Carbon-boosted stability of Cu-based Catalysts for Solar driven Photocatalysis

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A carbon-containing Cu-based photocatalyst was investigated for the degradation of a dye (tartrazine) under solar light at laboratory and in outdoor conditions in a pilot scale using a compound parabolic collector (CPC) photoreactor. The Cu@C catalyst is composed by ca. 20 wt.% of carbon and a nominal fraction of Cu of ca. 33 wt.%. The adsorption capacity, catalyst´s loading and initial concentration of the azo-dye were optimized. The potential use of the prepared catalyst was verified for the treatment of food-industry wastewaters containing tartrazine. Data revealed a 3 times faster degradation kinetics of tartrazine using the CPC photoreactor under natural solar light than in a slurry reactor under artificial solar light.

Introduction

Tartrazine -also known as yellow 5 (Y5)- is a synthetic azo dye used and accepted as a safe food additive in Europe and in US, frequently found in wastewaters derived from the food industry. Owing to some contradictory studies about its impact on health and its possible carcinogenic effects, the removal of Y5 from water courses has become an issue of concern. Heterogeneous photocatalysis is an effective solution for the degradation of azo dyes from wastewater. Although TiO_2 is the current benchmark photocatalyst, it presents important limitations that hinder large-scale application, such as a low surface area and limited absorptivity under solar irradiation (ca. 5–8%). This has triggered the interest for alternative semiconductors as photocatalysts. Among them, Cu-based oxides [1,2] have received much attention since copper is an abundant raw element. In this work, we report a comparative study of the catalytic performance of a C-containing Cu-based photocatalyst under artificial and natural solar light, in two photoreactor configurations, slurry and continuous flow.

Material and Methods

The C-containing Cu-based photocatalyst was prepared by a two-step procedure using furfural as carbon source and copper (II) acetylacetonate as metallic precursor [1]. The catalyst was labelled as Cu@C, and it was characterized by proximate and elemental analysis, gas adsorption, X-ray diffraction, and scanning and transmission electron microscopy. The performance of Cu@C catalyst for the degradation of Y5 dye was initially evaluated in at lab-scale in a batch slurry reactor under (artificial) simulated solar light. The optimized operating conditions (e.g., catalyst loading, dye initial concentration) were applied for the degradation at pilot scale using a (CPC) photoreactor in outdoor illumination conditions [2]. The results have been compared using different kinetic models.

Results and Discussion

Initially, the stability of the copper photocatalyst towards the leaching of the metallic species was evaluated in dark and irradiation conditions. Data revealed that the incorporation of a carbon phase in the photocatalyst prevents the lixiviation of the Cu-species [1]. The prepared Cu@C catalyst is composed by ca. 20 wt.% of carbon and a nominal fraction of Cu of ca. 33 wt.%. XRD patterns showed Cu, CuO and Cu_2O as the main crystalline phases; these are also considered the photoactive sites of the Cu@C sample, based on the optical characterization (e.g., a well-defined absorption edge above 600 nm ascribed to Cu_2O in the diffuse reflectance spectroscopy). Important parameters such as dark adsorption capacity, catalyst´s loading and initial concentration of Y5 were optimized under artificial light following the kinetics of degradation of the dye. These optimized conditions were applied also in the CPC photoreactor. Data revealed between 2.2 – 2.9 times faster degradation kinetics of tartrazine using the CPC photoreactor under natural sunlight than in the slurry reactor under artificial solar light (**Table 1**). This behavior is attributed to the combination of photoactive copper species and the carbon phase in the catalyst (boosting sunlight absorption) and the moderate photon flux conditions in the CPC (minimizing recombination). This is of paramount importance since most of the photocatalytic tests designed to evaluate the activity of novel materials are carried out under simulated solar light and disregard the impact of photon flux in outdoor conditions.

The mechanism of the photocatalytic degradation of yellow 5 (**Figure 1**) has been proposed in terms of the variation observed in scavenger kinetic studies. Additionally, total organic carbon (TOC) analysis revealed that organic carbon was photodegraded.

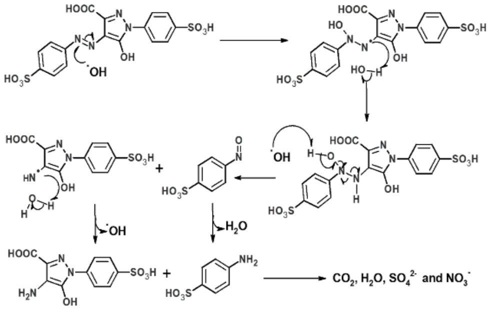

Figure 1. Proposed photodegradation pathway of yellow 5 with the Cu@C photocatalyst.

The photocatalyst was stable under natural solar irradiation in a continuous-flow CPC photoreactor. This is attributed to the protector role of the carbon matrix preventing the lixiviation of the copper species to the solution. Its photocatalytic performance is faster in natural solar light than under artificial irradiation. Overall, the prepared Cu@C photocatalyst is an economically sustainable, locally available, and efficient material to be applied for the degradation of Y5 dye from wastewater effluents by adsorption and heterogeneous photocatalysis under natural solar irradiation.

Conclusions

Table 1. Summary of adsorption in the dark and kinetic parameters of the photocatalytic degradation of Y5 using artificial UV-vis and natural solar irradiation. Initial concentration 2 ppm and 0.25 g L^{-1} catalyst loading.

Type of Irradiation	**η_{ads} (μmol g^{-1})** [a]	**k_{app} x 10^{-3} (min^{-1})** [b]	**R_1^2** [c]	**k_2 x 10^{-2} (L mol^{-1} min^{-1})** [d]	**R_2^2** [e]	**n_{deg} (%)** [f]
Natural solar irradiation	15.3 ± 0.3	5.5 ± 0.1	0.997	32.7 ± 0.9	0.968	100
Artificial irradiation	16.6 ± 0.5	2.5 ± 0.2	0.916	11.4 ± 0.8	0.932	63

[a] Y5 adsorption in the dark after 60 min; [b] 1st-order apparent rate-constant obtained from: $Ln(C_o/C_t) = k_{app}\cdot t$; [c] Quadratic factor according to a 1st-order reaction-rate; [d] 2nd-order apparent rate-constant obtained from: $(1/[C_t]) = [(1/[C_{Eq}] + k_2.t]$; [e] Quadratic factor according to a second-order reaction-rate; [f] Y5 conversion after 420 min irradiation defined by $n_{deg} = [1 – (C_t/C_o)].100$.

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References

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