</sup> each, was prepared in a domestic wastewater matrix. A catalyst dose of 0.5 g L<sup>-1</sup> was applied and the mixture kept stirring in the dark for 30 min to reach adsorption-desorption equilibrium. After the equilibration time, the solutions were irradiated with UV-A (365 nm) for up to 2 hours. The three best catalysts were then selected for kinetic assays. The degradation was monitored by HPLC-RF (LOD = 0.263 µg L<sup>-1</sup>, LOQ = 0.878 µg L<sup>-1</sup>, R<sup>2</sup> = 0.999 for OFX and LOD = 4.79 µg L<sup>-1</sup>, LOQ = 16.0 µg L<sup>-1</sup>, R<sup>2</sup> = 0.999 for DCF.

## Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the samples heat treated at 400 and 600 °C.

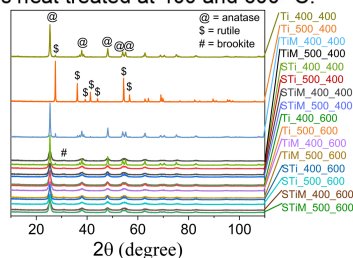


Fig. 1 – X-ray pattern of pure TiO<sub>2</sub> samples or doped with samarium. The samples were identified by DTiL\_P\_T, where D = presence of Samarium, L = presence of MDEL, P = microwave power, and T = heat treatment temperature

Samples heat treated at 600 °C showed an increase in crystallinity compared to samples treated at 400 °C, which can be confirmed by the better resolution of the diffraction peaks. Rietveld refinement analyses of the samples found the presence of anatase, rutile, and brookite polymorphs. The concentration of  $\text{Sm}^{3+}$ , determined by atomic absorption spectrometry, ranged from 0.59 to 0.84 mol% ( $\text{Sm}/\text{TiO}_2$ ), confirming low-concentration doping. The formation of oxides derived from samarium was not observed in any sample, confirming that  $\text{Sm}^{3+}$  was added to the  $\text{TiO}_2$  network. The bandgap energy ranged from 2.98 to 3.55 eV, and therefore, UV-A light was selected for degradation assays of emerging contaminants OFX and DCF prepared in a domestic wastewater matrix.

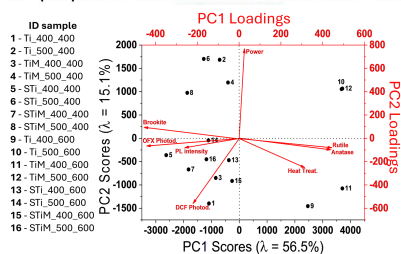


Fig. 2 – Graph of the principal component analysis (PCA) of each catalyst about its physicochemical properties and photoactivity. Degradation conditions: UV-A light,  $0.5\text{g L}^{-1}$  catalyst, 0-120 min.

The PCA results show the correlation of the different properties of the material (Fig. 2). The anatase-rutile phases are related to the heat treatment temperature, while the photoluminescence intensity is more related to the presence of the brookite phase. The photodegradation results for DCF and OFX also showed a greater relationship with the brookite phase, indicating that this polymorph has photoactivity on potential. Here, the contribution of adsorption and photocatalysis were separated to identify the response to the photoactivity of each material. The DCF adsorption is an effective mechanism in removing the compound, contributing up to 82% ( $\text{Ti}_500_600$ ). On the other hand, OFX adsorption was at most 11% ( $\text{STi}_500_400$ ) under the same conditions. This behavior occurs because at  $\text{pH} = 8.15$  (of the reaction), DCF ( $\text{pka} = 4$ ) is in its deprotonated form, while OFX ( $\text{pka}_1 = 6.1$ ,  $\text{pka}_2 = 8.28$ ) is in its protonated/neutral form. The presence of different carbon species in the wastewater was confirmed by the concentration of  $\text{TC} = 467.8\text{ mg L}^{-1}$ ,  $\text{IC} = 214.7\text{ mg L}^{-1}$ , and  $\text{TOC} = 253.0\text{ mg L}^{-1}$ . Thus, the interaction of DCF with the catalyst and organic matter present in the effluent was more effective compared to OFX. On the other hand, the removal of

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OFX by photodegradation was much superior to DCF. This occurs because the drug that remains available in the solution can be oxidized more efficiently by the hydroxyl radicals that are formed in the photocatalytic mechanism. The degradation profile of DCF (Fig. 3a) and OFX (Fig. 3b) over time was shown in Fig. 3. The photolysis of DCF and OFX in 2h were at most 8 and 9%, respectively. The pseudo-first-order kinetic constant was calculated and shown in Fig. 3c along with the linear correlation coefficients ( $R^2$ ). The highest  $k$  values obtained for OFX corroborate the results shown in Fig. 2, confirming that this contaminant is effectively degraded by the photocatalytic mechanism in the presence of UV-A light.

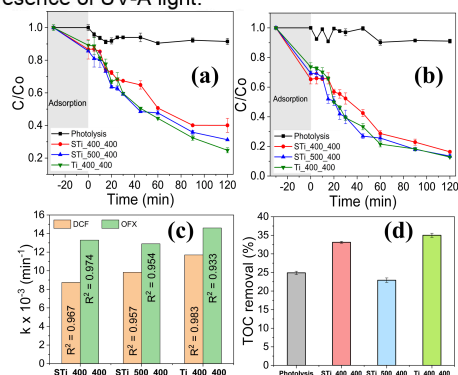


Fig. 3. Individual degradation profile (a), mixture (b), hydroxyl radical probe assays (c) and TOC removal (d). Degradation conditions: UV-A light,  $0.5\text{g L}^{-1}$  catalyst, 0-120 min.

The TOC removal (%) shown in Fig. 3d confirms that the photocatalytic process mediated by the  $\text{STi}_400_400$  and  $\text{Ti}_400_400$  samples was  $\sim 35\%$  within 2h. These data confirm that in addition to the removal of DCF and OFX especially, mineralization showed an improvement using photocatalysis. As the photolytic degradation of these compounds was not effective, the photocatalysts produced by the synthesis route proposed in this work were effective in the degradation of the respective drugs in domestic wastewater.

#### Conclusions

The synthesis of samarium-modified  $\text{TiO}_2$  using a still little-explored synthesis route produced samples with a high percentage of photoactive  $\text{TiO}_2$  phases. These photocatalysts proved to be effective for the degradation of DFC and OFX. The use of effluent as a complex matrix confirmed that, even under these conditions, the photocatalytic activity of the materials is highlighted, especially for the degradation of OFX.