Study on the photodegradation of pharmaceuticals using graphitic carbon nitride derivatives

Eleonora RUSSO[*,1], Eryk FERNANDES[2], João GOMES[2], Paolo SGARBOSSA[1], Rui C. MARTINS[2]
[1]*University of Padua, Department of Industrial Engineering, via F. Marzolo 9, 35131, Padova, Italy.*
[2]*University of Coimbra, Department of Chemical Engineering, rua S. Lima, 3030-790, Coimbra, Portugal*
** eleonora.russo.2@phd.unipd.it*

Significance and Relevance

Non-conventional derivatives of graphitic carbon nitride (g-C_3N_4) doped with bromine have been synthesized for the application to wastewater photocatalytic depollution from emerging pollutants. The influence of different brominated precursors was tested: melamine bis-hydrobromide, 2-Bromobenzonitrile, and 4-Bromo-N,N dimethylaniline. As model pollutant pharmaceuticals an antibiotic (sulfamethoxazole) and a beta-blocker (atenolol) were chosen. In the case of sulfamethoxazole, the removal efficiency with four of the photocatalysts tested reached a value higher than 95% after two hours of treatment, under irradiation with a visible light lamp. In the case of atenolol, similar results were obtained.

Preferred and 2nd choice for the topic: Water treatment or photocatalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Graphitic carbon nitride is a semiconductor material with stacked nanosheet structure that can be synthesized from easily applicable, economic, and eco-friendly procedures, such as thermal condensation. Nonetheless, pure g-C_3N_4 has drawbacks which limit its utilization as a photocatalyst, due to the fact that it can only absorb in the blue light region of the solar spectrum. Furthermore, it has a low specific area and fast recombination of the photogenerated election-hole pairs[1]. In order to overcome these drawbacks, some modifications such as heteroatom doping, copolymerization with non-metal compounds, deposition of noble metals, construction of heterostructures have been considered[2]. In the work by Bresolin et al. (2021)[3], the thermally induced copolymerization of melamine and 2-bromobenzonitrile was performed, producing a g-C_3N_4 derivative with a lower band gap of 2.55 eV and good photocatalytic properties in the degradation of Rhodamine-B. In this case, different doped graphitic carbon nitride materials have been synthesized. They were obtained starting from three different brominated precursors: melamine bis-hydrobromide, 2- Bromobenzonitrile, and 4-Bromo-N,N-dimethylaniline. The materials obtained were tested on the photodegradation of pollutants of emerging concerns.

Materials and Methods

Two different approaches were pursued for the thermal synthesis of the melamine mixture, namely a muffle treatment in air and in a vertical pyrolizer under inert atmosphere. In the muffle, a crucible was placed for 2h at 550 °C. The same procedure was carried out in the pyrolizer, with a N_2 constant flow of 1 mL/s, for 2h at 550 °C, aiming to make a comparison between different conditions of thermal treatment. The general testing procedure was performed as followed: 60 mg of photocatalyst were added to 200 mL of a 1 mg/L solution of pollutant to treat and stirred in a beaker. The first 30 minutes of the test were conducted in dark conditions to evaluate the adsorption effect. The system was then

irradiated with visible light. Samples of the solution were analyzed by HPLC to determine the pollutant concentration.

Results and Discussion

Concerning the results obtained for the photodegradation of sulfamethoxazole, the removal efficiency with almost all of the eleven photocatalysts tested reached a value higher than 95% after two hours of treatment under irradiation with a visible light lamp. Similar results have been obtained after 80 minutes of treatment in the case of irradiation with direct sunlight (Figure 1). In the case of atenolol similar results were observed.

Considering that nowadays pollutants of emerging concern are frequently detected in wastewater and aquatic environments worldwide at concentrations ranging from ng/L to µg/L and that they cannot be completely removed in conventional wastewater treatment plants, graphitic carbon nitride possess promising features to be an alternative to common wastewater treatment methods in the next future.

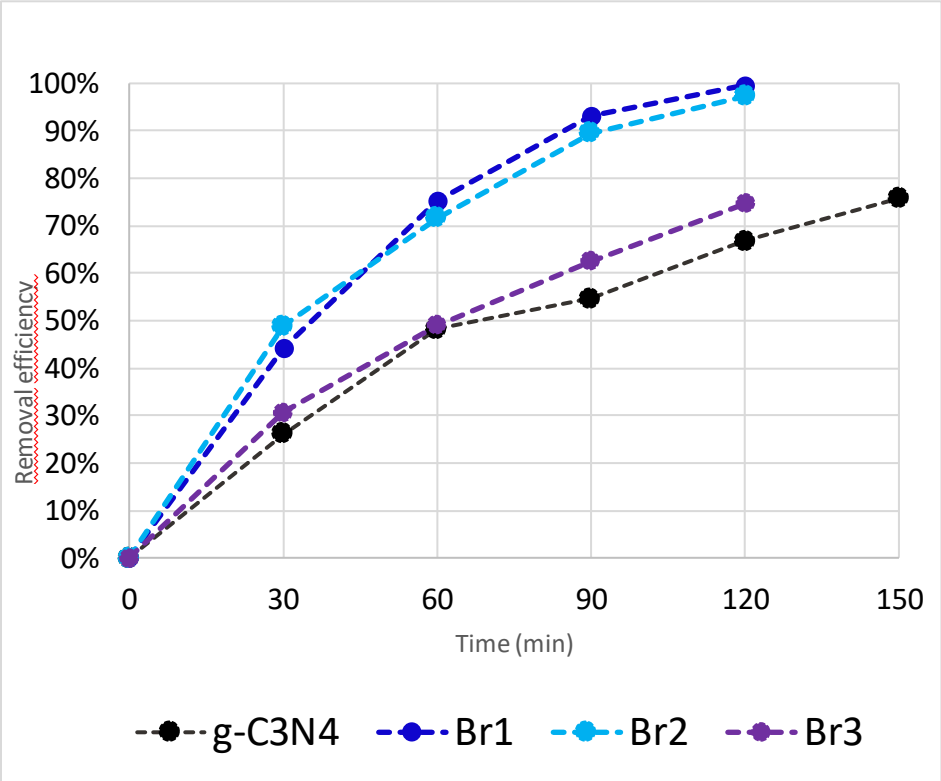

Figure 1 Removal efficiency of four of the produced photocatalysts in the degradation of sulfamethoxazole, under sunlight irradiation.

References

1. S. Patnaik, S. Martha, K. M. Parida, *RSC Advances* **2016**, 46929–46951, 6(52).
2. Y. Li, R. Jin, G. Li, X. Liu, M. Yu, Y. Xing, Z. Shi, *New Journal of Chemistry* **2018**, 6756–6762, 42(9).
3. B. M. Bresolin, P. Sgarbossa, D. W. Bahnemann, *Journal of Environmental Chemical Engineering* **2021**, 106389, 9(6).

Acknowledgements

The authors wish to thank the Department of Industrial Engineering (UniPD – DII) for financing the HYPURE SID2023 project and the Department of Chemical Engineering (DEQ – UC).