Graphitic Carbon Nitride Rare-Earth and Transition Metal Doping for Enhanced Photocatalytic Degradation of Contaminants

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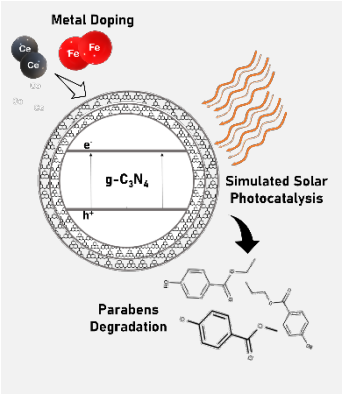

The use of graphitic carbon nitride light activated catalysts for the elimination of contaminants in water rises as an efficient and low-cost alternative. To increase the material's photoactivity, doping with foreign elements may be an option. The introduction of rare-earth and transition metals in the g-C_3N_4 structure was succesfully studied for parabens elimination under simulated solar light. The iron-doped and and cerium doped catalysts presented considerably higher degradations compared to the bulk material. The formation of inner electronic sub-levels, electron trapping sites and improved interaction between catalyst and medium possibly provided by metal doping may contribute for the design of a more efficient and feasible catalyst for water treatment. Further characterization and investigation of reaction parameters will also be studied.

Introduction

Water reclamation is one of the main challenges of current and future generations. Suitable water management is essential to ensure sufficient potable water availability. In order to achieve this objective, the development of efficient water treatment technologies is fundamental, especially due to the inefficacy of conventional treatments encompassed in wastewater treatment plants (WWTPs), that are not designed to eliminate a large group of contaminants [1]. In front of this issue, Advanced Oxidation Processes (AOPs), such as ozonation and photocatalysis, become good alternatives, as they are based upon the production of highly efficient and non selective radicals, especially hydroxyl (·OH) [2].

The use of graphitic carbon nitride (g-C_3N_4) for the photocatalytic treatment of contaminants in water have gradually increased in recent years. The material synthesis uses low-cost precursors, nitrogen and carbon-rich compounds such as melamine and urea, that are typically applied in thermal polymerization reactions to obtain the final catalyst. Besides, g-C_3N_4 is known to possess activity under visible radiation, resulting in a more efficient use of natural sunlight for its activation, instead of the use of artificial radiation sources [3].

Despite the advantages of g-C_3N_4 materials for water treatment, some typical drawbacks still exists [4]. The recombination of the e^-/h^+, low surface areas and a less positive valence band may occur, decreasing its photoactivity. Catalyst doping is an alternative for catalyst modification, based on the introduction of foreign elements on the material's structure, possibly resulting in the formation of new electronic sub-levels, increased surface areas and photocarriers trap sites, etc [2].

Thus, the main objective of this study is to evaluate the benefits of the incorporation of diferent metals, both rare-earth and transition, into the structure of graphitic carbon nitride, for the the degradation of contaminants in water under solar radiation.

Material and Methods

The g-C_3N_4 catalysts synthesis, melamine used as the C/N precursor, citric acid (CA) was used for catalyst modification, and iron and cerium nitrate were used as the Fe and Ce dopant precursors, respectively.

For the Fe-doped g-C_3N_4 (FeCN), melamine and iron nitrate were added to 100 mL of ultrapure water and stirred at 80 °C for 1 h. For the cerium doped (CeCN) and citric acid (CACN and CeCACN) catalysts, the precursors were simply combined and ground until fully mixed. After preparation, the materials were subjected to thermal polymerization, at 550 °C for 4h (5 °C min^{-1}) [3]. After cooled, catalysts were ground, washed with methanol then dried at 60 °C for 12 h. Undoped catalyst (CN) was also synthesized with the same procedures.

For the photocatalytic tests, a 250 mL glass reactor was used, under magnetic stirring. The contaminants solution used in all reactions was prepared using 1 mg L^{-1} methyl-, ethyl- and propylparaben in ultrapure water. The catalyst load was 200 mg L^{-1}. Prior to each test, catalysts were kept for a period in the dark, to obtain adsorptive equilibrium. Ossila Solar Simulator was used as light source, operating at 100 mW cm^{-2}.

Results and Discussion

Parabens degradation along the 120 min reaction time are present in Figure 1. To evaluate the influence of the radiation source, a photolysis reaction was also performed, and no significant removals oft he contaminants were found. The bulk g-C_3N_4, CN, alone presented only a slight decrease in contaminants concentration, 6-8% [3]. Additionally, no alterations of concentration in the dark test was found for any catalyst, ruling out the impact of adsoption on the contaminants removal.

Iron doping demonstrated a considerable increase in photocatalytic performance of g-C_3N_4, with FeCN resulting in around 23% removal of parabens. The Fe^{3+} introduced into the catalyst interlayers may act as an effective electron trapping site, easily been reduced into Fe^{2+}, delaying the photocarriers recombination. On the other hand, Fe^{2+} is unstable enough to also be oxidize to Fe^{3+} again, decreasing its deactivation after reaction [2].

The incorporation of cerium also improved the parabens elimination, to 21-23%, similarly to FeCN. Lanthanides such as cerium present a unfilled f-orbital, which not only may act as electron trapping sites, but may also form complexes with the functional groups of organic pollutants, optimizing the interaction of the catalyst with the medium [2].

The CACN catalyst resulted in a similar degradation profile of the bulk material, indicating that no significant alteration of the catalyst activity was obtained after citric acid modification for the tested conditions. Nonetheless, when the modified material was doped with cerium, CoCACN, the catalyst obtained the highest degradation among the analyzed materials, 30-32%, indicating a synergic effect. The combined incorporation of cerium and citric acid modification may provide a higher formation of oxygen and nitrogen vacancies, and modifications of the band gap energy.

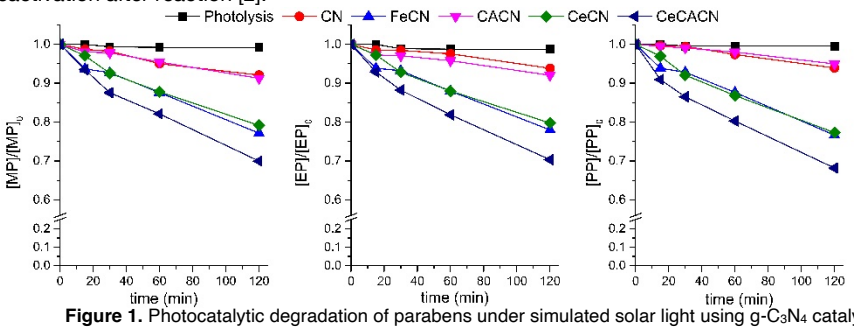

Figure 1. Photocatalytic degradation of parabens under simulated solar light using g-C_3N_4 catalysts.

Conclusions

The different doped materials were succesfully synthesized and applied for the parabens elimination. The performance of g-C_3N_4 under simulated solar radiation was significantly improved, except for the simple modified citric acid catalyst. The cerium codoped CeCACN had the highest degradation observed, benefiting from the synergic effects between the modificed catalyst and dopant. Further study of dopant amounts, evaluation of different reaction parameters and characterization of the synthesized catalyts may provide more detailed insights of the benefits of the g-C_3N_4 metal doping.

Acknowledgments

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