Statistical optimization of $g\text{-}C_3N_4/ZnCr_2O_4$ heterojunction preparation and improvement of photocatalytic efficiency

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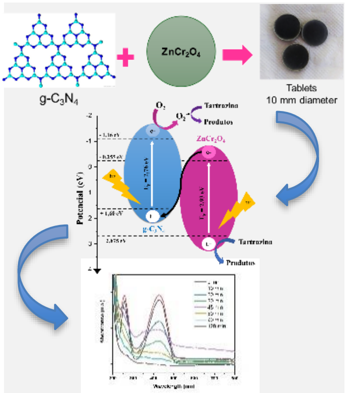

This study shows the statistical optimization of the preparation of $g\text{-}C_3N_4/ZnCr_2O_4$ heterojunctions in different proportions. The study showed that by designing Simplex-Centroid experiments, it is possible to obtain materials with improved photocatalytic properties and greater efficiency in the degradation of organic compounds, such as the azo dye tartrazine. The aggregation technique by the difference of surface load was used to prepare the g-CN/ZCO heterojunctions. g-CN is more significant than ZCO in the mixture, which indicates that when there is more g-CN the more efficient the heterojunction is in degradation, which was confirmed experimentally. The statistical desirability profile showed that the ratio of 75% g-NC and 25% ZCO is ideal and extremely showed higher efficiency in the removal of azo dye (99.5% efficiency).

Introduction

Heterogeneous photocatalysis (HP) is a promising technology to circumvent global environmental and energy problems. The degradation of organic contaminants and the production of hydrogen are examples of HP applications [1].

HP efficiently degrades persistent organic compounds such as azo dyes. Photocatalysis is based on the photoactivation of a semiconductor generating reactive species such as hydroxyl radicals (HO•) and superoxide (O_2^{-}•) with high oxidizing power, capable of degrading and mineralizing various organic compounds [1-2].

One of the main limitations of HP is the efficiency of the photocatalyst. The most applied semiconductors have limitations such as high bandgap energy (>3.0 eV), making it impossible to use visible and solar light; the high recombination rate of electron/gap pairs and the use of powder suspension that hinders the separation and reuse of the photocatalyst [3].

The search for ideal photocatalysts has led to the development of materials with improved photocatalytic properties, economically attractive with the possibility of long-term application [1-3].

Graphitic carbon nitride, $g\text{-}C_3N_4$ (g-CN), is a photocatalyst potential with electrical properties, active bandgap in visible light, high stability, non-toxic and easy synthesis [4]. Zinc chromate, $ZnCr_2O_4$ (ZCO), has been highly applied regarded due to its properties as active bandgap energy in visible light, high specific surface area, and stability, making this semiconductor attractive for photocatalytic applications [5].

The development of heterojunctions is an alternative to overcome the high recombination rate of electron/hole pairs in semiconductors [4].

Thus, this work aims to develop g-CN/ZCO heterojunctions with improved properties and photocatalytic activity in the degradation of tartrazine dye. Their use in the tablet form make them easily separated and reusable.

Material and Methods

1. $g\text{-}C_3N_4/ZnCr_2O_4$ heterojunction preparation

The aggregation technique by the difference of surface load was used to prepare the g-CN/ZCO heterojunctions with the preformed phases. Determining amounts of g-CN and ZCO were dispersed in 15 mL of ultrapure water and 15 mL of absolute ethyl alcohol, maintaining a pH between 6 and 8. The dispersion was maintained in an ultrasound bath for 40 minutes. The mixture remained for 12 hours in the greenhouse at 60ºC for complete drying. After drying, the sample was macerated and calcined for 2 hours at 300ºC. Finally, after calcination, the sample was pressed into a hydraulic press, forming 10 mm tablets used in the degradation tests of the organic pollutant. Figure 1(c) shows a simplified scheme for preparing g-CN/ZCO heterojunctions.

2. Statistical Optimization

For the statistical optimization of the preparation of heterojunctions, a Simplex-Centroid mixture experiment design was used (Table 1). The g-CN and ZCO components varied in percentage of mass. Two responses were evaluated: the percentage of efficiency in the degradation of the two absorption bands of the tartrazine dye, the first at 425 nm, the absorption band of the groups responsible for the color, and the band at 259 nm referring to the aromatic groups of the organic compound. Statistical optimization was performed using the Statistic 7.0 software.

3. Photocatalytic Tests

A batch photochemical reactor equipped with a cooling system and mechanical agitation was used for the photolysis and photocatalysis experiments. The radiation source was a low-pressure mercury vapor lamp (125 W, λ = 200-600 nm) coated with a glass bulb for visible radiation testing. Photocatalytic tests were performed with photocatalysts in the form of tablets deposited inside the reactor. Experimental conditions: azodye concentration 50 mg L-1; pH 6 (natural); 0.25g of photocatalyst; time 120 minutes; visible radiation.

Results and Discussion

The two components of the mixture are significant, i.e., both g-CN and ZCO play a key role in the efficiency of heterojunction. In addition to each isolated component, the interactions between the two components of the mixture are statistically significant. Despite the little difference between the photocatalysts, g-CN is more significant than ZCO in the mixture, which indicates that when there is more g-CN the more efficient the heterojunction is in degradation, which is confirmed experimentally (Figure 1).

One way to simultaneously optimize multiple responses is by applying a desirability function. This methodology is based on the transformation of each response into a dimensionless scale of individual desirability. The scale of individual desirability can range from 0 (for an unacceptable answer) to 1 (for the desired answer). When the desirability function is equal to 1 (Figure 2), we have that the ideal mixture between the components is 75% of the g-CN and 25% of the ZCO to obtain the desired responses. The highest degradation efficiency was 99.5% (at 425 nm) and 85.2% (at 290 nm).

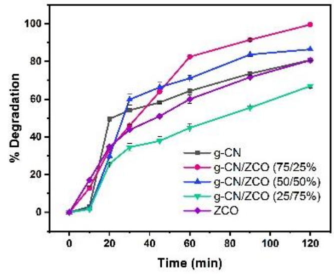

Figure 1. Comparison between the kinetics and degradation efficiency of tartrazine dye (425 nm) with the different prepared heterojunctions.

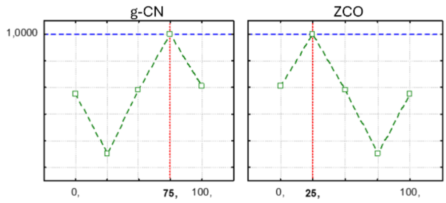

Figure 2. Desirability Profile.

Table 1. Experimental matrix of the design of Simplex-Centroid mixtures used to study the proportions in the preparation of g-CN/ZCO heterojunctions and efficiency in the degradation of tartrazine.

Experiment	$g\text{-}C_3N_4$ (%mass)	$ZnCr_2O_4$ (%mass)	%Degradation (425 nm)	%Degradation (259 nm)
1	100	0	80,7	68,5
2	75	25	99,5	85,2
3	50	50	86,5	70,3
4	25	75	67,0	35,6
5	0	100	80,6	68,6

Conclusions

In the preparation of new photocatalysts, such as heterojunctions prepared in this work, the statistical study of the proportions of each component is fundamental. The 75%g-CN/25%ZCO heterojunction showed improved photocatalytic activity compared to the isolated components and the other proportions tested. In addition, the use in the form of tablets allows easy separation and reuse of the heterojunction.

Acknowledgments

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