Photocatalytic Degradation of Azo Dye Reactive Orange 16 by TiO₂

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Abstract Photocatalytic degradation of hydrolyzed reactive orange 16 (RO16) using titanium dioxide (TiO₂) was analyzed in our study. The effects of various parameters, such as photocatalyst amount, RO16 concentration, light intensity, and temperature on photocatalytic degradation were investigated. Decolorization of hydrolyzed RO16 resulted in an decreasing of toxicity (EC₅₀=76.54±2.16). It was found that the decolorization efficiency was 87% after 20-min reaction and 100% after 80-min reaction. The total mineralization was 70% after 20 min and nearly 100% after 120 min, respectively. The results indicate that color degradation was faster than the decrease of total organic carbon. The photocatalytic degradation process was well described by first-order reaction. The final mineralization product was acetamide and the intermediate products were identified by gas chromatography–mass spectroscopy.

Keywords Photocatalytic degradation · Reactive orange 16 · TiO₂ · Mineralization

1 Introduction

Large amounts of dyes are annually used in textile, cosmetics, food, pharmaceutical, and paper industries (Zee and Villaverde 2005). Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes (Mariana et al. 2002). The fixation degree of azo dyes to fabrics is not complete, resulting in the contamination of the effluents in wastewater (Pekakis et al. 2006; Chen et al. 2006). Azo dyes are characterized by the existence of nitrogen nitrogen double bonds and the bright color is due to the azo bonds and chromophores (Lee et al. 2006). Furthermore, azo dyes also affect photochemical activities in aquatic systems by reducing light penetration. The removal of azo dyes is important because many azo dyes are toxic to aquatic organisms (Sharma et al. 2003). Many physical and chemical methods including adsorption, coagulation, membrane process, oxidation–ozonation, and biological treatment have been used for the treatment of azo dyes (Walker et al. 2003). The fixation degree of dyes to fabrics is not complete, resulting in the contamination of the effluents in wastewater (Farah et al. 2007). However, chemical techniques often give rise to other type of pollutants, which needs further treatment (Kansal et al. 2007). Some studies showed that azo dyes were difficult to be biodegraded (Shu et al. 2004). The utilization of advanced oxidation processes for the treatment of dyes are based on generation of hydroxyl radicals that
oxidize organic pollutants. Among these processes, heterogeneous photocatalysis is an emerging technology leading to mineralization of most of organic pollutants (Erdemoglu et al. 2008). In most cases, the degradation using UV-illuminated TiO$_2$ to treat dissolved organic pollutants (Khodja et al. 2001; Kusvuran et al. 2005).

Reactive orange 16 (RO16) is one of the azo dyes. Since RO16 is hard to be biodegraded and other treatment cost is too high, there is a need to search for better treatment methods for the pollutants. In the present study, it was aimed to investigate the degradation kinetics of RO16 by TiO$_2$ photocatalysis. Furthermore, identifying the end products of the reaction using gas chromatography–mass spectroscopy (GC-MS) was also performed.

2 Materials and Methods

2.1 Materials

All chemicals used in our experiment were of analytical grade. RO16 was purchased from Sigma Ltd. (USA). The physical and chemical characteristics of RO16 are listed in Table 1. The experiments were performed as follows: 300 mL of RO16 solution (10 mg/L) was put into a Pyrex reaction vessel and TiO$_2$ powder (anatase, purity 99.9%, diameter 230 nm, Sigma-Aldrich) was added to the solution to produce a given concentration of TiO$_2$ suspension (90 mg/L). The TiO$_2$ solution was stirred for 60 min in the dark to ensure the equilibration of adsorption of RO16 on the surface of TiO$_2$.

2.2 Characterization of Photocatalytic Degradation

Photocatalytic degradation of RO16 were performed in solution at 25°C, pH=7.0, in triplicates. The experiments were carried out in a (10-cm ID×20-cm H) quartz beaker with magnetic stirring, which was placed in the center of the UV photo-reactor, Rayonet RPR-200 (Southern New England Ultraviolet Co.). The reactor was equipped with four Xenon 254-nm lamps and the light intensity ranged from $1.00 \times 10^{-6}$ to $5.00 \times 10^{-6}$ Einstein l$^{-1}$ s$^{-1}$. For pH adjustment, 0.1 M HCl or 0.1 M NaOH was used. Total organic carbon (TOC) concentration was analyzed by Aurora 2009W OI Analytical TOC analyzer (OI Analytical, USA). Sulfate ions were analyzed by an ion chromatograph ( Dionex, model DX-100).

After UV light radiation, TiO$_2$ was separated by a Millipore 0.45-μm membrane filter. Then, the adsorption spectra were recorded and the decolorization efficiency was observed in light intensity of the dyes. The decolorization efficiency (%) has been calculated as follows:

$$\text{Efficiency} (%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where $C_0$ and $C_e$ correspond to the initial and final concentration of dye before and after photo-irradiation.

<table>
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<th>Parameters</th>
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<td>Molecular formula</td>
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