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Development of TiO_2-C photocatalysts for solar treatment of polluted water

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ABSTRACT

Two different types of Carbon-containing TiO_2 photocatalysts were studied in depth. A hybrid TiO_2-C spherical material was prepared by solvothermal synthesis from furfural and titanium isopropoxide and compared to a binary TiO_2-activated carbon composite prepared using the slurry method. A systematic study of the catalyst concentration, type of pollutant molecule, the concentration of H_2O_2 and the type of irradiation (simulated solar irradiation and pilot-scale photoreactors) was performed. The influence of catalyst weight and H_2O_2 concentration was verified by following the kinetics of phenol (PH), imidacloprid (IM) and dichloroacetic acid (DCA) photodegradation. It may be concluded from the results that activated carbon promotes higher efficiency in the photoactivity of TiO_2 than the hybrid TiO_2-C photocatalyst. The basic surface chemistry and significant contribution of micropores in the binary TiO_2-AC composite seem to be responsible for their higher TiO_2 photoactivity than the TiO_2-C hybrid materials which are characterized by a mesopore structure and an acid surface pH. This study shows the advantage of using a solar simulator to elucidate the efficiency of carbon materials in a thorough comparison including various photocatalytic reactions with several different substrates before testing at pilot scale.

1. Introduction

Since the earliest reports on the influence of carbon-based materials on the photocatalytic activity of TiO_2 [1–7] they have attracted growing attention [8–38]. The many interesting results can be summarized as follows. Synergy between carbon and TiO_2 in the photocatalytic degradation of organic molecules was the first influence reported [1–6,28]. This phenomenon was attributed to the significant diffusion of pollutant molecules from the activated carbon to photoactive semiconductors through a common interface. Another important physical effect reported is photo-assistance [7–9,16,23] by electron transfer from the π^*-orbital of oxygen functional groups in carbon materials to the conduction band of TiO_2 leading to enhancement of superoxo $O_2^{\cdot -}$ radical formation.

A remarkably positive effect of activated carbons on TiO_2 has also been reported in consecutive cycles of photocatalytic degradation of organic molecules [10,17,30]. TiO_2 is able to retain the photocatalytic activity after several cycles due to the high adsorption capability of both the original pollutant and the main intermediates. Furthermore, the textural properties and chemical surface of carbon-based materials reportedly also influence TiO_2 photoactivity [6,11,12,14,15,22,24]. This suggests that not only the carbon surface functional groups have an important role in the mass diffusion of pollutant molecules, but also their texture, especially the micro and mesoporous framework.

On the other hand, despite the influence of carbon materials on product selectivity during the photooxidation of aromatic molecules, which is not very uncommonly discussed in photocatalytic studies, some interesting results have also been reported

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[16,18,20,21], showing that carbons with acid surface pH induce a remarkable increase in the formation of ortho-products by electrophilic addition reactions compared to the unimolecular nucleophilic substitution reactions forming the para-products observed in carbons with basic surface pH.

A more recent challenge led to studies on the influence of carbon-based materials for hydrogen photo-production by water splitting under UV–visible irradiation [19,20,26]. It should also be mentioned that both the intrinsically photochemical reactivity of carbon under monochromatic light [25,27,29] and harvesting of solar energy into nanoporous carbon are strongly influenced by the presence of heteroatoms such as sulfur [25,32], nitrogen [19,20,22,28], and oxygen [27,29–31].

Recent publications [32–38] have suggested interesting novel explanations for the influence of carbon on TiO_2 photocatalytic activity. The influence of the confining effects of the nanoporous framework of carbon materials on TiO_2 photoactivity, and even on an intrinsically photochemical reactivity of nanoporous carbons has been reported [32–34]. These studies have shown that not only the chemical surface but also the micropore volume has an important role in photocatalytic reactions under UV–visible irradiation. Hollow carbon spheres [35] have an important application in catalysis and photocatalysis because of such properties as their encapsulation ability, controllable permeability, surface functionality, high surface-to-volume ratios, and high chemical and thermal stability. An important contribution of carbon quantum-dots to carbon spheres in solar cells and photocatalysis applications under visible irradiation has recently been reported [36].

Three-dimensional photocatalysts with a network structure [37], with important applications, including solar energy storage and conversion, and photocatalytic pollutant degradation have also been described. A recent insight into binary TiO_2@C composites [38] showed the crucial effect of an interfacial microstructure between the two solids, as reported earlier by our research group [4,6].

Concerning to the influence of molecular carbon networks such as nanotubes and graphene upon the photoactivity of TiO_2, recent works have interesting results [39–47]. For example, graphene and carbon nanotubes are responsible of a clear enhancement in the activity of TiO_2 for the photo inactivation of bacteria such as *E. coli* [39,42,43] under solar light irradiation. By contrast, controversial results showed that graphene-TiO_2 photocatalysts can be responsible of the destruction of certain nematodes [40]. In addition, the incorporation of graphene oxide and carbon nanotubes to TiO_2 under visible light irradiation have shown an enhancement of the photocatalytic activity of the semiconductor in the photodegradation of azo-dyes such as methyl orange [41] and carcinogenic aromatic such as phenol [44]. It is also important to remark an interesting study about the photo stimulation of human neural stem cells on graphene/TiO_2 materials for the differentiation into neurons. This study shows important results for the application in neural regeneration and brain repairs [45]. It must be point out that for the case of graphene-based photocatalysts, some studies have reported that graphene oxide sheets were photodegraded by TiO_2 [39,46] or ZnO [47] along irradiation which is an indicative that long term stability studies must be performed with these type of composites before an appropriate scaling-up. In short, these works have shown not only the important role of graphene-based materials upon the photocatalytic activity of TiO_2 but also warm us of the destruction of minuscule animals of the environment by extensive application of graphene-TiO_2 photocatalysts, so the photocatalysts must be handle with care and properly disposed after reaction.

In addition, these studies have made very important fundamental contributions leading to a better understanding of the role of carbon materials in TiO_2-based photocatalytic reactions. However, most of them were conducted under laboratory controlled conditions using UV–vis lamps or artificial solar irradiation. In addition, most employed only one test molecule or at best two. In contrast, very few studies of carbon materials in photocatalytic reactions under real solar conditions have been published [5,16,39,40], and to our knowledge, none of them have employed solar irradiation and hydrogen peroxide simultaneously to simulate a water treatment plant methodology with more than one test molecule.

This study evaluated the influence of two different carbon materials on the photocatalytic activity of TiO_2. Photoactivity was tested under identical conditions to determine the efficiency of the photocatalysts. Three different substrates were chosen as the model molecules: dichloroacetic acid DCA (aliphatic organochloride), phenol, PH (aromatic) and imidacloprid, IM (N-containing insecticide and non-aromatic, highly water-soluble and stable). IM is an important test molecule, because it contains both pyridyl and imidazolidine rings, which make it of particular interest for the study of N-containing compounds during photocatalytic treatment. Testing and comparing the photocatalytic degradation of pollutants with different structures is of great interest, because it enables detection of any change in catalyst activity due to change in the nature of the pollutant. This strategy differs from that of most studies based on the degradation reaction of a single pollutant. It is well known that in photocatalysis the nature of the substrate affects the behavior of the catalyst. DCA, PH and IM have often been used to study photocatalysis and have been proposed for verifying the activity of photocatalysts under solar irradiation [48].

2. Materials and methods

2.1. Reagents and chemicals

Analytical grade furfural and titanium (IV) isopropoxide from Sigma-Aldrich, ethanol from VWR and ultra-high purity CO_2 were used for the synthesis of hybrid and binary samples. All solvents used for liquid chromatography analyses, acetonitrile (ACN) and ultrapure water (MiliQ) were HPLC-grade. The three compounds selected as model contaminants for this study were phenol (PH), imidacloprid (IM) and dichloroacetic acid (DCA), all high purity grade (>98%), also purchased from Sigma-Aldrich. Reagent-grade hydrogen peroxide (35% wt.) was provided by Panreac. All experiments were performed using 100–500 mg L^{-1} photocatalysts because this is the optimum concentration range for the solar photoreactors used in this study [49] as described in Section 2.5.

2.2. Synthesis of hybrid TiO_2-C photocatalysts

0.5 g furfural (Fu) and 0.5 g titanium (IV) isopropoxide were dissolved in 9 mL ethanol for typical solvothermal synthesis. The resulting solution was sealed in a glass vial inside a Teflon-lined autoclave, followed by the overnight solvothermal treatment at 180 °C. The resulting brown solid was filtered and thoroughly washed with absolute ethanol. The material was dried under static air at 100 °C for 2 h and labelled TiO_2-C.

Activated carbon powder was prepared from *Tabebuia Pentaphyla* sawdust by gasification under CO_2 flow at 800 °C for 1 h. This activated carbon was labelled AC. Then, a 10:1 TiO_2:AC binary composite was obtained by the slurry method by mixing about 250 mg TiO_2 P25 with 25 mg AC in 80 mL deionized H_2O. The slurry was vigorously stirred for 20 min at room temperature, and then filtered and dried for 2 h at 100 °C. The binary photocatalyst prepared by this method was labelled TiO_2-AC.