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PHOTOCATALYTIC COMPOSITE BEADS FOR METHYLENE BLUE AND IMIDACLOPRID REMOVAL FROM WASTEWATERS

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Introduction

The photocatalytic process is intensively investigated for advanced wastewater treatment targeting reuse, following its efficiency in removing organic emergent pollutants at low concentrations. Titanium dioxide, TiO_2, is the most commonly reported photocatalyst because it exhibits good stability in aqueous environments over a wide pH range, is easily manufactured, and is non-toxic. However, TiO_2 is a wide-bandgap semiconductor (E_g = 3.0–3.2eV) activated under UV irradiation, which leads to significant process costs. Various strategies have been proposed to extend the activation range towards the visible (Vis) spectral range. Recently, TiO_2 was coupled with graphitic carbon nitride (g-C_3N_4), a narrower bandgap semiconductor, to produce Vis (solar)-active composites with reduced electron-hole recombination, leading to higher photocatalytic efficiency. This paper reports on sol-gel photocatalytic composites with a TiO_2 matrix and g-C_3N_4 filler deposited on spherical glass substrates (beads), for advanced wastewater treatment.

Materials and methods

Vis/solar active composite films were deposited on glass beads (2 mm diameter) by the sol-gel method. The composite sol containing titanium tetra-isopropoxide, ethanol, acetylacetone, acetic acid, water, and different amounts of g-C_3N_4 dispersion was used for depositing thin films containing up to 10% (wt) of g-C_3N_4. In the diluted sols (sol: ethanol (v/v) = 1:1), glass beads covered with a TiO_2 thin seeding layer were immersed (30 min), under orbital stirring. The composite coated beads were dried (110 °C, 1h) and annealed (450 °C, 3h) to get crystalline films. The investigation of thin films structure (XRD), morphology (SEM, AFM) and composition (EDX, XRF) proved the incorporation of g-C_3N_4 in the TiO_2 -matrix and the formation of continuous composite films.

The influence of an intermediate TiO_2 seeding layer on the stability and photocatalytic performance of the films was also investigated.

The photocatalytic properties of the composites beads were tested in static regime, using methylene blue (MB) and imidacloprid (IMD) solutions, each with a 10 ppm concentration, and under low irradiance radiation, with different spectral composition: solar simulated radiation (UV + VIS, G_{total} = 55 W/m^2, G_{UV}= 3 W/m^2) and UV radiation (G_{UV}=3W/m^2), up to 8h.

Results and conclusions

Structural characterization (XRD) indicated a limited crystallinity degree of around 50% in both cases (with or without the intermediate TiO_2 layer). At the same time, XRF confirmed the presence of the g-C_3N_4 filler in the composite films. From a morphological point of view, the thin films present a continuous thin layer on which aggregates of different sizes and shapes can be found. These increase the area available for the pollutant molecules to adsorb and are pretty stable (they were not washed out even after 24 h testing in a static regime).

Promising MB photodegradation efficiencies of 55-65% were recorded after 8 hours of UV+VIS irradiation, with higher values (up to 10%) compared to those obtained under UV irradiation. IMD degradation showed a similar behaviour, but with lower efficiencies (~20-25%), indicating photocatalyst sensitisation when using MB.

Three successive photocatalytic cycles (~24 h) using MB or IMD (10 ppm) and UV-VIS radiation were conducted to assess the stability of the composite beads. Photocatalytic efficiency decreased after each successive cycle, indicating that the surface area becomes clogged with photocatalytic by-products. This necessitates the regeneration of the thin films for up-scaling.

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