Preparation and Application of Floating Chitosan and TiO_2-Graphene Oxide Based Photocatalysts for the Degradation of Antibiotic Drug Mixture Under Simulated Solar Irradiation

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Introduction

TiO_2 is characterized by low quantum efficiency and wide band gap (3.0–3.2 eV, located at the ultraviolet (UV) wavelength range), resulting to limited performance under visible light, which reflects the highest percent of solar irradiation. Graphene oxide (GO) has been also used to extend the visible light response and improve the photocatalytic activity of the TiO_2 materials. as a promising support. Additionally, using chitosan as a carrier for TiO_2, chitosan-supported TiO_2 (CS–TiO_2) adsorbent has exhibited multifunctional performance for enhancing the adsorption–photocatalytic process of organic pollutants. Floating TiO_2 photocatalysts have also gained attention lately. Floatable photocatalyst can maximize the illumination/light utilization processes, especially in a system using solar irradiation. Under this light, the main goal of this study was the preparation and characterization of novel floating nanocomposite photocatalysts based on CS, TiO_2 and GO at different concentrations of TiO_2/GO in CS. The novel photocatalysts were applied under simulated solar light irradiation at the potocatalytic degradation of an antibiotic drug mixture, since the occurrence of this group of pharmaceuticals in the environment pose a large threat, due to their biological activity.

Experimental

Photocatalyst synthesis

Nanocomposite catalysts based on CS, TiO_2-P25 and GO were prepared with the solution mixing method. The amount of GO in each phocatalyst was 20 % of the weight of TiO_2. Briefly, a proper amount of CS was dissolved in an aquatic solution of 2% v/v CH_3COOH followed by the addition of a predetermined amount of GO. The mixture was stirred and sonicated for 1 h to achieve good dispersion. After that, TiO_2 was also added in the mixture and was stirred and sonicated for 1 more hour. The mixture containing CS, TiO_2 and GO was consequently stirred for 1 h, and finally it was precipitated in acetone, filtered and washed with deionized water. The final nanocomposites were freeze dried for the removal of the solvent. The final concentrations of TiO_2/GO in CS were 5, 10, 15 and 20 wt%.

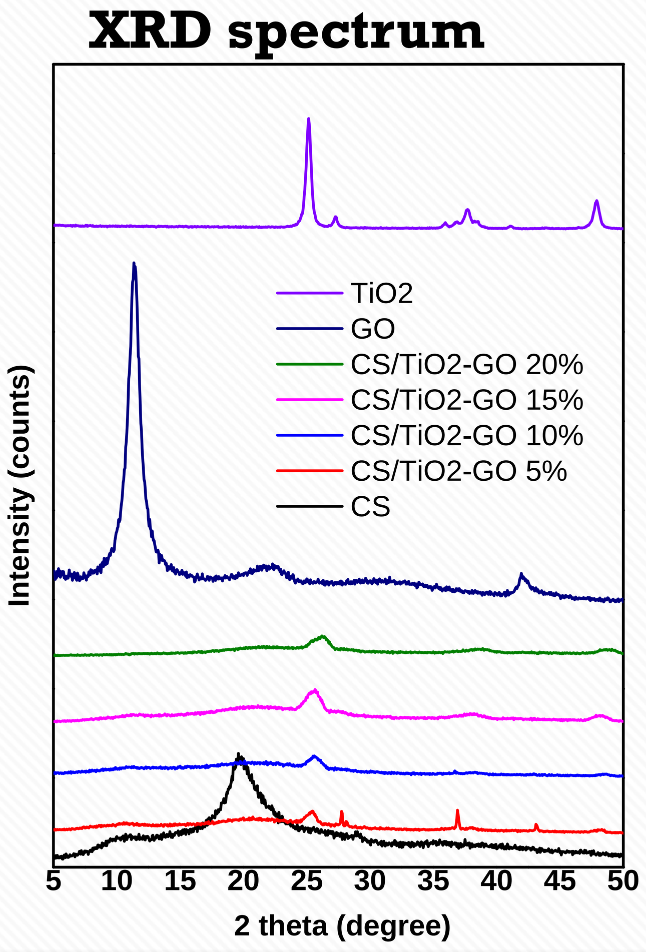
Photocatalytic degradation experiments

Photocatalytic experiments under simulated solar irradiation were carried out in a solar simulator Atlas Suntest CPS+ (Germany). Illumination was provided with a xenon lamp (1.5 kW) at an irradiance of 700 W m^{-2}. Irradiation experiments were performed using a Pyrex glass reactor containing 50mL of aqueous solutions, at 1g L^{-1} catalyst, while the pH was the inherent of ultrapure water, approximately 6.

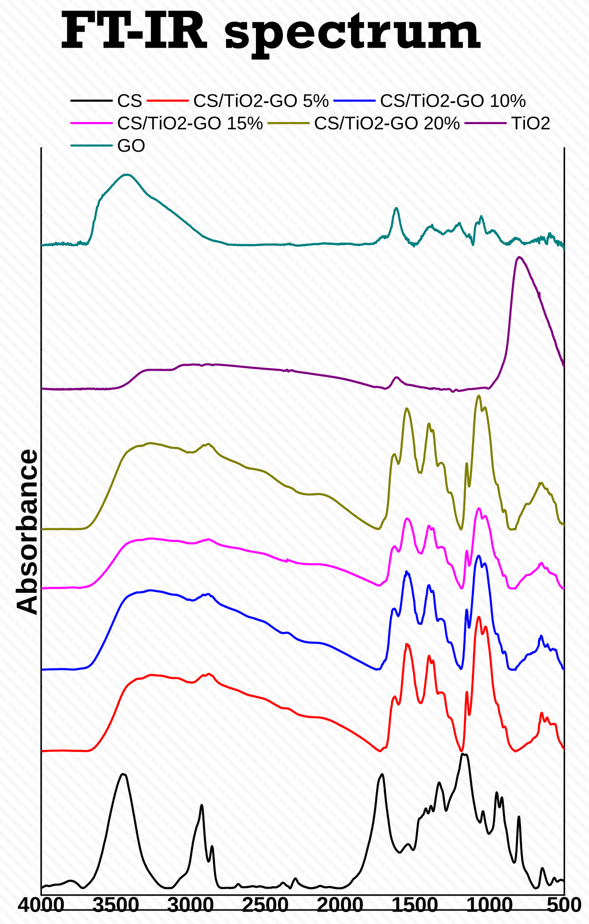
Sample	CS (g)	TiO_2 (g)	GO (g)
CS/TiO_2-GO 5%	1.9	0.08	0.02
CS/TiO_2-GO 10%	1.8	0.16	0.04
CS/TiO_2-GO 15%	1.7	0.24	0.06
CS/TiO_2-GO 20%	1.6	0.32	0.08

Results

XRD spectrum

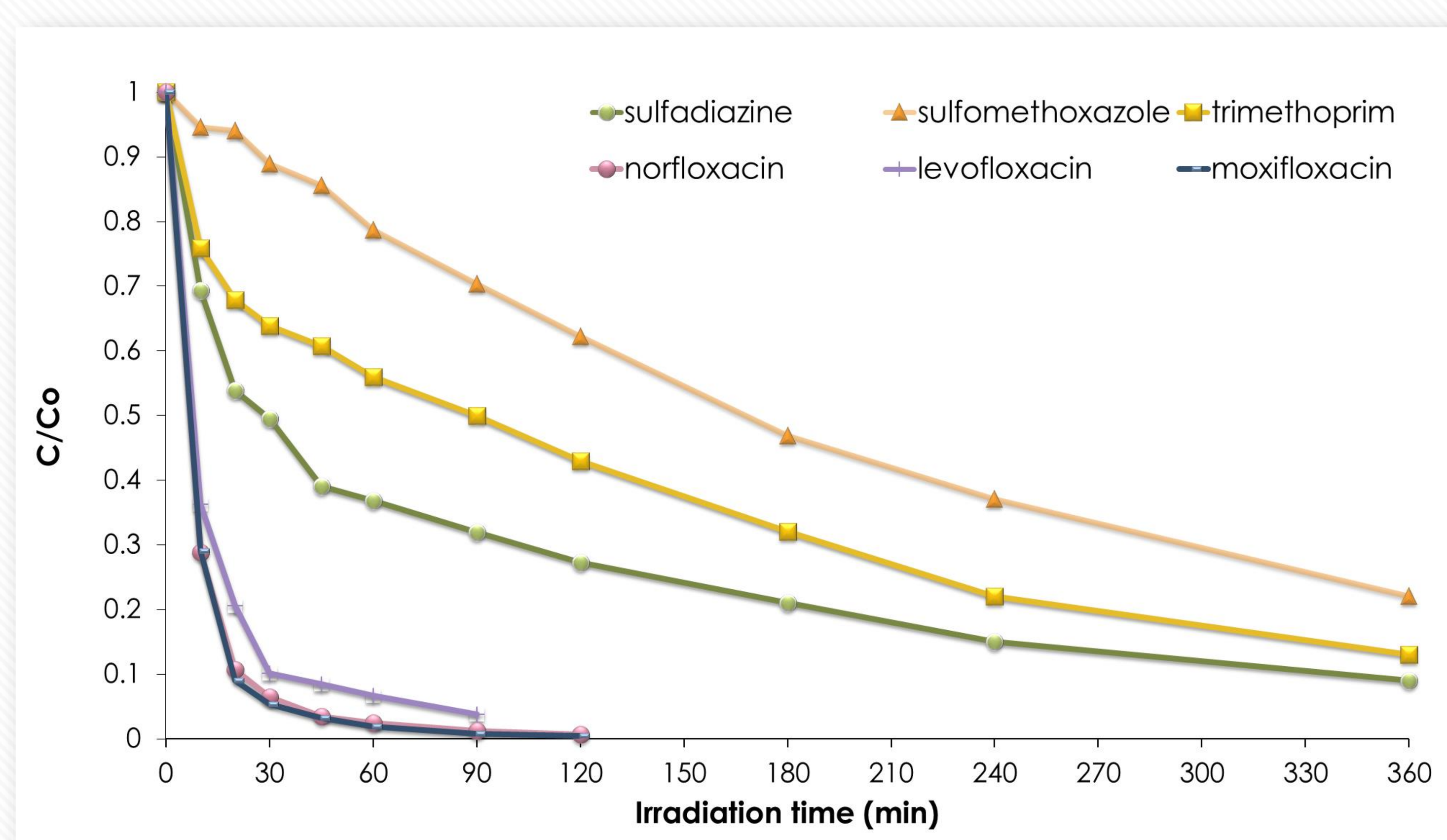


FT-IR spectrum



- *Composites exhibited diffraction peaks only ascribed to P25, which contained both anatase and rutile. The absence of the diffraction peak of GO suggests its full exfoliation in the CS matrix due to the sonication process that helps expand and separate the GO layers.*
- *The peaks at 1658 cm^{-1} and 1595 cm^{-1} that are due to the vibrations of NH_2 groups of CS shift to smaller wavenumbers in the nanocomposites and that shift is usually observed after the formation of hydrogen bonds between polymeric matrices and nanofillers. The hydroxyl groups of TiO_2 as well as the hydroxyl, carboxyl and epoxide groups of GO have the ability to bond with the hydroxyl and amino groups of CS.*

Degradation kinetics for CS/TiO_2-GO 20%



Conclusions

- All the synthesized materials maintained the photocatalytic properties of TiO_2.
- The mixture of selected antibiotics (1 mg/L of each) were almost completely eliminated in 360 min (except for sulfomethoxazole), under simulated solar irradiation, for 1 g/L of all the studied materials.
- An increase at the photocatalytic rate of antibiotics was observed at higher concentrations of TiO_2/GO in CS.
- However, at higher concentrations of TiO_2/GO, the hydrophilicity of the materials increases, leading to possible decomposition.

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