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TiO_2–PANI/Cork composite: A new floating photocatalyst for the treatment of organic pollutants under sunlight irradiation

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ABSTRACT

A novel photocatalyst based on TiO_2–PANI composite supported on small pieces of cork has been reported. It was prepared by simple impregnation method of the polyaniline (PANI)–modified TiO_2 on cork. The TiO_2–PANI/Cork catalyst shows the unique feature of floating on the water surface. The as-synthesized catalyst was characterized by X-ray diffraction (XRD), scanning electron micrograph (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectra (UV–vis DRS) and the Brunauer–Emmett–Teller (BET) surface area analysis. Characterization suggested the formation of anatase highly dispersed on the cork surface. The prepared floating photocatalyst showed high efficiency for the degradation of methyl orange dye and other organic pollutants under solar irradiation and constrained conditions, *i.e.*, no-stirring and no-oxygenation. The TiO_2–PANI/Cork floating photocatalyst can be reused for at least four consecutive times without significant decrease of the degradation efficiency.

Introduction

TiO_2–anatase is one of the most studied and efficient photocatalysts for the decomposition of a wide range of organic pollutants by transforming them into inorganic species or converting them into readily biodegradable organic species. However, despite its good chemical and biological inertness and its low production cost, the scale-up use of TiO_2 in real water treatment and environmental remediation is still limited and below expectations. One major difficulty to this development is related to the problem of powder recovery and recycling of titania photocatalyst when used in slurry. Another shortcoming of TiO_2 photocatalyst limiting its wide use lies in its large band gap, limiting the photocatalytic activation to radiation with energy larger than 3.2 eV (in ultraviolet range), and on the fast recombination rate of photogenerated electron/hole pairs.

The immobilization of TiO_2 onto a floating support is a convenient method to alleviate the problems of powder filtration and the catalyst recovery. It offers flexibility in photocatalyst handling for a water purification system. Examples of floating supports include fly-ash cenospheres

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(Huo et al., 2010), perlite (Faramarzpour et al., 2009), polystyrene beads (Singh et al., 2014) and exfoliated vermiculite (Machado et al., 2006).

Floating photocatalysts have received considerable attention because they integrate, in a single high performance material, the benefits of a floating support, such as lightness and flexibility. Due to their proximity to the air/water interface, the floating photocatalysts have also the advantage to be subjected to optimal solar irradiation and maximal oxygenation. As a result, the radical formation rate and the oxidation efficiency are highly improved (Machado et al., 2006). In addition, the floating photocatalysts do not need stirring or artificial oxygenation during the photocatalytic reaction and it can be easily collected from the surface. All these reasons make the floating photocatalysts easily used in practice and more economical than that of slurry TiO_2 in suspension. In particular, floating photocatalysts can be effectively used in the removal of floating or insoluble organic pollutants from the wastewater surfaces without any special equipment or installation. Specifically, it can be directly applied in the contaminated wastewater reservoirs located in remote places.

In order to extend the light absorption property of TiO_2 to drive the photocatalytic activity to visible light, the coupling of TiO_2 with a narrow band gap semiconductor such as a conducting polymer, polyaniline (PANI), may be considered. Why considering PANI? In fact, PANI aroused interest for different reasons: (1) PANI has a low band gap of 2.8 eV which makes it a potential sensitizer for TiO_2 under visible light irradiation (Chen et al., 2007), (2) the conduction band (CB) of PANI is located at a more negative level than that of TiO_2 which thermodynamically favors the electron transfer from PANI to TiO_2, leading to the improvement of the photocatalytic performance of the TiO_2–PANI hybrid material, and (3) PANI is easy to synthesize by various methods.

On the other hand, cork is a low density natural material, non-toxic, readily available and having a large surface area. Besides, it is a hydrophobic material that can pre-concentrate organics from water on its surface improving their removal and oxidation efficiency. For these reasons and others, such as compressibility, resilience, thermal stability and corrosion resistance, the cork may well be a suitable support for photocatalytic applications. To the best of our knowledge, the literature is very poor in research studies about cork material as a floating support for photocatalytic processes. So, the main purpose of this research work is to investigate the feasibility and the efficiency of TiO_2–PANI/cork as a floating photocatalyst. To do, the degradation reaction of methyl orange (MO) dye and other organic pollutants under solar irradiation and constrained conditions, *i.e.*, no-stirring and no-oxygenation, is investigated.

1. Materials and methods

1.1. Materials

Aniline, tetrahydrofuran (THF), sodium dodecyl sulfate (SDS) and titanium tetraisopropoxide (TTiP) were purchased from Aldrich Chemicals, USA. Ammonium peroxodisulfate (APS), sulfuric acid, MO, ethanol and acetic acid were purchased from Merck Company, USA as analytical grade; commercial vinyl binder was purchased from STPC Tunisia. All products were used as received.

1.2. Preparation of TiO_2 photocatalyst

The TiO_2 photocatalyst was prepared through the sol–gel process. The two precursor solutions, here denoted as precursors A and B were prepared as follows. Precursor A: TTiP (22.5 mL), ethanol (50 mL) and acetic acid (3.0 mL). Precursor B: H_2O (27.0 mL), ethanol (50 mL) and SDS (0.43 g). Each precursor was stirred for 10 min at room temperature. Afterwards, precursor B was added to precursor A drop wise with vigorous stirring. The resultant mixture was further stirred for 20 min. The sol was placed in a culture dish for 1.0 day to finish the sol–gel transition and filtered. Filtered residue was rinsed with water repeatedly, and then dried at 110°C for 24 hr to get a dried gel. The dried gel was ground and heat treated at 350°C for 6.0 hr to get a stable TiO_2 photocatalyst.

1.3. Synthesis of PANI

The method used in the preparation of PANI is the oxidative polymerization of aniline monomer by ammonium persulfate (APS) in aqueous solution of sulfuric acid at a pH = 1–3. In a typical synthesis, 50 mL of sulfuric acid solution containing 1.4 g of APS was added dropwise to 50 mL of sulfuric acid solution containing 1.82 mL of aniline. The polymerization was allowed to proceed by stirring the mixture for 2.0 hr at ambient temperature. The obtained dark green precipitate corresponding to PANI was then filtered and washed with distilled water and methanol. The resulting PANI was finally dried for 24 hr at 80°C.

1.4. Surface modification

The TiO_2–PANI composite was prepared by the direct impregnation method. In a typical procedure, 1.0 g of TiO_2 nanoparticles was dispersed in 50 mL of solution (PANI + THF) containing 45 mg of PANI. A constant magnetic stirring was conducted for 60 min at room temperature until the adsorption equilibrium. Thus, a dark green coloration of the surface of TiO_2 has appeared, inferring that a chemical reaction took place (chemisorption) between PANI and TiO_2. After filtration, the surface-modified titania nanoparticles (TiO_2–PANI) were washed three times with ethanol and water respectively, and dried for 24 hr at 80°C. The obtained powder was then ground to get fine particles.

1.5. TiO_2–PANI/Cork photocatalyst preparation

The TiO_2–PANI/Cork floating photocatalysts were prepared from a suspension of TiO_2–PANI on the cork surface. TiO_2–PANI/Cork ratios (*W/W*) of 50%, 70% and 100% were used. The cork (1 g) was divided into small pieces and stirred in a vinyl binder solution (3 mL binder + 30 mL distilled water) for a few minutes before the addition of TiO_2–PANI nanocomposite. The binder was used to immobilize the TiO_2–PANI onto the cork surface. The resultant mixture was further stirred vigorously for 30 min. After filtration, the recovered product was dried in an oven at 60°C for 3.0 hr. Subsequently, the

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