Assessment of toxicity removal from the BaTiO3 + UV process applied to the degradation of amicarbazone

POSTER
Ph.D. Student: N
Journal: JECE

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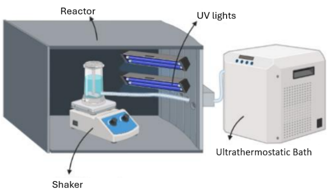

Graphical abstract. Scheme of the photochemical reactor.

This study investigated the removal of toxicity from an alternative treatment for water contaminated with the pesticide amicarbazone (AMZ), which is widely used in sugarcane cultivation in Brazil, has been detected in water bodies in the state of São Paulo[1] and can cause many risks to human health[2]. The treatment involves the degradation of AMZ by photocatalysis + UV with barium titanate ($BaTiO_3$), a very promising material with limited in-depth studies, and the evaluation of toxicity removal followed a methodology that considers the development of lentils (*Lens culinaris*) in a substrate moistened with AMZ solutions before and after treatment[3,4]. The results show that this treatment was not effective in degrading the pesticide under the studied conditions, with a maximum removal of 10%, however, the toxicity test indicates that the process is not toxic. Therefore, as this treatment is not toxic, it can be optimized under new conditions to improve pesticide degradation, making it an innovative solution for the treatment of persistent pollutants.

Introduction

Pesticides are recognized as pollutants of emerging concern due to their potential to affect human health. In Brazil, among the most used pesticides in sugarcane cultivation, is amicarbazone, detected in rivers located in the state of São Paulo [1].

Advanced Oxidative Processes (AOPs) are alternative water treatments capable of removing persistent organic pollutants, as AMZ, from the aquatic environment. Among different configurations of advanced oxidative processes studied in recent years are UV photoirradiated processes [5]. The photocatalysis of barium titanate, a promising material for its properties, low cost, low toxicity, and availability in different sizes and morphologies, began to be studied recently (after 2007), for the removal of pollutants from the aquatic environment [6]. Even so, there are few works dedicated to studying the removal of pesticides through UV photocatalysis of $BaTiO_3$.

Although AOPs perform the complete mineralization of certain pollutants, they can also produce degradation intermediates that can be more toxic than the original pollutant. Therefore, it is crucial to verify the removal of toxicity from the treated samples to assess the effectiveness of the treatment process [7].

This way, the objective is to develop a study for the degradation of AMZ by the UV photocatalysis process with $BaTiO_3$ and perform the analysis of toxicity removal from the test with *Lens culinaris*, which has been used for this purpose[3].

Material and Methods

Amicarbazone was provided by *Arysta LifeScience Corp*. and $BaTiO_3$ was prepared via hydrothermal synthesis by a collaborating research group. To determine the concentration of an AMZ solution, a calibration curve was created in the Agilent UV-vis spectrophotometer.

To determine the efficiency of the photocatalysis process, control experiments were carried out with all the mechanisms involved in degradation: hydrolysis, photolysis, and adsorption. For hydrolysis, AMZ solutions, with a concentration of 10 ppm, were placed in Erlenmeyer flasks, shaking in a shaker incubator (temperature controlled at 25°C), for two hours, samples were taken throughout the processes and the concentrations were measured.

For photolysis, an 10 ppm AMZ solution was placed in a UV reactor (Graphical abstract), with thermal control and constant agitation, for two hours, samples were taken and measured during this period.

Adsorption was carried out in the shaker incubator, with controlled temperature and agitation, for a period of 24 hours. Solutions of AMZ (10 ppm) and $BaTiO_3$ (10 ppm) were placed to react, isolated from light. Samples were collected, which went through the bench centrifuge (2 minutes, 4000 rpm), and their concentrations were also determined. All experiments were performed in triplicate.

The photocatalysis experiment was performed using the UV reactor (Graphical abstract), following the 2^2 factorial planning (Table 1), in which the variables are [AMZ] and [$BATiO_3$].

Table 1. Factorial planning of photocatalysis

Experiment	[AMZ]	[BaTiO]
1	10	50
2	10	10
3	5	50
4	5	10

Concentrations in ppm.

The solutions were kept in the reactor for 2 hours each, samples were collected, and the concentrations were measured.

After the photocatalysis, phytotoxicity tests were carried out, following the methodology described by Aksoy *et al* [4] and Mercado. Seir, Caleño. Jesús, Suárez. Jhan [3]. In this way, it is possible to identify whether the AMZ degradation process removed toxicity from the solution or not. The index used to measure phytotoxicity was the germination index, IG = (N/A)*100, where N is the number of germinated seeds and A is the total number of seeds.

Results and Discussion

The control experiments indicated that the AMZ was not affected by hydrolysis or photolysis. In the adsorption experiments, a slight adsorption was observed in the first 5 minutes followed by almost total desorption. The results of the photocatalysis tests are present in Figure 1.

The results indicate that barium titanate photocatalysis showed a minor removal of AMZ within two hours under the studied conditions. The experimental setup that exhibited the best performance in pesticide removal was Experiment 1 ([AMZ]=10ppm and [$BaTiO_3$]=50ppm).

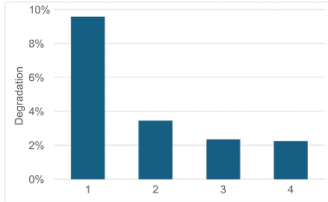

Figure 1. Relative degradation.

The result of the germination index calculation can be observed in Table 2. It is possible to identify that Experiment 1 presented the best performance, indicating lower toxicity. The index presented by the control was lower than the others, indicating that the photocatalysis of AMZ, using barium titanate, did not increase the toxicity levels of the solution.

Table 2. Germination index from phytotoxicity test

Experiment sample	Germinated seeds	GI
1	10	50%
2	7,5	37,5%
3	2	10%
4	5,5	27,5%
Control	4	20%

The number of germinated seeds considered is the average of the duplicate test performed.

Conclusions

The photocatalysis of barium titanate under UV radiation did not exhibit significant percentages of amicarbazone pesticide removal under the studied conditions. The best performance achieved was 10% removal of AMZ, obtained with $[AMZ]_0$=10ppm and $[BaTiO_3]_0$=50ppm; this condition also showed the highest germination rate. Toxicity tests indicate that despite the low removal of AMZ, the final solutions showed no toxicity, that is, the process of photocatalysis + UV with barium titanate for the treatment of water contaminated with amicarbazone can be studied under other conditions to achieve greater degradation, making it a viable alternative for the removal of persistent pollutants, especially AMZ, which are not removed in conventional water treatment.

Acknowledgments

I would like to thank the *Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq – Brasil* for Financial Support (process 123205/2023-9).

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