Photocatalytic Materials Development Based on Heterojunctions g-C_3N_4/MoO_3 and g-C_3N_4/MoS_2 Active by Solar Radiation

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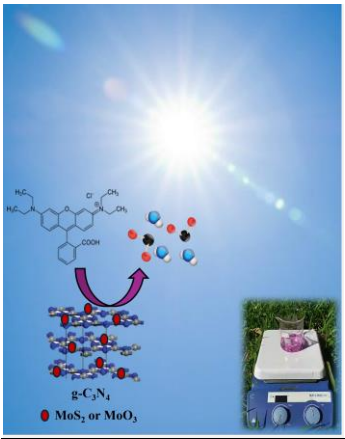


Organic dyes, such as RhB, are pollutants due to their potential to reduce photosynthetic activity and accumulation in the environment, in addition to their toxicity. The development of more efficient methodologies is necessary. The use of g-C_3N_4 is interesting, however it presents a high recombination rate of the photogenerated pairs. The combination of this material with MoO_3 or MoS_2 increases visible radiation absorption and reduces the recombination rate. Composites were formed with different proportions of MoO_3 or MoS_2 in relation to g-C_3N_4, using an ultrasonic bath in ethanolic solution. Photodegradation of 2.5 mg L^{-1} of RhB was carried out using solar radiation for 1 hour. The use of the catalyst MoO_3 10% and MoS_2 5% showed the best results, reaching 99% removal from the solution after 1 hour of photodegradation by sunlight, the proposed mechanism for degradation was direct for MoO_3 and indirect for MoS_2

Introduction

The presence of dyes in aquatic environment reduces photosynthetic activity. These dyes represent a serious environmental problem due to their high toxicity and potential accumulation in the environment and affecting public health and ecosystem biota [1]. Therefore, it is necessary to seek new, more efficient technologies than conventional methods, among which AOPs are included [2]. Among AOPs, heterogeneous photocatalysis stands out for its use of semiconductors. g-C_3N_4 has a band gap of 2.7 eV and is therefore a material with a response in the visible region [1]. However, it exhibits a high recombination rate, hence the importance of developing heterojunctions with other materials such as MoO_3 and MoS_2 to improve its photocatalytic response. these materials have an interesting activity and possible applied with visible light [3]. In this study, we aimed to develop new photocatalytic materials based on g-C_3N_4/MoO_3 and g-C_3N_4/MoS_2 heterojunctions activated by solar radiation.

Material and Methods

The g-C_3N_4 was synthesized using 6g of melanin, 4g of KCl, and 3g of NaCl, which were mixed and heated at 520 ºC for 2 hours. For the synthesis of MoO_3, a citric acid solution and ammonium molybdate in a 3:1 ratio was prepared, with the addition of ethylene glycol, and the mixture was kept at 90 ºC for 30 min. The resulting resin was subjected to heat treatment at 500 ºC. The synthesis of MoS_2 was carried out with 0.01 mol of MoO_3 in 15 mL of water, stirred for 30 min, and then added 0.035 mol of thiourea, maintaining stirring for another 15 min. The solution was then transferred to a hydrothermal reactor and maintained at 200 ºC for 24 hours.The g-C_3N_4/MoO_3 and g-C_3N_4/MoS_2 heterojunctions were prepared with 1 g of g-C_3N_4 for concentrations of 5%-20% of MoO_3 or MoS_2, 30 mL of ethanol in an ultrasonic bath for 5 hours, then dried in an oven at 100°C. All materials were analyzed by Infrared (IR) and UV-Vis. Photocatalytic study, 0.025 g of the photocatalyst in 50 mL of RhB (2.5 mg/L) for 1 hour in sunlitgth. The samples were analyzed using UV-Vis and a fluorimeter (PL).

Results and Discussion

The FTIR results of the synthesized samples showed peaks at 1237 and 1315 cm^{-1} corresponding to out-of-plane flexion vibrations, characteristic of the heptazine rings[4]. The low-intensity broad band centered at 3203 cm^{-1} can be attributed to the amine terminations derived from the heptazine rings, as well as to the stretching and folding of the N-H and N-H_2 groups, indicanting indicating the g-C_3N_4 formation [4]. Heterojunctions with fractions of 5-20% exhibit peaks in both the MoO_3 and MoS_2 profiles. Figure 1 displays the photoluminescence spectra for the samples synthesized in this work.

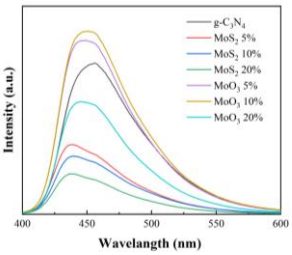
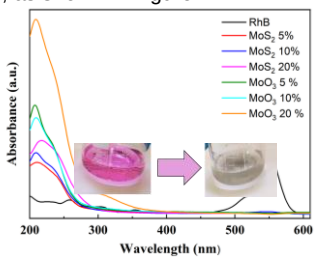


Figure 1: Espectro de emissão das amostras sintetizadas

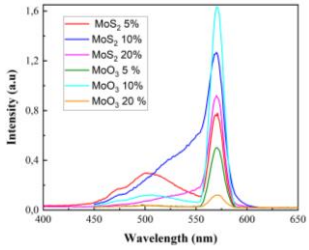
The PL and photocatalytic activity of semiconductor materials can be related considering the dynamic behaviors of photoinduced charge carriers. The literature reports that the reduction in PL spectrum intensity, either for band-to-band transitions or excitonic transitions, may be related to increased photocatalytic activity [5]. Thus, samples doped with

MoS_2 showed lower photoluminescence intensity, indicating their potential for better photocatalytic activity. Photodegradation tests were therefore conducted and are presented in Figures 2 to 4. RhB solutions exhibited significant discoloration after photocatalytic degradation under visible light irradiation, as shown in Figure 2.



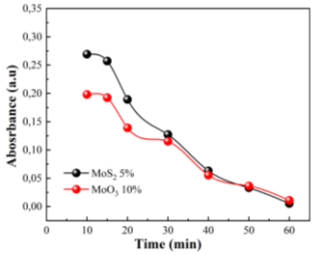
Figrue 2: UV-Vis absorption spectrum of the solution after photodegradation using solar radiation

After 1 hour of irradiation, the band between 500-580 nm related to the RhB molecule disappeared, leading to the emergence of a band in the 200-300 nm region, which can be attributed to the formation of smaller molecules such as carboxylic acids, indicating the degradation of the RhB molecule. Regarding the removal efficiency, the MoO_3 10% and MoS_2 5% solutions stood out by showing a lower signal in the 200-300 nm region, indicating a lower quantity of molecules originating from degradation. This relationship is justified by Lambert-Beer's law, where absorbance is directly proportional to concentration.To support these results, Figure 3 shows the RhB solution fluorescence spectrum o band profile in the 600-450 nm region, where a second band in the 550-450 nm region was observed, possibly indicating the formation of other smaller compounds due to RhB degradation. Once the most efficient photocatalysts like MoS_2 5% and MoO_3 10% were chosen, it was possible to evaluate the degradation kinetics of the RhB solution (2.5 mg/L).



Figrua 3: Fluorescent emission spectrum of RhB solutions using the different synthesized materials.

In Figure 4, it is shown that both photocatalysts achieved satisfactory discoloration within 1 hour. However, it is important to note that the MoO_3 10% sample exhibited significant adsorption. This indicates that the degradation mechanism of the solution was direct. In contrast, for MoS_2, there was no adsorption, indicating that the degradation process was indirect.



Figrue 4: Variation of RhB concentration at different photodegradation times.

Conclusions

The synthesis of the proposed materials proved to be efficient. All synthesized materials showed photocatalytic activity when irradiated with sunlight. The MoS_2 5% and MoO_3 10% composites exhibited the best photocatalytic activity, achieving a 99% removal efficiency of RhB under sunlight. It is worth noting that the degradation mechanism was indifferent between the materials, being direct for MoO_3 10% and indirect for MoS_2 5%.

Acknowledgments

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