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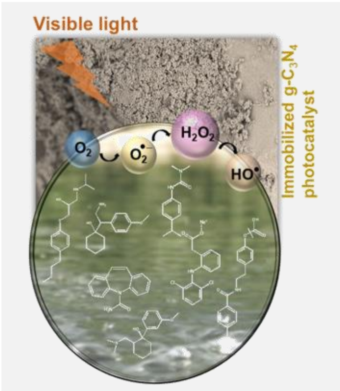
Innovative Solutions for Efficient Photocatalytic Removal of Micropollutants with Immobilized Carbon Nitride Materials

Maria J. Sampaio[1,2]*, Manuel Peñas-Garzón, Ana Rita L. Ribeiro*[1,2]*, Adrián M.T. Silva*[1,2]*, Cláudia G. Silva*[1,2] *Joaquim L. Faria. (1) LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, Porto, 4200-465, Portugal, (2) ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, Porto, 4200-465, Portugal. Email: mjsampaio@fe.up.pt*



Despite the progressive advances in technologies employed in Urban Wastewater Treatment Plants - UWWTPs, the presence of organic micropollutants (MPs) in the environment has been raising a great concern, in particular those found in surface waters (levels of ng L^{-1} and µg L^{-1}). Thus, the exploitation of far-sighted and holistic technologies to attenuate harmful emerging pollutants in water are imperative nowadays. In the field of photocatalytic applications, the catalysts are mostly used as slurries, and several practical problems arise from the use of a catalyst in powder form. Here, we propose efficient photocatalytic systems based on immobilized polymeric carbon nitride materials responsive to solar light to remove MPs commonly found in actual wastewaters.

Introduction

The technologies employed in UWWTPs are quite efficient to remove most of the organic compounds. However, the identification of organic micropollutants (MPs) in water matrices, such as river, tap, wells, lakes, etc., has been a matter of considerable concern. Some recommendations were launched in the European Union (EU) to monitor harmful substances in water environments, such as Directive 2013/39/EU, which identifies a group of 45 priority substances/groups and recommends the development of new treatment strategies. The current Watch List of CECs, published in Decision 2022/1307, includes 26 compounds (such as pharmaceuticals and metabolites, pesticides, and sunscreen agents). These findings suggest that conventional processes are ineffective for the degradation of these refractory contaminants, which led to intense research into the use of heterogeneous photocatalysis as a promising quaternary method for water treatment. This technology can generate highly reactive species (*e.g.*, hydroxyl and superoxide radicals), photogenerated holes and electrons that can interact in a non-selective manner with the persistent MPs, leading to their degradation. Graphitic carbon nitride (g-C_3N_4) has been pointed out as a promising catalyst for photocatalytic application operating under solar energy [1, 2].

This work describes the synthesis and characterization of g-C_3N_4, seeking enhanced photocatalytic performance towards removing MPs using a low-cost and energy-efficient LED visible light source. The study presents a solution for eliminating these pollutants using a responsive solar light material immobilized as a film and on a cylindrical structure of poly(lactic acid) (PLA) designed by 3D printing technology. This approach avoids an additional step to recover the catalyst from treated water and prevent the leakage of nanoparticles into the environment.

Material and Methods

A g-C_3N_4 photocatalyst synthesized by thermal condensation of dicyandiamide with a post-treatment at 500 °C (CN-D) and a g-C_3N_4 synthesized using urea as precursor (CN-U) were immobilized in as a polymeric film and on a 3D printed structure, respectively. The efficiency of the immobilized photocatalysts was evaluated in the degradation of MPs detected in both a spiked distilled water sample, containing various MPs, and a non-spiked UWW sample under visible LED irradiation. In addition, the robustness of CN-D and CN-U immobilized supports were examined under batch and continuous flow modes.

Results and Discussion

The SEM images revealed that the morphologic characteristic of carbon nitride materials remained after the immobilization on both supports (film and 3D structure (Fig. 1a). Different areas of the g-C_3N_4-

film revealed that this coating is constituted by two phases, *i.e.*, by PVDF polymer (dashed squares) and g-C_3N_4 powder (dashed circles). Comparing the cross-section micrographs of the g-C_3N_4-3Dstruct photocatalyst to the neat PLA support (Fig. 1a and 1b), it can be observed that the g-C_3N_4 particles are successfully anchored over the surface.

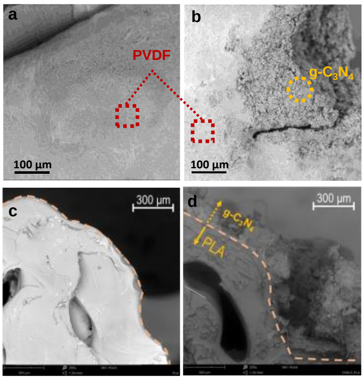


Figure 1. SEM images of (a) neat PVDF, (b) g-C_3N_4-film, (c) neat PLA structure and (d) g-C_3N_4-3Dstruct.

Considering the complexity of environmental matrices and to better understand the effect of the presence of the several species involved in the reaction medium, the photocatalytic performance of the g-C_3N_4-3Dstruct was examined [1]. This was done using a spiked distilled water sample for the degradation of different MPs (1.8 µM of each MPs) (Fig. 2).

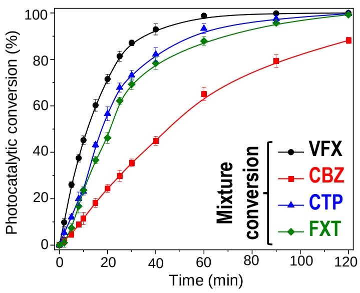


Figure 2. Conversion of a mixture of emerging pollutants using the g-C_3N_4-3Dstruct under visible LED irradiation.

An apparent similarity can be observed between the individual and the mixture of contaminants, yielding the total degradation of compounds with differences in their chemical structure, as in the case of venlafaxine (VFX), citalopram (CTP), and fluoxetine (FXT). On the other hand, a lower conversion tendency was displayed by carbamazepine (CBZ), probably ascribed to a superior refractory character for the breakdown of the olefinic double bond on the central heterocyclic ring.

The photocatalytic performance of the g-C_3N_4-film was examined in a non-spiked WW sample for the degradation of other MPs found in the UWWTP effluent (Fig. 3). For that, the samples collected before and after treatment, were pre-concentrated by SPE to ensure the quantification of the MPs [2].

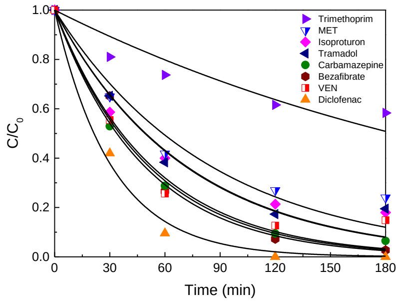


Figure 3. Photocatalytic degradation of MPs detected in the non-spiked WW sample using g-C_3N_4-film under visible LED irradiation.

The g-C_3N_4-film revealed high efficiency for the degradation of MPs found in an actual non-spiked UWW sample. These results corroborate that the presence of numerous and unknown species present in the water matrix are responsible for the decrease on the efficiency of the photocatalytic process.

Conclusions

Despite the challenging technological solution attained with this study, further research is still needed concerning the optimization of various parameters, aiming to enhance the process performance under continuous flow mode. This includes the study of the light distribution inside the reactor, the area of the immobilized catalyst, the design and volume of the reactor, the flow rate, and the development of empirical kinetic models to predict the effect of the species occurring in water streams.

Acknowledgments

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