Application of Ag_3PO_4-MOF composites for wastewater remediation

ORAL/POSTER
Ph.D. Student: Y
Journal: ESPR

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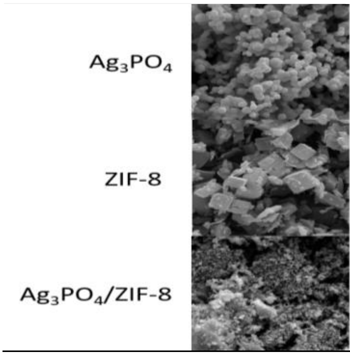

This study investigates the efficacy of heterojunction formation to enhance photocatalysis, focusing on Ag_3PO_4 and ZIF-8. The Ag_3PO_4/ZIF-8 heterojunction was synthesized and characterized via XRD and SEM. Degradation tests using methylene blue dye revealed superior photocatalytic activity of the heterojunction compared to individual components. Ag3PO$_4$/ZIF-8 exhibited excellent stability and inhibition of electron-hole pair recombination, while pure Ag_3PO_4 showed high catalytic activity despite low photostability. ZIF-8 displayed efficient degradation kinetics but lesser efficacy compared to Ag_3PO_4. In summary, the study highlights the potential of the Ag_3PO_4/ZIF-8 heterojunction for efficient photocatalysis in dye degradation, offering insights for improving wastewater treatment processes.

Introduction

Around 15% of the total world production of dyes is lost during the dyeing process and is released into textile effluents causing eutrophication and disturbances to aquatic life. Technological systems for removing organic pollutants, such as dyes, have been recently developed **[1]**. Photocatalysis is a promising technique for the degradation of organic extractants in wastewater, a semiconductor that has been widely used is Ag_3PO_4 for photocatalystsis, due to its simple preparation method, low toxicity and strong oxidative capacity **[2]**. However, it is still a big challenge for the practical application of a single Ag_3PO_4 photocatalyst, which is mainly because of the uncontrollable photocorrosion by the photogenerated electron-hole (e^-/h^+) pairs and the speedy recombination **[2]**. The construction of heterojunction has been proven to be an effective modification method in Ag_3PO_4.**[2]** Another compound that has been studied in photocatalysis is ZIF-8, a metalorganic such as ZOU et al. used ZIF-8 in a heterojunction with Cu_2O, where it exhibited a better tetracycline degradation rate constant 1.9 times greater than pure Cu_2O. Cu_2O/ZIF-8 could still degrade tetracycline effectively after four cycles, which proved that it had good stability **[3]**. In this research, the same principle as previously seen will be used, associating Ag_3PO_4 with ZIF-8. The objective of this research is to verify the photocatalytic activities of Ag_3PO_4 in association with ZIF-8 and separately in the degradation of methylene blue.

Material and Methods

Ag_3PO_4 crystals were obtained by the precipitation method using $AgNO_3$ and anhydrous K_2HPO_4 solutions. A methodology adapted from the literature was used such that an aqueous solution of 100 mL of K_2HPO_4, 0.06 mol L^{-1} was dripped into a solution of 100 mL of $AgNO_3$, 0.018 mol L^{-1}, in an aqueous medium. At the beginning of dripping, the solution obtained a pale yellow and cloudy appearance, later replaced by a yellow color (Ag_3PO_4). After synthesis, the precipitate was filtered and washed with isopropyl alcohol placed in the oven for drying at 100ºC for 24 h. For the synthesis of ZIF-8, a molar ratio of 1:8:700 of $Zn(NO_3)_2$. $6H_2O$, 2-methylimidazole and methanol was used, respectively. First, 2-methylimidazole was added to a beaker and dissolved in methanol and in another beaker the $Zn(NO_3)_2.6H_2O$ was dissolved in methanol, then the two solutions were mixed and left to stir for materials were characterized by XRD and scanning electron microscopy SEM. In the heterojunction, a mass ratio close to 1:10 of ZIF-8 and Ag_3PO_4, respectively. 0.1g of ZIF-8 was added to 50 mL of water, in the same solution Ag_3PO_4 was synthesized, the Ag_3NO_4 solution was added beforehand and left under stirring for 3 h and then added K_2HPO_4. In methylene blue degradation tests (10 mg L^{-1}) 0,5 g of the compound was added to 100 mL of methylene blue solution and aliquots were removed at times of -210, -180, -120, -90, -60,-30, 0, 15, 30, 45, 60, 90 min. (where the negative time refers to the time when the light was off) and then centrifuged to remove the compound powder and UV-Vis spectrometry was performed to check degradation.

Results and Discussion

Initially, to confirm the formation of the compounds Ag_3PO_4 and ZIF-8 and their heterojunction, as well as evaluate the crystallinity and the crystalline phase formed, X-ray diffractometry analyzes were carried out, as shown in Figure 1.

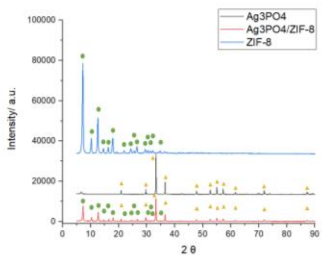

Figure 1. X-ray diffraction patterns of Ag_3PO_4, ZIF-8 and Ag_3PO_4/ZIF-8.

Peak identification was performed using Crystallography Search-Match software (free trial version). In the case of the synthesized Ag_3PO_4 semiconductor, it was related to PDF nº 71-1836, demonstrating the absence of secondary phases resulting from the syntheses carried out and the cubic system. Regarding ZIF-8, the software did not have the ZIF-8 compound in the database, so it was compared with the XRD of Nordin et al.**[4]** Where it was shown to be identical to the XRD found by the author and his collaborators. The XRD of the heterojunction, it maintained peaks equal to Ag_3PO_4 and ZIF-8, demonstrating that it maintained the characteristics of the compounds.

Scanning microscopy images are used to confirm the surface morphology of the obtained materials. The Ag_3PO_4 semiconductor presents homogeneity in the size and morphology of the particles, which are rounded in Figure 2a, similar to those presented by Huang, K., et al., 2015 **[5]**. The micrograph of the ZIF-8 sample in figure 2b, cubic structures of 2 µm size were obtained, similar to those obtained by Mousavi et al **[6]**. In the Ag_3PO_4/ZIF-8 heterojunction, it can be seen that the ZIF-8 and Ag_3PO_4 were not very well distributed, with the physical mixing of the precursor materials not being very effective, as shown in figure 2c.

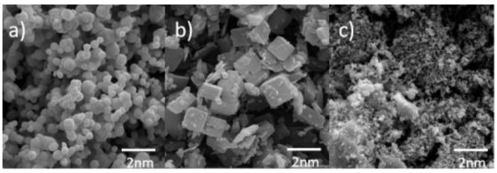

Figure 2. Micrographs obtained by Scanning Electron Microscopy for the samples: a)Ag_3PO_4 ,b) ZIF-8, c) Ag_3PO_4/ZIF-8.

The photocatalytic activity of the pure compounds of Ag_3PO_4, ZIF-8 and the Ag_3PO_4/ZIF-8 junction, all in powder form, was evaluated through the photocatalytic degradation of the methylene blue dye, using an LED lamp as an illumination source. The C/C0 graph obtained from these solutions, are shown in figures 3.

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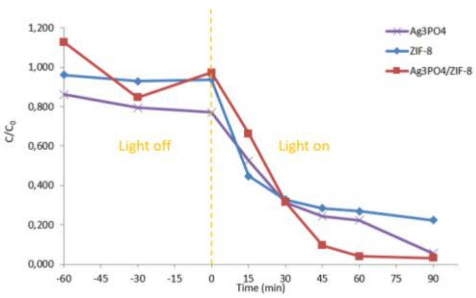

Figure 3. C/C_0 graph of Ag_3PO_4, ZIF-8 samples and the Ag_3PO_4/ZIF-8 junction.

Degradation tests were carried out with the aim of verifying the photocatalytic activity of the synthesized samples, this activity being confirmed by the degradation of the dye evidenced by the decrease in absorbance values. The photocatalysis power of the samples is also verified, showing that the Ag_3PO_4/ZIF-8 heterojunction has one of the best results, degrading all the dye, then Ag_3PO_4 and then ZIF-8. Thus, Ag_3PO_4/ZIF-8 presents excellent catalytic activity, inhibiting the recombination of electron-hole pairs (e-/h+) and increasing stability. Pure Ag_3PO_4 shows excellent catalytic activity. However, studies show that it has little photostability due to the photocorrosion process. In this process, Ag is leached into Ag_3PO_4. ZIF-8 was effective in the kinetics of the degradation process, presenting a less efficient degradation than Ag_3PO_4. ZIF-8 was effective in the kinetics of the degradation process, presenting a less efficient degradation than the other compounds.

Conclusion

The materials were successfully synthesized through chemical studies with the crystalline phases confirmed by XRD. ZIF-8 in particular showed a cubic morphology according to the SEM images. The model molecule degradation tests showed efficiency after 60 min of testing. Pure ZIF-8 has high adsorption capacity. However, together with the Ag_3PO_4/ZIF-8 semiconductor, it showed high photocatalytic degradation efficiency compared to other pure components.

Acknowledgments

The authors thank CAPES, Fundação Araucária, CNPQ and C-Labmu-UEPG.

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