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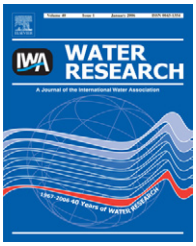

Preparation, stabilization and characterization of TiO_2 on thin polyethylene films (LDPE). Photocatalytic applications

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ABSTRACT

An innovative way to fix preformed nanocrystalline TiO_2 on low-density polyethylene film (LDPE-TiO_2) is presented. The LDPE-TiO_2 film was able to mediate the complete photodiscoloration of Orange II using about seven times less catalyst than a TiO_2 suspension and proceeded with a photonic efficiency of ~0.02. The catalyst shows photostability over long operational periods during the photodiscoloration of the azo dye Orange II. The LDPE-TiO_2 catalyst leads to full dye discoloration under simulated solar light but only to a 30% TOC reduction since long-lived intermediates generated in solution seem to preclude full mineralization of the dye. Physical insight is provided into the mechanism of stabilization of the LDPE-TiO_2 composite during the photocatalytic process by X-ray photoelectron spectroscopy (XPS). The adherence of TiO_2 on LDPE is investigated by electron microscopy (EM) and atomic force microscopy (AFM). The thickness of the TiO_2 film is seen to vary between 1.25 and 1.69 μm for an unused LDPE-TiO_2 film and between 1.31 and 1.50 μm for a sample irradiated 10 h during Orange II discoloration pointing out to a higher compactness of the TiO_2 film after the photocatalysis.

1. Introduction

In the field of environmental chemistry, semiconductor mediated photocatalysis has been the focus of recent attention since it aims at the destruction of contaminants in water under mild conditions. The objective in this field is to find innovative low cost processes that can use sunlight as the source of irradiation (Oppenlaender, 2003; Mills and Lee, 1997). Suspensions of TiO_2 as photocatalysts present two major drawbacks: (a) the separation of TiO_2 after the treatment, and (b) the low quantum efficiency of these processes. Suitable supports for TiO_2 have been reported recently such as: Nafion (Fernandez et al., 1999), Raschig rings (Bozzi et al., 2004), polyethylene-maleic anhydride copolymer (Dhananjeyan et al., 2001) and synthetic fabrics (Bozzi et al., 2005). Suitable thin film supports should present four properties: (a) withstand reactive oxidative radicals attack during light, (b) maintain adequate long-term catalytic stability, (c) preclude TiO_2 leaching during the light irradiation, and (d) allow photocatalytic reaction to proceed with an acceptable kinetics. The photocatalyst presented in this work shows these properties suitable for reuse during long-term reactor operation.

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The commercial use of polyethylene thin films is due to the single bond presence that makes this material stable towards chemical and/or corrosive agents. This film is a flexible semi-transparent low-cost commercial product. Polyethylene has excellent electrical properties making it widely used as insulator. The low-density polyethylene used consists of highly branched low crystalline units with the formula $H(CH_2CH_2)_nH$.

Few studies have reported the use of TiO_2 on thin polyethylene films as photocatalyst. Recently, TiO_2 films by sol–gel processing (Yu et al., 2000; Sung et al., 2004) and the degradation of organic compounds under light by TiO_2 fixed on foamed polyethylene sheet have been recently reported (Naskar et al., 1998).

This study presents LDPE-TiO_2 films as photocatalysts showing a stable performance during the photoinduced discoloration of Orange II. The photodiscoloration process will be shown to proceed with an acceptable kinetics having the advantage over nanocrystalline suspensions of TiO_2 requiring a much lower TiO_2 concentration per unit volume to photodegrade azo dyes. LDPE-TiO_2 films avoid the screening of the incident light as it is the case of TiO_2 suspensions. Studies involving the abatement of azo-dyes in suspensions of TiO_2 have been previously reported (Morrison et al., 1996).

In this study we report LDPE-TiO_2 thin films as photocatalyst in processes activated by simulated solar irradiation. We will present the details of the TiO_2 loading procedure. The use of XPS spectroscopy will give detailed information on the surface composition and profile of the outermost catalyst layers (at a few nanometers) involved in the dye discoloration process. The detailed dynamics of the photocatalysis leading to Orange II discoloration and the characterization of the catalyst structure are presented by suitable physical techniques.

2. Methods and materials

2.1. *Reagents and materials*

Reagents like acid and bases, dye material and H_2O_2 were pro-analysis (p.a.) from Fluka AG Buchs, Switzerland and used without further purification. Millipore-Q tri-distilled H_2O was used throughout this study. The photocatalyst TiO_2 Degussa P25 powder was a gift from Degussa AG, Bäar, Switzerland (Degussa, 1997). The LDPE (0.1 mm thickness) was obtained from Longfellow (ET3112019), had a density of $0.92\,g/cm^3$, an upper working temperature of 90 °C and a flowing point of 185 °C. The LDPE was prepared by Blown Film Extrusion manufacturing (blownfilm@reifenhauser.com, 1999). This process involves extrusion of a plastic through a circular die, followed by a bubble-like expansion allowing the production of flexible and tough polyethylene multi-layer films.

2.2. *Catalyst preparation*

A 10 g/l TiO_2 Degussa P25 solution was added to 200 ml isopropanol and aged for a day. The polyethylene film was then introduced in this suspension for 10 h and the film was dried afterwards in air at room temperature (23 °C). The dried film was then heated in an oven at 180 °C for 10 h to diffuse or entrain the nanocrystalline TiO_2 into the polyethylene film. Finally the LDPE-TiO_2 was sonicated for 15 min and washed with tri-distilled water four consecutive times to eliminate the loosely bound TiO_2 particles from the film surface. The pieces of LDPE do not deform at 180 °C and no pyrolysis of LDPE was observed. The Ti^{3+} centers were not observed since they would have induced blue color on the LDPE film (Kiwi, 1986).

2.3. *Irradiation procedures and analyses of the irradiated solutions*

The photodegradation of Orange II was carried out in small batch cylindrical photochemical reactors made from Pyrex glass (cutoff $\lambda = 290\,nm$) of 70 ml capacity containing 50 ml aqueous solution. The strips $48\,cm^2$ films of LDPE-TiO_2 were positioned immediately behind the reactor wall. Irradiation of the samples was carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air cooled at 35 °C. The light intensity in the cavity of the Suntest simulator at tuned at $100\,mW/cm^2$ (AM 1) was 2×10^{16} photons/sxcm^2. The Suntest Xe-lamp emitted 7% of the photons in the 290–400 spectral range. The integral radiant flux in the reactor cavity was monitored with a power-meter from YSI Corp. Colorado, USA. The absorption of the solutions was followed in a Hewlett-Packard 38620 N-diode array spectrophotometer. The disappearance of Orange II was measured in the spectrophotometer at $\lambda = 486\,nm$ (the absorption peak). The peroxide concentrations in the solutions were measured using Merckoquant® paper (Cat Merck No 1.10011.01) for the quantitative detection of peroxides. This is a colorimetric test in which the peroxidase transfers oxygen from the peroxide to the organic redox indicator (o-toluidine) converting it in a blue colored oxidation product. The intensity of the blue color is a function of the peroxide found in solution. This was also carried out for reactions with initially added H_2O_2 to determine its concentration in the course of the reaction.

2.4. *Transmission electron microscopy (TEM) and scanning electron microscopy (SEM)*

A field emission TEM microscope Philips EM 430 (300 kV) was used to measure the particle size of the nanocrystalline TiO_2 nanocrystalline aggregates on the LDPE surface. Energy dispersive X-ray spectroscopy (EDS) was used to identify the deposition of TiO_2 on the LDPE film. The LDPE film was coated with EPON 812 epoxy resin polymerized at 60 °C and then cut with a microtome at room temperature to a thin layer of ~50 nm thickness. Magnification of 10 000 up to 450 000 × were used to characterize the samples. The resolution normally used was of 0.5 nm.

2.5. *Atomic force microscopy (AFM)*

The AFM images were acquired in contact mode using a PSIA Xe-100 AFM. The AFM uses a sample driven x–y scanner that is independent from the probe-drive z-scanner, eliminating the background curvature inherent to tube AFM scanners.