

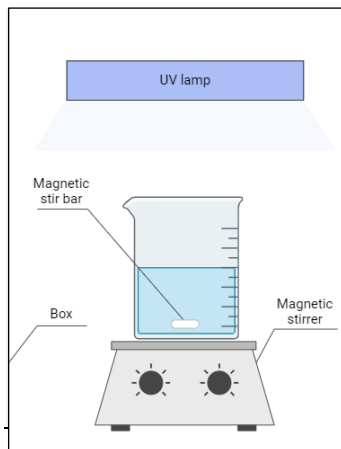
## Effect of BaTiO<sub>3</sub> photocatalyst doping on AMZ removal from aqueous medium

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Increased use of the herbicide amicarbazone (AMZ) in sugarcane production, raises concerns about ecosystem contamination. Advanced Oxidation Processes (AOP) emerge as an alternative for this. The AOP studied was the photocatalysis to remove AMZ from water applying BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5% as the photocatalysts and this study is not found in the literature. Powders were synthesized by microwave-assisted hydrothermal method and characterized by X-ray diffraction analysis (XRD) and Raman spectroscopy. The photocatalysis experiments were developed in a photochemical reactor, it was collected aliquots at different time intervals and analyzed in the spectrophotometer UV-Vis. Characterization demonstrated the formation of a crystalline tetragonal phase and the bond formation between the titanium, oxygen, barium and silver. The photocatalysis of AMZ with BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5% did not have a significant difference and showed a low removal rate.

### Introduction

São Paulo state represented 50,04% of the total harvested area of sugarcane production in Brazil, in 2022/2023 harvest [1]. Furthermore, its planted area in the mesoregion of Presidente Prudente showed an increase of approximately 490 thousand to 523 thousand hectares between 2021 and 2022 [2]. However, this contributes to the rise of pesticide use, in which this crop constituted 10% of the consumption of pesticides in the country, in 2016 [3].

One pesticide applied in sugarcane fields is amicarbazone (AMZ), an herbicide belonging to the triazolinone chemical class responsible for inhibiting the photosystem II. Moreover, this herbicide persists more in aerobic aquatic environments than terrestrial environments, with a half-life time of around one year and 87 days, respectively [4, 5]. When reaching these mediums, it becomes necessary to apply methods for the degradation of this substance, such as the advanced oxidative process (AOP).

Among the AOP, stands out the photocatalysis reaction, that is activated when a semiconductor material absorbs photons with equal or higher energy than its band gap [6] and to improve the properties of these materials, it is possible to apply doping [7].

In this context, this research aimed to study the effect of barium titanate (BaTiO<sub>3</sub>) photocatalyst undoped e doped with 5% of silver on AMZ removal from aqueous medium.

### Material and Methods

The reagents used in the experiments were the

herbicide amicarbazone C<sub>10</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub> (CAS 129909-90-6) and BaTiO<sub>3</sub>(Ag) 5% synthesized by microwave-assisted hydrothermal method and characterized by X-ray diffraction analysis (XRD) and Raman spectroscopy.

Control experiments of hydrolysis, photolysis and adsorption were carried out to evaluate the degradation pathways of AMZ in water solution and with the photocatalyst without light radiation.

Afterward, the photocatalysis experiments were developed in a photochemical reactor (as shown in the Graphical Illustration) and the reaction was initiated by the UV lamp, under agitation and constant temperature at 25°C. It was collected aliquots at different time intervals, submitted to centrifugation and analyzed in the spectrophotometer UV-Vis.

Thus, it was evaluated the removal of 10 mg /L of AMZ with BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5%, varying in 10 and 50 mg/L.

### Results and Discussion

The XRD analysis (Figure 1), shows the formation of the crystalline tetragonal phase of BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5%. Moreover, the Raman spectroscopy (Figure 2), demonstrates the bond formation between titanium, oxygen, barium and silver.

The control experiments demonstrated an insignificant degradation of AMZ by hydrolysis and photolysis. However, the adsorption with BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5% demonstrated a similar behavior, showing a sharp reduction in AMZ concentration between 0 and 5 minutes. After this, a small increase in its concentration was observed

until the last sample collection in 120 minutes, demonstrating desorption.

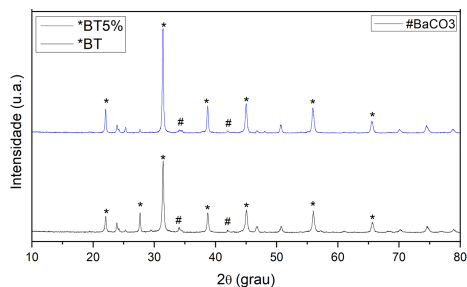


Figure 1. XRD for BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5%.

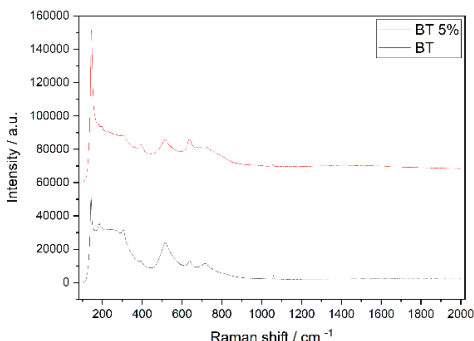


Figure 2. Raman for BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5%..

The photocatalysis experiments revealed a low removal rate of AMZ with both photocatalysts, in which it was under 10% in all samples. As shown in Table 1, the BaTiO<sub>3</sub> doped with 5% of silver did not have a significant difference in comparison with pure BaTiO<sub>3</sub>. Moreover, it is possible to verify the increase of AMZ degradation with the increase of the photocatalyst concentration.

Table 1. Removal of AMZ in photocatalysis with BaTiO<sub>3</sub> and BaTiO<sub>3</sub>(Ag) 5%

| [photocatalyst] | BaTiO <sub>3</sub> | BaTiO <sub>3</sub> (Ag) |
|-----------------|--------------------|-------------------------|
| 10 mg/L         | 3,45%              | 3,30%                   |
| 50 mg/L         | 9,59%              | 9,36%                   |

## Conclusions

The results showed an insignificant difference between the BaTiO<sub>3</sub> and the doping of this material with 5% of silver for the degradation of AMZ from aquatic environments. Furthermore, both photocatalysts demonstrated a low removal rate, indicating that barium titanate and its doping with silver are not effective for AMZ removal.

## Acknowledgments

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