Visible Light Photodegradation of Selected Antibiotics with g-C_3N_4 Thin Films in a Photo-Microreactor

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Highlights

- g-C_3N_4 was synthetized from melamine and cyanuric acid
- Photodegradation of antibiotics (tetracycline, trimethoprim, sulfamethoxazole) with g-C_3N_4 was observed under visible light
- g-C_3N_4 in form of powder and thin film was tested in a batch photoreactor and in a photo-microreactor respectively
- Specific initial reaction rates of all pollutants obtained from both reactor types were compared

1. Introduction

Graphitic carbon nitride (g-C_3N_4) has emerged as a noteworthy metal-free photocatalyst, capturing considerable attention from researchers due to its advantageous physical, chemical, and electronic properties. Its utility extends to applications in photo and electrocatalysis, pollutant degradation, water splitting, heterogeneous catalysis, and various other fields. Notably, g-C_3N_4 possesses a lower band gap (2.7 eV) compared to TiO_2 (3.2 eV), suggesting promising light harvesting capabilities, particularly within the visible solar light spectrum. This contribution focuses on the development of thin films of g-C_3N_4 and their evaluation in pollutant photodegradation through testing in a photo-microreactor (PMR) with a slit geometry.

2. Methods

In this study, g-C_3N_4 was synthesized through the calcination of a supramolecular complex comprising melamine and cyanuric acid at 550°C in nitrogen atmosphere, yielding g-C_3N_4 with enhanced photocatalytic activity [1]. Films of g-C_3N_4 were then prepared using a mixture of ball-milled g-C_3N_4 and a binder. These thin films, with an average thickness of 27 µm, underwent surface modification through plasma treatment to impart excellent hydrophilic properties. The resulting photocatalytic films were tested in a photo-microreactor (PMR) featuring a slit geometry and results compared to tests conducted in a batch photoreactor (BPR) with photocatalysts in form of a slurry. Rhodamine B (RhB), a fluorescent dye, was used as a reference substance, further the study focused on the degradation of three specific antibiotics—tetracycline (TC), trimethoprim (TMP), and sulfamethoxazole (SMX)— as emerging wastewater pollutants. The degradation products were analyzed using HPLC-MS, and potential degradation pathways were elucidated.

3. Results and discussion

The flow-through PMR was operated as a differential reactor with negligible conversion at single pass. In case of PMR, the reaction volume of 432 µl was irradiated continuously, while the reaction mixture of 25 ml was circulated within a loop at the flowrate of 63 ml/min. This is in contrast to the BPR, where the whole reaction volume of 25 ml was irradiated continuously. To be able to compare the data from BPR and PMR, the effective time of irradiation was calculated in case of PMR. The effective irradiation

time in case of PMR was obtained by dividing the common time by the ratio of reaction mixture volume and a PMR volume. The dependencies of pollutant concentration as functions of time were obtained via HPLC-MS analysis. The kinetics constants were calculated assuming first order of reaction with respect to pollutant concentration. The data from both reactors were compared by a specific initial reaction rate r_0 evaluated by the formula below, where k is the kinetic constant, c_0 pollutant initial concentration and m_{cat} mass of the used catalyst in the reaction volume.

$$r_0 = \frac{k \times c_0}{m_{cat}}$$

The described reactor comparison required identical irradiating conditions that were ensured by having the same frontal irradiated area of BPR and PMR, the same distance from the light source and all other relevant conditions of the tests identical.

Pollutant	$r_{0,BPR}$ [$mg_{poll}\ mg_{kat}^{-1}\ l^{-1}\ min^{-1}$]	$r_{0,PMR}$ [$mg_{poll}\ mg_{kat}^{-1}\ l^{-1}\ min^{-1}$]	$\frac{r_{0,PMR}}{r_{0,BPR}}$
RhB	0.140 ± 0.002	1.5 ± 0.4	10.5
TC	0.153 ± 0.005	1.45 ± 0.35	9.5
TMP	0.05 ± 0.01	1.32 ± 0.04	25.4
SMX	0.0016	0.30 ± 0.02	186

The table above shows higher specific initial reaction rates obtained in PMR compared to BPR. Surprisingly, the reaction rate enhancement in PMR, as evidenced by the ratio r_{PMR}/r_{BPR}, differed among tested pollutants. The highest enhancement of the specific initial reaction rate was achieved for the photodegradation of SMX, namely the specific reaction rate was 186 times higher in the PMR compared to BPR. The second highest improvement was achieved for photodegradation of TMP, followed by RhB and the last was TC. It is worth noting that the achieved conversions of SMX in BPR was 11% and 45% in PMR. Only a partial mineralization of pollutants was obtained since the reaction intermediates of high molecular weight were detected after 60 min of reaction. Nevertheless, the conversion of TC, TMP and RhB in both PMR and BPR was always higher than 87%.

4. Conclusions

Three chosen antibiotics were subjected to photodegradation under visible light using the g-C_3N_4 catalyst in form of a powder (batch photoreactor, BPR) or in form of a thin film (photo-microreactor, PMR). The highest specific reaction rates in PMR were achieved during the photodegradation of tetracycline (TC), followed by trimethoprim (TMP) and then sulfamethoxazole (SMX). Even though the biggest rate enhancement of photodegradation rate of g-C_3N_4 in PMR was achieved with SMX, the overall relatively low SMX conversion suggests its high stability under the conditions of the experiments. On the other hand TC and TMP showed much lower stability in comparison with SMX due to their significantly higher conversions in both BPR and PMR, however their mineralization was only partial even after 60 min of reaction.

Acknowledgments

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References

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Keywords

Photochemistry; g-C_3N_4; antibiotics; photo microreactor; thin film