$g\text{-}C_3N_4$/PDMI@MOF-74(Ni) mediated photocatalytic degradation of metoprolol and propranolol under UV/visible radiation

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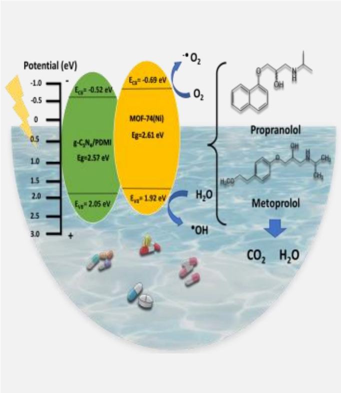
V.A. Herrera-Doñez, L. Hinojosa-Reyes, A. Hernández-Ramírez, ***M.L. Maya-Treviño****, J.L. Guzmán-Mar*, Universidad Autónoma de Nuevo León, UANL, Facultad de Ciencias Químicas, Av. Universidad S/N, Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66455. México. *E-mail* jorge.guzmanmr@uanl.edu.mx



Heterogeneous photocatalysis using MOF-74(Ni) 5.0% wt. coupled in $g\text{-}C_3N_4$/PDMI material was evaluated in the degradation of metoprolol (MET) and propranolol (PRO). The $g\text{-}C_3N_4$/PDMI@MOF-74(Ni) 5.0% (CNP@MOF 5%) catalyst was synthesized by the solvothermal route and characterized by UV-Vis/DRS, PL spectroscopy, XRD, and N_2 physisorption techniques. The photocatalytic experiments were carried out in an aqueous medium at pH 7 under UV/Vis light. The prepared composite showed improved activity compared to $g\text{-}C_3N_4$ and $g\text{-}C_3N_4$/PDMI in MET and PRO degradation, allowing complete degradation of the compounds in 90 and 105 min, respectively. The enhanced activity was related to the mesoporous properties of the material (surface area, 6.56 m^2/g; and average pore size, 24.44 nm) as well as its reduced recombination rate.

Introduction

Emerging contaminants (ECs) in water have generated scientific concern due to these pollutants are unregulated and often adversely impact the environment. Among the drugs group considered ECs, MET, and PRO from the β-blockers family are commonly used to treat cardiovascular diseases and have been detected in wastewater treatment plants (WWTP) effluents (2 μg/L) [1]. Heterogeneous photocatalysis (HP) has been evaluated as an alternative for efficient EC degradation through the hydroxyl radicals (•OH) generation that exhibits a high oxidation potential. Graphitic carbon nitride ($g\text{-}C_3N_4$) is a widely used visible light response photocatalyst (Eg=2.7 eV) that shows low toxicity, photostability, and chemical stability in a wide pH range. However, its usage in HP is limited by the high e^-/h^+ pair recombination and low specific surface area (SSA, 15.31 m^2/g) [2,3]. Thus, polymeric structures such as pyromellitic diimide (PDMI) that present excellent photostability have been combined with photocatalysts acting as electron mediators [4], increasing the photocatalytic activity of semiconductors such as $g\text{-}C_3N_4$ [5].

On the other hand, the photocatalytic properties of semiconductors have been modified by incorporating metal-organic frameworks (MOFs) [6],[7] that retarded the recombination rate of photogenerated carriers and increased the SSA. The MOF-74(Ni) coupled in $g\text{-}C_3N_4$/PDMI catalyst was evaluated under UV/Vis light for the degradation of two drugs of the β-blocker family (MET and PRO) in an aqueous solution.

Material and Methods

The $g\text{-}C_3N_4$ was synthesized by direct heating of melamine in a muffle at 520°C for 4 h. Subsequently, $g\text{-}C_3N_4$ was pulverized, and PDMI was incorporated by heating at 280°C for 4 h ($g\text{-}C_3N_4$/PDMI, 50:50 % wt.). The $g\text{-}C_3N_4$/PDMI@MOF-74(Ni) composite was synthesized by the solvothermal method at 120°C for 24 h using 2,5-dihydroxyterephthalic acid and $Ni(NO_3)_2{\bullet}6H_2O$ as MOF precursor. The prepared materials were characterized by XRD, UV-Vis-DRS, PL spectroscopy, and N_2 physisorption techniques. The photocatalytic experiments were conducted in a batch reactor (100 mL Pyrex glass vessel) under UV-Vis light (100 W Hg lamp) with the lamp positioned above the reactor (7 cm). A 1 g/L catalyst amount was suspended in MET and PRO (8 mg/L each) solution at pH 7, and the suspension was stirred for 60 min in the dark for adsorption/desorption equilibrium; then, the lamp was turned on for up to 3 h of reaction. The samples were analyzed by HPLC to monitor the degradation of pollutants.

Results and Discussion

The diffractograms of the materials are shown in Figure 1A, demonstrating the successful preparation of the individual materials. $g\text{-}C_3N_4$ showed the crystallographic planes (100) and (002) (Figure 1A (a)) while MOF-74(Ni) showed the planes (100), (101), (200), (020), (221), and (331) (Figure 1A (b)) [2, 8]. In the $g\text{-}C_3N_4$/PDMI (Figure 1A (c)), the diffraction peaks related to the PDMI were observed at high intensity, while the (002) plane characteristic signal of $g\text{-}C_3N_4$ was appreciated at low intensity. Figure 1A (d) corresponds to the CNP@MOF 5% composite, where only crystallographic planes of g-

C_3N_4 were detected that could indicate the PDMI and MOF-74(Ni) were randomly assembled layer by layer on the surface of C_3N_4. However, the crystallite size of CNP@MOF 5% (4.87 nm) was larger than that of g-C_3N_4 (2.64 nm) and is related to better stability and enhanced charge transfer, which can lead to improved photocatalytic activity [10].

The intensity of PL spectra of CNP@MOF 5% (Figure 1B) ensured a decreased value after MOF-74(Ni) incorporation compared to g-C_3N_4/PDMI and g-C_3N_4, suggesting delayed e^-/h^+ pair recombination rate [10].

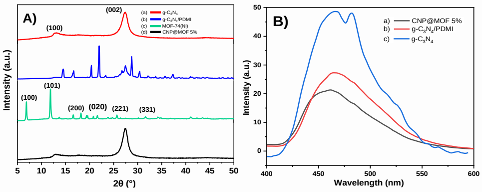


Figure 1. A) Diffractograms of **(a)** g-C_3N_4, **(b)** g-C_3N_4/PDMI, **(c)** MOF-74(Ni), and **(d)** CNP@MOF 5% and **B)** photoluminescence spectra of **a)** CNP@MOF 5% **(b)** g-C_3N_4/PDMI, **(c)** g-C_3N_4

Table 1 presents the results obtained by N_2 physisorption analysis. The materials are classified as mesoporous materials (2.29-24.44 nm), and the incorporation of the MOF-74 in g-C_3N_4/PDMI enhanced the surface area and pore size compared to g-C_3N_4/PDMI, which could increase the contact surface between material and pollutants during degradation. The Eg values of the materials calculated using the UV-Vis/DRS and Kubelka-Munk function (Table 1) indicated that incorporating MOF-74 to g-C_3N_4/PDMI did not modify the Eg showing visible light response.

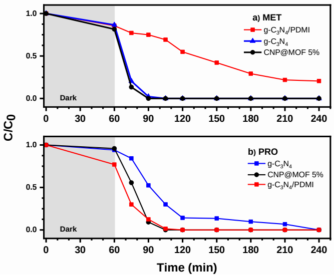


Figure 2. Degradation **a)** MET and **b)** PRO with g-C_3N_4, g-C_3N_4/PDMI, and CNP@MOF 5%.

The degradation of MET and PRO with the individual materials and CNP@MOF 5% are shown in Figure 2. As can be seen, the CNP@MOF 5% composite presented enhanced performance under UV/Vis light allowing the complete degradation of MET and PRO mixture in 90 and 105 min, respectively, than that of the pure g-C_3N_4 and g-C_3N_4/PDMI.

Table 1. Eg and textural properties of the prepared materials.

Material	S_{BET} (m²/g)	Pore size (nm)	Eg (eV)
g-C_3N_4	8.19	23.90	2.72
g-C_3N_4/PDMI	3.13	19.16	2.67
MOF-74(Ni)	256.32	2.29	2.45
CNP@MOF 5%^{a}	6.56	24.44	2.62

^{a}g-C_3N_4/PDMI@MOF-74(Ni)

Conclusions

The visible-light-driven mesoporous structured material was successfully synthesized by the solvothermal route. The incorporation of MOF-74(Ni) into g-C_3N_4/PDMI retarded the recombination rate of photogenerated carriers compared to g-C_3N_4 and improved the specific surface area than that of g-C_3N_4/PDMI, allowing superior photocatalytic activity in the degradation of MET and PRO mixture.

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