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Photocatalytic degradation of methyl orange dye in water solutions in the presence of MWCNT/TiO_2 composites

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ABSTRACT

The textile and dyestuff industries are the primary sources of the release of synthetic dyes into the environment and usually there are major pollutants in dye wastewaters. Because of their toxicity and slow degradation, these dyes are categorized as environmentally hazardous materials. In this context, carbon nanotubes/TiO_2 (CNTs/TiO_2) composites were prepared using multi-walled CNTs (MWCNTs), titanium (IV) propoxide and commercial TiO_2 (P25®) as titanium oxide sources, to degrade the methyl orange dye in solution through photocatalyst activity using UV irradiation. The composites were prepared by solution processing followed by thermal treatment at 400, 500 and 600 °C. The heterojunction between nanotubes and TiO_2 was confirmed by XRD, specific surface area. The coating morphology was observed with SEM and TEM.

1. Introduction

Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora [1,2]. They are also esthetically objectionable for drinking and other purposes [3]. Dyes can cause allergy, dermatitis, skin irritation [4] and also provoke cancer [5] and mutation in humans [6].

Two efficient methods for the degradation of synthetic dyes are the adsorption procedure [7] and the photocatalytic process [8,9]. The first process transfers the dyes from the water effluent to a solid phase, thereby keeping the effluent volume to a minimum [10–12]. Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment [13]. In the other process, dye molecule degrades when irradiated by energy.

Multi-walled carbon nanotubes (MWCNTs) can be considered good supports for materials with photocatalytic properties due to their good mechanical properties, chemical stability and the presence of mesopores, which favor the diffusion of reagent species [8]. The use of composites of MWCNTs and TiO_2 can therefore have very interesting potential applications in photocatalysis.

In order to optimize the catalytic properties of TiO_2, MWCNTs have been used as support, providing easier passage in the electron transfer process and, therefore, increasing the catalytic activity of titania [14]. Among the oxide semiconductor photocatalysts, titania (TiO_2) is a great option due to its high oxidizing properties, absence of toxicity and photostability. It is believed that the dispersion of TiO_2 on the surface of MWCNTs favors the appearance of many active sites for photocatalytic degradation [15].

According to Leary and collaborators [14], the performance of MWCNTs in the presence of TiO_2 in photocatalysis, can be understood as the CNT acting as a receptor or electron donor under UV irradiation, forming a very reactive superoxide or hydroxyl radical. These ions react on the surface of the oxide and become responsible for the degradation of organic compounds.

The recombination of the electron–hole pair formed in the generation of superoxide radical and hydroxyl ions is undesirable in photocatalytic reactions. The addition of electron acceptors can inhibit the recombination of the pair since it increases the amount of electrons confined to the conduction band, avoiding the recombination and generating more radicals and oxidants. It is believed that CNTs can hinder the recombination processes.

Photocatalytic applications of wide reaching importance include water splitting for hydrogen generation, degradation of environmental pollutants in aqueous contamination and wastewater treatment, carbon dioxide remediation, self-cleaning activity and air purification [14,16].

In the present study, MWCNTs/TiO_2 composites were obtained and used to degrade organic dyes in water. The methyl orange (MeO) dye was used in aqueous media as a model dye to evaluate the photocatalytic activity of the CNTs/TiO_2 composites. The adsorption capacities in the dark and the photocatalytic activities

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of the CNTs/TiO_2 composites under UV light were studied as well as the structural characterization of the composites.

2. Experimental design

2.1. Synthesis

The following precursors were employed for the functionalization process of MWCNT with TiO_2: titanium (IV) propoxide $Ti(OPr)_4$ (*TPP*), as alkoxide precursor of TiO_2, provided by Sigma–Aldrich; commercially available TiO_2 (AEROXIDE® – P25) made by Evonik; nitric acid P.A., produced by Synth; isopropyl alcohol and deionized water. The Baytubes® were supplied by Bayer®, and were employed as the MWCNT source.

The composites were prepared by a modified sol–gel method. The production of the samples was basically divided into two systems: (i) using *TPP* and (ii) using P25. The molar ratio for system (i) and (ii) is 6:140:5:1 = $Ti(OPr)_4$/P25:R-OH:H_2O:HNO_3, with 0.33 g of MWCNT being mixed in 29 ml of solution for each sample. The liquid systems containing precursors were kept under magnetic stirring and heated up to 40 °C for 1 h. After this period, MWCNTs were added to the liquid systems, which remained under stirring for another hour. The process was completed before of the samples started the gelation process, i.e. there was no complete transformation of sol in gel. Thereafter, the liquid systems were filtered and the material was kept at 100 °C for 24 h. The samples of system (i), called T4, T5 and T6 were subjected to heat treatment at 400 °C, 500 °C and 600 °C for 1 h, respectively, using a heating rate of 2.5 °C in a muffle type furnace in air atmosphere. The heat treatment of the sample of system (ii), called PA, was not necessary because the precursor was already crystallized.

2.2. Characterization

Scanning electron microscopy (SEM – JEOL JSM-6060) operating between 12 and 15 kV, and transmission electronic microscopy (TEM – JEM 1200EXII-120 kV) operating to 80 kV were employed for the morphological analysis of the samples. The crystallinity of the composites obtained was evaluated by the X-ray diffraction (XRD) technique using a PHILIPS diffractometer (Model X'Pert MPD) equipped with a graphite monochromator and a copper anode, operating at 40 kV and 40 mA. Analyses were performed in a 2θ range of 20–70°, with steps of 0.05° for 2 s, with Cu Kα radiation. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method, using N_2 as gas adsorption media, using a Quantachrome Autosorb Automated Gas Sorption System (NOVA 1000). Thermogravimetric analysis (TGA) of the NTCPMs–TiO_2 composites were performed in a Mettler apparatus (A851e) using an O_2 atmosphere and with a heating rate of 10 °C/min until the temperature of 900 °C, with alumina as the reference material.

2.3. Photocatalytic activity

The photocatalytic activity of the composites was evaluated by following the decomposition of the methyl orange dye (MeO) under UV light. Initially, the MWCNTs/TiO_2 composites were added to a MeO solution and kept in the dark for 1 h. Subsequently, the solution was dispersed using ultrasound for 10 min. After this period, the solution was irradiated with UV light. The photocatalytic activity of MWCNT/TiO_2 composites, as well as of the MWCNT/P25 samples, was evaluated using 12 UVA lamps (wavelength 365 nm or 3.39 eV) of 8 W each. The dye concentration was set at 1.0×10^{-5} mol/L. The concentration of composites in suspension was 0.4 g/L and 0.8 g/L in the MeO solution. The first dispersed dye sample was collected at the end of the adsorption period in the dark, before the sample was exposed to UV irradiation.

The reaction recipient consisted of a quartz Dreschel bottle fitted with a silicone septum to facilitate withdrawal of samples from the reaction dispersion. Samples were collected periodically with a syringe from the reactor every 10 min during a 70 min time interval and then filtered (pore diameter 0.2 μm) into a 4 mL PMMA cuvette. The absorbance at the wavelength of 465 nm was recorded (Bioespectro SP 200) for each sample containing the composites and the MeO in a solution with pH 7.

3. Results and discussion

XRD spectra (Fig. 1) were collected to analyze the effect of CNTs on the crystallization of the nanocomposites. A sample of pure TiO_2-P25 shows the anatase phase with well-defined peaks and some peaks of the poorly crystalline rutile-type phase. However, in the presence of CNTs its characteristic crystallinity apparently decreases, as can be observed in the XRD spectra of the PA sample (Fig. 1). A similar effect occurs with the MWCNT samples: in the presence of TiO_2, apparently there is a decrease in the intensity of the CNT characteristic peak.

According to Wang and collaborators [17], the disappearance of characteristic CNT peaks in the XRD patterns of the composite materials is consistent with a homogeneous coverage of TiO_2 on MWCNT, which is additionally supported by the absence of MWCNT aggregated pores in the composite materials. On the other hand, the introduction of MWCNT to TiO_2 favors less extended crystallized TiO_2 domains on the MWCNT surface, thus avoiding TiO_2 particle agglomeration. All factors account for the increase in surface areas of the composite materials.

The 2θ positions at 26° and 43.4°, on the (0 0 2) and (1 0 1) planes, respectively, correspond to characteristic peaks of CNTs [8]. These peaks can be visualized on the spectra of the MWCNT sample, which has no TiO_2. The main peak of the anatase phase is observed at 25.4° on the (1 0 1) plane [15,18]. This could explain the overlap of peaks on this position in the T4, T5 and T6 samples, which hinders the observation of the typical diffraction peak of graphite at 26° corresponding to the (0 0 2) plane [19,20].

In general, the amorphous TiO_2 shows lower photocatalytic activity. However, if it is heat treated at 450 °C in air, part of the material can be transformed into the anatase phase and promote photocatalytic activity [17].

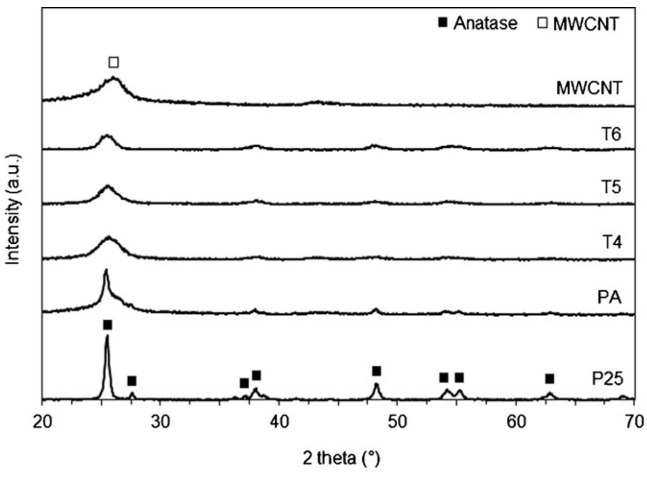

Fig. 1. XRD pattern of the MWCNT/TiO_2 composites, P25 used as reference for the presence of pure TiO_2 and MWCNT.