TiO_2/*Luffa cylindrica* Composites for Photocatalytic Degradation of Atrazine

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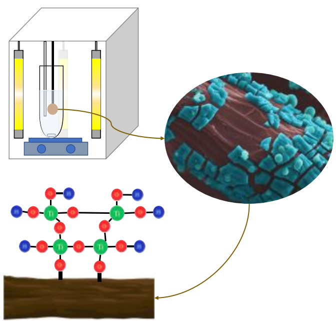

Environmental contamination by herbicides is a serious problem that affects ecosystems and human health. Therefore, it is essential to develop efficient and economical methods to degrade them. This study synthesized composites of TiO_2 immobilized on *Luffa Cylindrica* by the microwave-assisted solvothermal method, aiming to reduce reaction time and obtain crystalline anatase TiO_2. The composites were applied for the photocatalytic degradation of the atrazine herbicide in water. The characterization showed the deposition of a TiO_2 film adhered to the *L. cylindrica* fibers. The composites outperformed photolysis results of 22% of atrazine degradation, with the microwave-produced materials reaching 53% efficiency after 24 hours. These results indicated that these composites are viables for the effective treatment of contaminant herbicides at low concentration in water.

Introduction

Human activities such as mining, agriculture and energy production are among the main causes of chemical pollution of water resources, impacting marine life, ecosystems and human health. Brazil is one of the world's largest consumers of pesticides, including the atrazine (ATZ) herbicide for weed control [1]. This compound is highly persistent, contaminating soils, and surface and groundwater [2]. Thus, it becomes necessary to develop effective and economical technologies for the proper treatment and disposal of these pollutants [3]. Heterogeneous photocatalysis using titanium dioxide (TiO_2) as a photocatalyst emerges as a promising strategy for the degradation of pesticides [4]. TiO_2 can be applied in suspension or immobilized on a solid support. Immobilization facilitates its recovery, with cellulose being an efficient option due to its advantageous properties, such as high strength and stiffness, renewable chatacter, recyclability, low cost, and low density [5]. *Luffa cylindrica* (LC), a renewable and inexpensive vegetable fiber, stands out as a 3D cellulosic support [6]. The solvothermal method allows for the nucleation and growth of TiO_2 particles directly on the cellulosic fibers. Additionally, microwave assisted solvothermal synthesis provides high efficiency, reduced costs, and time optimization [7]. However, studies on TiO_2 immobilized on cellulose by the microwave assisted solvothermal method are scarce. El-Roz et al. (2013) [6] studied the TiO_2 immobilized on LC for the photocatalytic degradation of methanol under UV radiation. Composites showed coverage of LC by TiO_2 synthesized through the hydrothermal method in autoclave, exhibiting good stability. Therefore, this work aims to develop TiO_2/*Luffa cylindrica* composites by the microwave-assisted solvothermal method to degrade atrazine in water under UV light.

Material and Methods

The *LC* (Vegetable sponge, Brand: Santa Clara) was pretreated with a 1M NaOH solution for 90 min at room temperature under constant stirring. After washing, the fibers were dried in an oven at 80 °C for 24 h.

Titanium isopropoxide (TTIP) (Sigma Aldrich, 99%) was used as TiO_2 precursor. For TiO_2 immobilization, LC pieces were immersed in the TTIP/ethanol solution for 1 h. After the addition of acetic acid and stirring for an additional hour, the solution was transferred to the microwave reactor (CEM, Discovery Synthesis model) and treated at 140 °C for 1 or 2 h. The TiO_2/Luffa composites were filtered, washed, and dried at 80 °C for 24 h. They were identified as TiO_2/Luffa_X, where X is the synthesis time. The samples underwent physicochemical characterization using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FTIR).

A solution of ATZ (Sigma Aldrich, 99.9%) with a concentration of 3 mg/L was prepared in ultrapure water. Photodegradation tests were carried out in a quartz reactor containing 50 mL of the solution, under constant agitat ion at 25 °C. The photocatalyst was immersed in the solution and kept in the dark for 30 minutes to establish adsorption-desorption equilibrium. The solution was then exposed to UVA radiation from an 8 W lamp for 24 hours. Both photolysis and photocatalysis experiments were conducted in duplicate to ensure reproducibility. ATZ degradation was analyzed by HPLC/UV-vis (Shimadzu LC-20AT, UV-vis detector) at 221 nm.

Results and Discussion

TGA analyses showed that the content of TiO_2 immobilized on *L. cylindrica* fibers was 17% for TiO_2/Luffa_1 and 18% for TiO_2/Luffa_2, suggesting that the reaction time did not significantly affect the loading of nanoparticles.

FTIR spectra (Fig. 1.1) showed that characteristic bands of LC decreased in intensity after TiO_2 immobilization. Both composite samples displayed a pronounced decrease in vibrations 3330 cm^{-1} (O-H bond associated to cellulose), 2990 cm^{-1} (C-H bond associated with lignin) and 1022 cm^{-1} (peak due to C-H, C-N, C-O bonds) [8]. Also, were observed an increase in the peak at 1630 cm^{-1}, which is attributed to the bending vibrations of TiO-H, a peak around 1400 cm^{-1} related to Ti-O modes and a broadening of band at 3250 cm^{-1} related to symmetric stretching vibration of O-H on the surface of TiO_2 [9]. These results clearly show that TiO_2 formed a uniform film on *Luffa* fibers, independently of the synthesis time of the composites.

SEM analysis revealed directed growth of TiO_2 on the *Luffa* surface, forming an adhered film (Fig. 1.2 and 1.3). At first, TTIP precursor interacted with cellulose hydroxyls, followed by its hydrolysis and condensation of the titanium oxo-hydroxide supported in the form of a thin layer on the Luffa fiber. The TTIP which hydrolysed without contact with the cellulosic support, nucleated and created spherical TiO_2 particles dispersed on the film phase.

In the photocatalytic degradation of ATZ (Fig. 1.4), the TiO_2/Luffa composites exhibited superior performance compared to photolysis. While photolysis resulted in approximately 22% degradation, the TiO_2/Luffa_1 composite showed an efficiency of 47%. TiO_2/Luffa_2 composite, achieved the highest degradation of ATZ at 54%. Reuse tests of TiO_2/Luffa_2 over 5 cycles of ATZ degradation under UVA radiation were carried out. Its performance remained above 98% until the third cycle, decreasing to 74.4% in the fifth cycle.

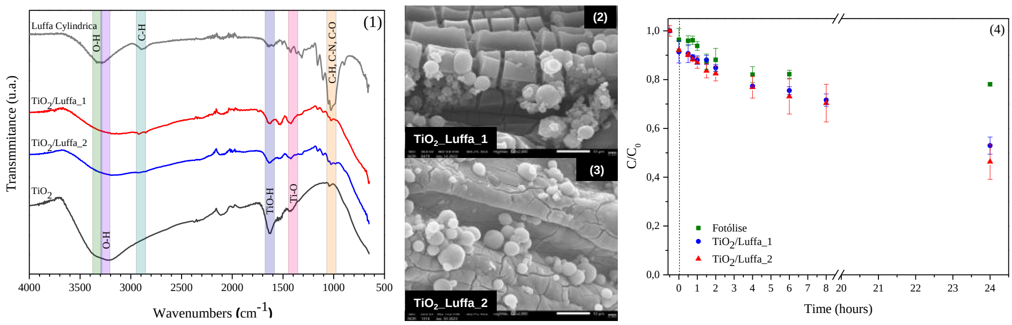

Figure 1: (1) FTIR spectra of samples. **(2)** SEM analysis of TiO_2/Luffa_1 and **(3)** TiO_2/Luffa_2. **(4)** Atrazine photocatalytic degradation in water at initial concentration of 3 mg/L.

Conclusions

The study assessed the synthesis of TiO_2 and its immobilization on *Luffa cylindrica* using the microwave-solvothermal method for the photocatalytic degradation of atrazine. Characterizations revealed the formation of a thin layer of TiO_2 on the *Luffa* fibers. The results of photocatalytic tests indicated that the TiO_2/Luffa composites prepared by microwave-assisted technique were efficient concerning the UV degradation of atrazine. The TiO_2/Luffa_2 sample exhibited the best performance. Furthermore, the composites proved to be reusable, maintaining good activity even after five reaction cycles.

Acknowledgments

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References

[1] SINDIVEG, disponível em: https://sindiveg.org.br/wp-content/uploads/2020/08/SINDIVEGPaper_REVa_FINAL2020bx resolucao.pdf. Acesso em 15/05/2021.
[2] F. P. De Albuquerque,J. L. De Oliveira, V. Moschini-Carlos, L. F. Fraceto, *Sci. Total Environ.*, 700 (2020) 134868.
[3] F. E. Titchou, H. Zazou, H. Afanga, J. E. Gaayda, R. A. Akbour, P. V. Nidheesh, M. Hamdani, *Chem. Eng. Process.: Process Intensif.*, 169 (2021) 108631.
[4] A. H. C. Khavar, G. Moussavi, A. R. Mahjoub, M. Satari, P. Abdolmaleki, *Chem Eng J.* 345 (2018) 300-311.
[5] H. Hamad, E. Bailón-García, S. Morales-Torres, A. F. Pérez-Cadenas, F. Carrasco-Marín, F. J. Maldonado-Hódar, *In Bio-Based Materials and Biotechnologies for Eco-Efficient Construction*, Woodhead Publishing, 2020, 329-358.
[6] M. El-Roz, Z. Haidar, L. Lakiss, J. Toufaily, F. Thibault-Starzyka, *RSC Advances*, 3 (2013) 3438–3445.
[7] J. F. De Conto, M. R. Oliveira, M. M.Oliveira, T. G. Brandão, K. V. Campos, C. C. Santana, S. M. Egues, *Chem Eng Commun*, 205 (2018) 533-537.
[8] Ghali, L., Aloui, M., Zidi, M., Bendaly, H., M'sahli, S., and Sakli, F.. *Bio Resources.* 6(4) (2011) 3836-3849.
[9] León, A.; Reuquen, P.; Garín, C.; Segura, R.; Vargas, P.; Zapata, P.; Orihuela, P.A. *Appl. Sci.*, 7 (2017) 49.