Evaluation of the degradation of 2,4-D using 8% Ag/ZnO synthesized by a new Sol-Gel route

POSTER

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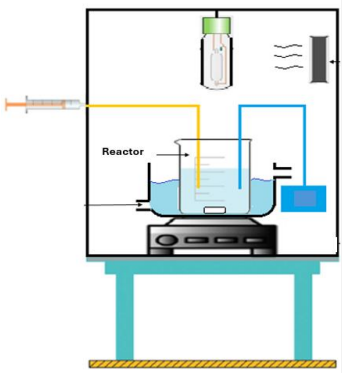

Pesticides are micropollutants that have generated significant concern because even in minimal quantities, they can be extremely toxic. Among these is the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), which is widely used. The resistance of this contaminant to conventional treatments motivates research for the development of new technologies. Heterogeneous photocatalysis presents itself as an option for treating this pollutant. Few studies have sought to apply new synthesis routes to obtain low-cost and environmentally friendly photocatalysts. Thus, this study aimed to apply pure zinc oxide (ZnO) and silver (Ag)-promoted zinc oxide in the degradation of 2,4-D, prepared by a new sol-gel route. Of the synthesized materials, the one that showed the highest degradation capacity was 8% Ag/ZnO, achieving 94.4% degradation.

Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is an active component used widely as a plant hormone regulator and is considered an endocrine disruptor. It's also the second most used pesticide in Brazil (De Souza et al., 2019)[1]. Residues of 2,4-D, after being used in agricultural lands or through improper disposal, contaminate and pose a threat to water bodies. Its biodegradation in water is very slow (with a half-life of 6 to 170 days), requiring intentional exclusion from water bodies (Aly; Faust, 1964)[2].

Advanced oxidative processes (AOPs) have been extensively studied as an alternative to conventional treatments for contaminated water. Zinc oxide is a semiconductor that has attracted significant interest due to its stability after repeated catalytic cycles, as well as its good chemical and thermal stability, non-toxicity, and low cost. These properties have enabled its widespread application in water treatment through heterogeneous photocatalysis (Debnath and Gupta, 2018)[3].

In light of the foregoing, the present study aimed to investigate heterogeneous photocatalysis as a promising technique for degrading 2,4-D in the presence of artificial radiation (UV), using pure ZnO and silver-doped ZnO synthesized via the modified Sol-Gel method

Material and Methods

The procedure used for the synthesis of zinc oxide and silver-doped zinc oxides with different metallic silver loads (2, 5, 8, 10%, by mass) is presented below and was analogous to that used by Ferreira et al., (2016)[4]. The method essentially involved slowly adding a homogeneous solution containing 1.6963 mol.L^{-1} of Zn $(NO3)2{\cdot}6H_2O$ to another solution containing native cassava starch at a concentration of 400 g L^{-1}, at a temperature of 25 °C. The resulting solution was maintained under constant magnetic stirring for 50 min at 80°C until complete gel formation of starch. The obtained gel was dried in an oven for 24 h at 100°C to obtain the xerogel (amorphous solid). The xerogel was then calcined for 4 h at 400°C. The obtained material was washed with ultrapure water to remove residual salts from the synthesis and finally was again placed in the oven for 24 h at 100°C. The same methodology was used for the synthesis of catalysts doped with silver (2, 5, 8, 10%), with the addition of the silver nitrate ($AgNO_3$) solution in the desired amount during the mixing step of the zinc nitrate and cassava starch solutions. After synthesis, part of the obtained material was sent for X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) characterization. The experimental assays of photolysis, adsorption, and photocatalysis under artificial UV radiation were conducted in a reaction system isolated from the environment by an aluminum metal box. The reaction system consisted of a Pyrex glass reactor operating in a batch system, on a bench scale, with a capacity of 1000 mL, equipped with a magnetic stirrer. The UV radiation was provided by a 125 W mercury vapor lamp, positioned at a distance of 10 cm from the solution

to be treated. The reactions were carried out under continuous air flow (provided by an aquarium pump), at a temperature of 20°C and atmospheric pressure, which was kept constant by a thermostat bath. The quantification of the analyte was performed using a UV-Vis spectrophotometer.

Results and Discussion

Figures 1(a) and 1(b) present the results obtained from the X-ray diffraction (XRD) of the samples of pure ZnO and 8% silver-doped ZnO, respectively. For all samples, both pure ZnO and silver-doped ZnO, the main diffraction peaks observed were associated with the hexagonal structure of wurtzite (ISCD-065120). This structure belongs to the P 63/mc space group, and the most intense peaks correspond to the crystalline planes (100), (002), and (101). These results are consistent with those reported by Naqvi et al. (2014)[5]. For the catalysts containing silver, it was also possible to identify low-intensity peaks at approximately 2θ equal to 38°, 44°, and 64°. These peaks are associated with the cubic phase of silver (ISCD-064994). Based on these results, it can be stated that doping ZnO with silver resulted in the formation of secondary phases in the material, similar to what was obtained by Yildirim et al. (2003)[6], who also studied silver-doped ZnO and identified the cubic phase of Ag, as well as the wurtzite structure of zinc oxide.

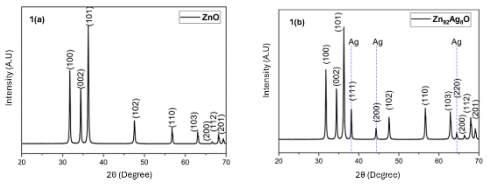

Figure 1. XRD 1(a) ZnO and 1(b) 8% Ag/ZnO.

Figure 2(a) presents the images obtained with the TEM for the 8% Ag/ZnO with a magnification of 100,000 times (it is worth noting that a similar result was obtained for pure ZnO). From the micrographs (Figure 2b), it was also possible to generate histograms of particle size distribution and thus calculate the average size of crystallites for the catalyst samples. The values obtained were 32.95 nm and 30.16 nm for ZnO and 8% Ag/ZnO, respectively. The images clearly show that the material is composed of clusters of nearly spherical-shaped rounded particles. These results are in agreement with those obtained by Nagaraju et al. (2017)[7].

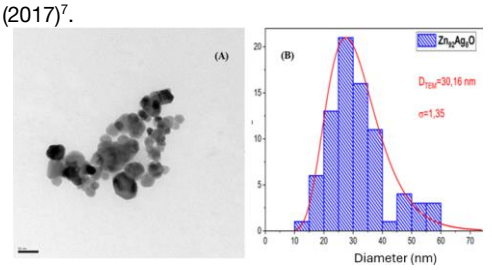

Figure 2. TEM 8% Ag/ZnO 2(a) Figure and 2 (b) Histograms.

The result obtained from photolysis showed that only in the presence of UV radiation was the degradation of 2,4-D very low, reaching a value of approximately 27% at the end of 120 minutes of reaction, highlighting the need for the presence of the photocatalyst to achieve a higher efficiency in degrading this contaminant.

The adsorption results indicate that this process is not the main step for contaminant removal, as the amount removed was very low, reaching an approximate value of 1% for both catalysts. Finally, applying photocatalysis yielded degradation values of 79.89% for pure ZnO and 94.4% for the 8% Ag/ZnO catalyst, demonstrating that the presence of metal increases the herbicide degradation capacity.

Conclusions

The nanoparticulate catalysts of pure ZnO and Ag-doped ZnO were successfully obtained through the modified sol-gel method, using cassava starch as a polymerizing agent, proving to be an efficient, simple, low-cost, and environmentally friendly synthesis route. The material showed promise for application in the degradation of 2,4-D, achieving values of 94.4% degradation, as in the case of 8% Ag/ZnO

Acknowledgments

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