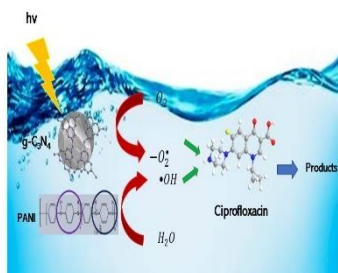


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The heterogeneous photocatalysis is an effective method for eliminating emerging contaminants. In this study investigates the use of composite catalysts formed by graphitic carbon nitride (CN) and polyaniline (PANI) for the elimination of ciprofloxacin in solution. The CN was synthesized using the hydrothermal method in the presence of cyanuric acid as a supramolecular agent. PANI was synthesized by chemical oxidation in the presence of 1M HCl as a doping agent. The g-C₃N₄/PANI (CN/PANI) composite was synthesized in - situ in the following mass proportions: 75:25, 85:15, and 95:5. The materials were characterized by FTIR-ATR and XRD to study their crystalline structure and morphology, respectively. According to the photocatalysis results, CN/PANI (95:5) eliminates 98% of the initial compound after 180 min of irradiation.

Introduction

The consumption of medicines can release active compounds known as emerging pollutants. Continuous exposure to these contaminants can lead to microbial resistance, endocrine disruption, and bioaccumulation in plants and animals.

Heterogeneous photocatalysis is an alternative to eliminate this emerging pollutant, in this research it is proposed to use metal-free catalysts such as semiconductor polymers instead of metal catalysts. These materials possess stability and optical properties that make them effective photocatalysts. Among the extensively studied semiconductor polymers are polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and others. Additionally, metal-free semiconductors, such as graphitic carbon nitride (g-C₃N₄), have shown promised results. However, g-C₃N₄ suffers from drawbacks such as the rapid recombination of photo degenerated electron-hole pairs and insufficient absorption of visible light [2]. In this research work, a synthesis method for the g-C₃N₄/PANI composite was studied to determine its structural and morphological properties and its influence on the photocatalytic degradation of ciprofloxacin in aqueous solution.

Material and Methods

Characterization

The crystalline phases and chemical compositions of the synthesized materials were investigated by FTIR-ATR on a PERKIN Elmer Spectrum 65 and X-ray diffraction spectroscopy with Bruker D2 Phaser diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), respectively.

g-C₃N₄ synthesis

g-C₃N₄ (CN) was synthesized by the hydrothermal method. 4g of melamine was mixed with 4g cyanuric acid in distilled water. The mixture was placed in an autoclave and heated at 180°C for 24h. Subsequently, the crystals were filtered and washed with water and ethanol several times. The material was dried in an oven at 60°C before being subjected to calcination at 550°C for 2h.

Synthesis of PANI and g-C₃N₄/PANI

PANI was synthesized by chemical oxidation in a semicontinuous system. A 1.19 mol/L solution of aniline was prepared with 1M HCl, the solution was placed in a cold bath at 2°C with constant stirring. Simultaneously, a 0.48 mol/L solution of ammonium persulfate (APS) was prepared with 1 M HCl as a solvent. This solution was added dropwise to the aniline solution using a Masterflex Model 07516-00 peristaltic pump over 6 h. A dark green powder was obtained, which was filtered and washed with water and dried in an oven at 60°C for 24 h. The synthesis of the g-C₃N₄/PANI (CN/PANI) was in-situ with the same previous methodology in a mass ratio of 75:25, 85:15 95:5.

Photocatalysis process

Heterogeneous photocatalysis of a 20 mg/L ciprofloxacin solution (CPX) prepared with distilled water was conducted in a 200 mL flat-side batch reactor. A catalyst concentration of 0.1 g/L was used. The reactor was irradiated during 180 min with two 400 nm, 50 W LED chip lamps placed at a 90° angle. The solution was continuously stirred at 300 rpm with a magnetic stirrer. The CPX elimination was monitored using HPLC.

Results and Discussion

Characterization

In figure 1b, the infrared spectrum of CN were identified at 3170 cm^{-1} , $1623 - 1217\text{ cm}^{-1}$, and 807 cm^{-1} . These correspond to the stretching vibration of the non-condensed N-H amino groups, C-N and C=N vibration in aromatic heterocyclic ring, and the triazine ring vibration of the nitride, respectively.

In contrast, figure 1a for PANI, the band at 1039 cm^{-1} is a vibrational mode of B-NH⁺=Q or B-NH⁺-B, which forms during doping reactions. The peaks at 1623 cm^{-1} and 1217 cm^{-1} are attributed to the C-N band stretching and the C-H vibration in the benzene ring. In figure 1c, the composite, the band at 1039 cm^{-1} disappears, likely because these charges interact with the CN [3].

In figure 2a, for CN, the peak at 12.8° corresponds to the (100) plane attributed to tris-s-triazine. The main peak is observed at 27.04° with an interplanar distance of 0.327 nm , corresponding to the (002) plane, interpreted as the graphitic structure. For PANI in the figure 2b, peaks at 20.6° and 25.3° correspond to the crystalline planes (020) and (200), respectively, confirming that PANI is in the emeraldine salt form. In figure 2c, the composite, with a higher proportion of CN, the peaks for CN are observed along with a slight shift of the 27.04° peak to 27.6° [4].

Evaluation

Figure 3 shows the comparison of photocatalytic processes (CN, CN/PANI (75:25,85:15 and 95:5)) used in the ciprofloxacin removal during 180 min. The CN/PANI 85:15 and 95:5 composites have CPX removal profiles like CN profile, probably the amount of generation of photogenerated species was similar. Nevertheless, the composites (CN/PANI) eliminated 95% of the initial concentration of CIPX at 150 min of irradiation. According to these results, there is not a significant difference between the photocatalytic activity of CN and CN/PANI during CPX removal. However, the effect of the presence of composite in photocatalyst was observed in the byproducts because their concentration was lesser than CN (data no showed). This demonstrated that

Conclusions

In the current work, a CN/PANI binary composite was developed via simple in-situ polymerization of aniline. While the composite displayed similar photocatalytic degradation efficiency for CPX compared to CN alone, it showed better efficiency in eliminating byproducts. This improvement is attributed to the composite's ability to enhance photogenerated charge separation, increasing redox capacity

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the composite favored the photogenerated species, eliminating not only the main compound but also its byproducts.

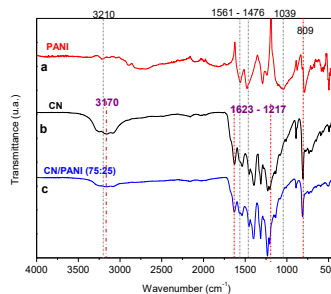


Figure 1. FTIR spectra a. PANI, b. CN y c. CN/ PANI (75:25)

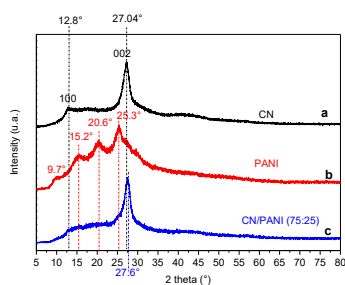


Figure 2. X-ray diffraction (XRD) patterns, a. CN, b. PANI y c. CN/PANI (75:25)

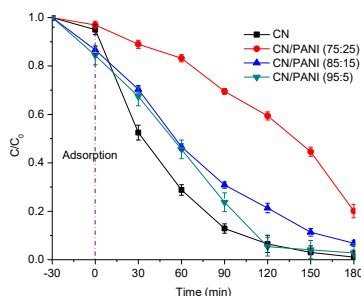


Figure 3. Comparison of photocatalysis of ciprofloxacin for system with CN, CN/PANI (75:25, 85:15, 95:5) 180min.