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ORIGINAL ARTICLE

1st Nano Update

Solar active nano-TiO_2 for mineralization of Reactive Red 120 and Trypan Blue

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Abstract Nano-TiO_2 was synthesized by sol–gel method. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) images, transmission electron microscope (TEM), BET surface area measurement and DRS analysis. The formation of anatase phase nano-TiO_2 was confirmed by XRD measurements and its crystalline size is found to be 15.2 nm. SEM images depict the crystalline nature of prepared TiO_2. The BET surface area of prepared TiO_2 is found to be 86.5 $m^2\ g^{-1}$ which is higher than that of commercially available TiO_2–P25. The photocatalytic activity of prepared anatase phase TiO_2 has been tested for the degradation of two azo dyes: Reactive Red 120 (RR 120) and Trypan Blue (TB) using solar light. The photocatalytic activity of nano-TiO_2 is higher than TiO_2–P25 under solar light. The mineralization of dyes has been confirmed by chemical oxygen demand (COD) measurements.

1. Introduction

Reactive azo dyes are widely used in the textile industries because of their simple dying procedures and good stability during washing process. But the main drawback of these dyes is low fixation rate on the fabrics. Hence dye wastewater introduces intense color and toxicity to aquatic system. Due to the complex structure and stability of the dyes, conventional biological treatment methods are ineffective for degradation (Huang et al., 1979; Pagga and Brown, 1986; Ince and Gonenc, 1997).

Heterogeneous photocatalysis has been considered as a cost-effective alternative as pre- or post-treatment of biolog-

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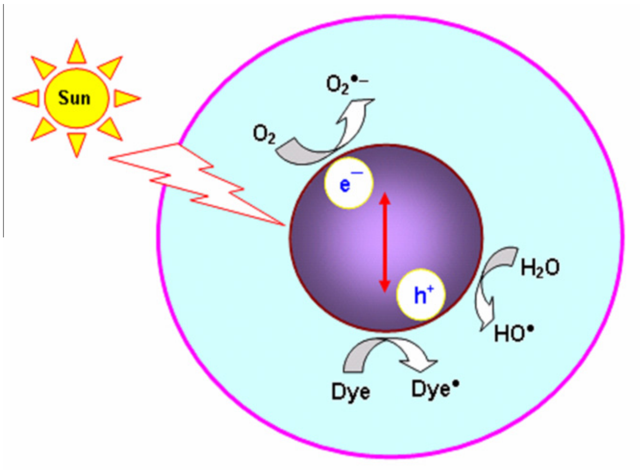


Scheme 1 Electron–hole pair generation in an illuminated semiconductor particle with solar light.

ical treatment process for the purification of dye-containing wastewater (Collins et al., 1978; Luthy and Talton, 1980; Kiwi et al., 1993; Tanaka and Ichikawa, 1993; Wang, 2000). Heterogeneous photocatalysis is based on the irradiation of a photocatalyst, usually a semiconductor such as TiO_2, with light energy equal to or greater than the band gap energy. This causes a valence-band electron to be excited to the conduction band, causing charge separation (Scheme 1). The conduction band electrons and valence band holes can then migrate to the surface and participate in interfacial oxidation–reduction reactions. The oxidative degradation of an organic pollutant is attributed to indirect reaction of positive hole at the surface where adsorbed water or hydroxyl groups are oxidized to hydroxyl radicals (OH•), which then react with the pollutant molecule (Turchi and Ollis, 1990). Recently, much attention has been paid to the photocatalytic degradation of dyes with TiO_2 particles under UV or visible light (Toor et al., 2006; Aarthi et al., 2007). We have reported photodegradation of a number of toxic chemicals with commercial ZnO and TiO_2 using UV and solar light (Sobana and Swaminathan, 2007; Muruganandham and Swaminathan, 2006; Ravichandran et al., 2007; Krishnakumar and Swaminathan, 2010). The present work focuses on the preparation and characterization of nano sized TiO_2 and its photocatalytic activity on the degradation of RR 120 and TB with solar light.

2. Experimental

2.1. Materials

The commercial azo dyes, Trypan Blue (Fig. 1a), from SD Fine and Reactive Red 120 (Fig. 1b), from Balaji Colour Company, Dyes and Auxiliaries (Chennai) were used as such. A gift sample of TiO_2–P25 was received from Degussa (Germany). It is a mixture of 80% anatase and 20% rutile with the particle size of 30 nm and BET specific area $50\ m^2\ g^{-1}$. AnalaR grade tetraisopropyl orthotitanate (Himedia, 98.0%), isopropanol (99.5%, Spectrochem) were used as received. The double distilled water was used to prepare experimental solutions.

2.2. Preparation of nano-TiO_2

Nano-TiO_2 was prepared by sol–gel method. 12.5 mL of tetraisopropyl orthotitanate was dissolved in 100 mL of isopropanol (Spectrochem $\geqslant$99.5%) and to this solution 3 mL of water was added drop wise under vigorous stirring. The resulting colloidal suspension was stirred for 4 h. The gel obtained was filtered, washed and dried in an air oven at 100 °C for 5 h. The sample was calcinated at 400 °C in a muffle furnace for 12 h.

2.3. Irradiation procedure

Solar photocatalytic degradation experiments were carried out under similar conditions on sunny days between 11 am to 2 pm in the month of May, 2010. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 12.6 mm diameter was used as the reaction vessel. Fifty milliliters of RR 120 (2×10^{-4} M) or TB (1×10^{-4} M) with the appropriate amount of catalyst was stirred for 30 min in the dark prior to illumination in order to achieve maximum adsorption of dye onto the semiconductor surface. Irradiation was carried out in the open air with continuous aeration by a pump to provide oxygen and for the complete mixing of reaction solution. During the illumination time no volatility of the solvent was observed. In all cases, 50 mL of reaction mixture was irradiated. At specific time intervals, 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the sample was suitably diluted and dye concentration was determined from the absorbance at the analytical wavelength (RR 120–285 nm, TB –313 nm).

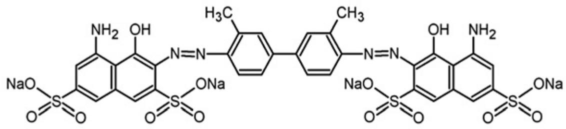
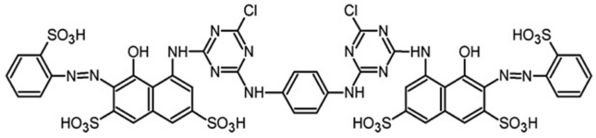
	Name	Chemical structure	Absorption maxima (nm)
(a)	TB		313, 581
(b)	RR 120		285, 512

Figure 1 The chemical structures and absorption maxima of (a) TB and (b) RR 120.