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Photocatalytic degradation of methyl orange in aqueous suspension of mesoporous titania nanoparticles

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Abstract

The photodegradation of methyl orange (MO) was investigated in aqueous suspension containing titania nanoparticles with mesostructures (m-TiO_2) under UV irradiation. The experimental results show that 98% MO can be mineralized in the 1.0 g l^{-1} m-TiO_2 suspension (pH 2.0) after 45 min illumination. Particular attention was devoted to the identification and the transformation of the fragments retaining the chromophoric group. The photodegradation mechanism of the quinonoid MO mainly involves three intermedial processes: demethylation, methylation and hydroxylation. Among those processes, demethylation is more favorable than the hydroxylation, but the hydroxylation results in the largest number of intermediates. The degradation pathway of quinonoid MO under the optimal conditions is also proposed.

Keywords: Mesoporous TiO_2 nanoparticle; Photocatalysis; Methyl orange; Degradation mechanism

1. Introduction

In the past decades, photocatalytic technique has been shown to be one of the most promising processes for the wastewater treatment due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range, etc (Zainal et al., 2005; Zhang et al., 2005a,b; Chen and Liu, 2007; Dillert et al., 2007). The photocatalytic treatment of wastes containing dyes has also been widely reported in the literature (Qaradawi and Salman, 2002; Kyung et al., 2005; Liu et al., 2005; Yang et al., 2005; Zhang et al., 2005a,b; Monteagudo and Durán, 2006; Pedroza et al., 2007). In this case, photosensitization of the dye may also occur upon excitation by visible light in addition to the hydroxyl radical attacking the dye molecules. The photogenerated electrons might also transfer from the excited dye to the semiconductor particle. It can also reduce the adsorbed oxygen in the suspensions to form superoxide radicals, then the reaction between the dye radical and the other active oxygen-containing species might also occur, which can accelerate the photodegradation process of the dye (Kamat, 1993).

Most previous publications on the photodegradation of dyes have mainly focused on the optimization of the photoreaction conditions and the examination of the so-called primary process through monitoring the decolouration or the substrate abatement (Qaradawi and Salman, 2002; Zainal et al., 2005; Zhang et al., 2005a,b), whereas less attention has been devoted to the investigations on the photodegradation mechanism of dyes. Spadaro et al. (1994) have proposed that the oxidation of aminoazobenzene dyes proceeds by the addition of a hydroxyl radical to the carbon atom linking with the azo bond, and the ring with the amino group is the first target for the hydroxyl radical reaction. It is believed that a series of transient intermediates have formed and/or decomposed after the destruction of the chromophore group of dye (Augugliaro

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et al., 2002; Baiocchi et al., 2002; Bianco-Prevot et al., 2004; Zhang et al., 2005a,b), which are usually invisible and unavoidable during the photodegradation process. Therefore, it is necessary to determine which intermediates appear in the effluent and whether there are some long-life byproducts during the photocatalytic process. The possibility of molecular fragments, which may be more toxic than the parent compound (Galindo et al., 2000), also makes it obligatory to identify the degradation mechanism. HPLC-MS technique has already been proposed for the separation and determination of methyl orange (MO) and/or its sulfonated azo intermediates during the photodegradation process under a simulated solar light (Jardim et al., 1997; Riu et al., 1997; Bianco-Prevot et al., 2004). A general picture of the overall process has been proposed (Bianco-Prevot et al., 2004) including the evolution of the molecules retaining chromophore group as well as the sequence of reactions occurring among them.

Recently, titania nanoparticles with mesostructures (m-TiO_2) have been fabricated and shown much better photoactivities than that of the commercial photocatalyst P25 (Degussa) due to its high specific surface area and well-crystallized mesoporous wall (Peng et al., 2005a,b). In the present work, the effect of the photocatalytic conditions on the efficiency for the photodegradation of MO was investigated in detail. The structures and transformations of the intermediates retaining the chromophore group during the photocatalytic process were identified by a HPLC-MS system. Finally, the degradation mechanism of MO was also inferred.

2. Experimental section

2.1. Photocatalysis tests of methyl orange

Methyl orange is obtained from commercial sources as analytical reagent grade. Acetonitrile and ammonium formate are chromatographically pure grade. The m-TiO_2 with highly crystallized mesoporous walls (anatase) was prepared as previous publication (Peng et al., 2005a,b). The properties of m-TiO_2 calcined at 400 °C are as follows: mean particle size (*ca.* 17.6 nm), crystallite size (*ca.* 3.1 nm), specific surface area (317.5 $m^2\,g^{-1}$).

A pair of photocatalytic reactions under the same conditions was performed at room temperature in the outer-irradiation-type reactors. A 250 W mercury lamp (100 mm long, $\lambda_{max} = 365$ nm, Beijing Yaming Lamp Works, China) with a light flux of 8.81 mW cm^{-2} after the empty reactor was applied as the light source and positioned inside the cylindrical vessel surrounded by a circulating water jacket (Pyrex). Pyrex glass vessels were used as the photoreactors. The 50 ml m-TiO_2 suspension containing 20 ppm MO was magnetically stirred before and during illumination. Prior to the irradiation, the pH value of suspension was adjusted with 3 M H_2SO_4. The suspension was stirred for 15 min in the dark (for the adsorption–desorption equilibrium of the dye on the m-TiO_2 surfaces), and then exposed to the UV light. After a defined irradiation time, a small quantity of solution was centrifuged and filtered through 0.45 μm Millipore membrane filter to remove the catalyst before analysis.

2.2. Determination of intermediates

For the convenience of detection for the intermediates originated from the photocatalytic reaction, a larger concentration of MO (100 ppm) was applied in this case. The m-TiO_2 amount in the suspension was also enlarged proportionally. The other photoreaction conditions are the same with the optimal photodegradation experiments of MO (pH 2.0). The intermediates of MO produced from different irradiation periods were analyzed through HPLC-MS system (Agilent 1100 series).

HPLC analyses were performed with a binary pump, 1100 UV–Vis diode array detector, an auto-sample and a column thermostat. The HPLC-MS system was equipped with a Zorbax SB-C18 column (150 mm × 2.1 mm). The eluent was 10.0 mM acetonitrile-ammonium formate (20/80, v/v) solution (pH 6.8) at a flow rate of 0.3 ml min^{-1}. A 3 μl of sample was injected by using autosampling device. The eluent from the chromatographic column successively enter the UV–Vis detector, the electrospray ionization (ESI) interface and then the mass analyzer. The UV detector was operated at 465 nm since the pH value of the mobile phase is 6.8.

MS and MS^2 analyses in the negative mode were performed on 1100 MSD ion trap mass spectrometer equipped with an atmospheric pressure ionization (API) interface and an ESI ion source. The flow rate of the high purity nitrogen (heater temperature, 300 °C) was maintained at 7 l min^{-1}. The spectrometer was scanned from $m/z =$ 100–350 at 0.3 ml min^{-1} during the recording mass spectra.

3. Results and discussion

3.1. Optimization of photocatalytic conditions

Preliminary blank experiments conducted in the photoreactor without m-TiO_2 showed that less than 1.0% MO was decomposed after 1 h irradiation, indicating that MO has a good photostability under the UV light irradiation and acidic condition. Wang et al. (2005) had studied the effect of different MO concentrations ranging from 5 to 25 ppm on the photocatalytic reaction rate in an anatase titania suspension system, and found the best degradation efficiency at MO concentration of 20 ppm. Therefore, 20 ppm MO solution was used in this study. The relationships of the degradation rate and the pH values are shown in Fig. 1. As can be seen, the photooxidation of MO takes place following the pseudo-first-order kinetic law in the presence of m-TiO_2 according to the relationship curves between the MO concentration and the irradiation time, which is consistent with the previous literature on most