

Photooxidative *N*-de-ethylation of anionic triarylmethane dye (sulfan blue) in titanium dioxide dispersions under UV irradiation

Chiing-Chang Chen^a, Chung-Shin Lu^a, Fu-Der Mai^{b,*}, Chyan-Syang Weng^b

^a Department of General Education, National Taichung Nursing College, Taichung 403, Taiwan, ROC

^b Department of Applied Chemistry, Chung-Shan Medical University, Taichung 402, Taiwan, ROC

Received 13 March 2006; received in revised form 26 April 2006; accepted 27 April 2006

Available online 30 May 2006

Abstract

The TiO₂-mediated photocatalysis process has been successfully applied to degradation of dye pollutants. Our results indicate that the TiO₂ surface is negatively charged, and the sulfan blue (SB) adsorbs onto the TiO₂ surface through the positive di-ethylamino groups while the TiO₂ surface is positively charged and the SB adsorbs onto the TiO₂ surface through the negative sulfonyl groups. In order to obtain a better understanding of the mechanistic details of this TiO₂-assisted photodegradation of the SB dye with UV irradiation, five intermediates of the processes were separated, identified, and characterized by the HPLC-ESI-MS technique, which included a positive- and negative-ion mode. The results indicated that the *N*-de-ethylation process continues until the *N*-de-ethylated SB dye is completely formed. The probable photodegradation pathways were proposed and discussed. The reaction mechanisms of UV/TiO₂ proposed in this study should be useful for future applications of the technology to the decolorization of dyes.

© 2006 Elsevier B.V. All rights reserved.

Keywords: UV/TiO₂; Triarylmethane; Sulfan blue; Dye; *N*-de-ethylation

1. Introduction

Synthetic textile dyes and other industrial dyestuffs constitute the largest group of chemicals produced in the world. In the dyeing process, 10–20% of dyes are reportedly lost to wastewater as a result of inefficiency [1]. Dyestuffs from the textile and photographic industries are becoming a major source of environmental pollution. The large amount of dyestuffs used in the dyeing stage of textile manufacturing represents an increasing environmental danger due to their refractory carcinogenic nature [2]. To de-pollute the dyeing wastewater, a number of methods have been investigated, including chemical oxidation and reduction, chemical precipitation and flocculation, photolysis, adsorption, ion pair extraction, electrochemical treatment, and advanced oxidation.

Advanced oxidation is one of the most promising technologies for the removal of dye-contaminated wastewaters due to its high efficiency. This technology is mainly based on the oxidative

reactivity of HO• radicals generated by various methods such as O₃/UV, H₂O₂/UV, H₂O₂/vis, O₃/H₂O₂/UV photolysis, photoassisted Fe³⁺/H₂O₂, and TiO₂-mediated photocatalysis processes [3].

The TiO₂-mediated photocatalysis process has been successfully used to degrade pollutants during the past few years [4–16]. TiO₂ is broadly used as a photocatalyst because of its nontoxicity, photochemical stability, and low cost [17–20]. The initial step in the TiO₂-mediated photocatalysis degradation is proposed to involve the generation of an (e⁻/h⁺) pair, leading to the formation of hydroxyl radicals (•OH), superoxide radical anions (O₂^{•-}), and hydroperoxyl radicals (•OOH). These radicals are the oxidizing species in the photocatalytic oxidation processes. The efficiency of the dye degradation depends on the concentration of the oxygen molecules, which either scavenge the conduction band electrons (e_{cb}⁻) or prevent the recombination of (e⁻/h⁺). The adsorbed dye molecules, leading to the formation of dye radical anions and the degradation of the dye, can pick up the electron in the conduction band [20].

Triarylmethane dyes are used extensively in the textile industry for dyeing nylon, wool, cotton, and silk, as well as for coloring of oil, fats, waxes, varnish, and plastics. The paper,

* Corresponding author. Tel.: +886 4 2473 0022; fax: +886 4 2324 8189.
E-mail address: davismai@csmu.edu.tw (F.-D. Mai).

leather, cosmetic, and food industries consume a high quantity of triarylmethane dyes of various kinds [1,21]. Additionally, the triarylmethane dyes are applied as staining agents in bacteriological and histopathological applications. The photocytotoxicity of triarylmethane dyes, based on the production of the reactive oxygen species, is tested intensively with the regard to their photodynamic treatment [22–24]. However, there is a great concern about the thyroid peroxidase-catalyzed oxidation of the triarylmethane class of dyes because the reactions might form various *N*-de-alkylated primary and secondary aromatic amines, the structures of which are similar to aromatic amine carcinogens [25].

In earlier reports [26–28], only one photodegradation of the anionic triarylmethane dyes, sulforhodamine-B, was investigated. The *N*-de-ethylation process was presumed to exist on the basis of the wavelength shift that occurs during the maximal absorption of the dyes. Only some of the photodegradation intermediates of this dye have been separated and identified, and the detailed mechanisms are still unclear. However, the photodegradation of SB dye has not been studied, and the intermediates have not been isolated or identified by the HPLC-ESI-MS technique.

Accordingly, identification of the reaction intermediates was performed using HPLC-ESI-MS, which reveals the degradation mechanism and reaction pathways of the photodegradation of SB dye in the UV/TiO₂ process, which in turn can serve as a foundation for future applications.

2. Experimental

2.1. Materials

The TiO₂ nanoparticles (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20–30 nm; BET area, ca. 55 m² g⁻¹) were supplied by Degussa. The SB dye was obtained from Tokyo Kasei Kogyo and used without further purification. The chemical structure of the SB dye is shown in Fig. 1. Stock solutions containing 1 g L⁻¹ of SB dye in water were prepared, protected from light, and stored at 4 °C. HPLC analysis was employed to confirm the presence of the SB dye as a pure organic compound.

Reagent-grade ammonium acetate, sodium hydroxide, nitric acid, and HPLC-grade methanol were purchased from Merck.

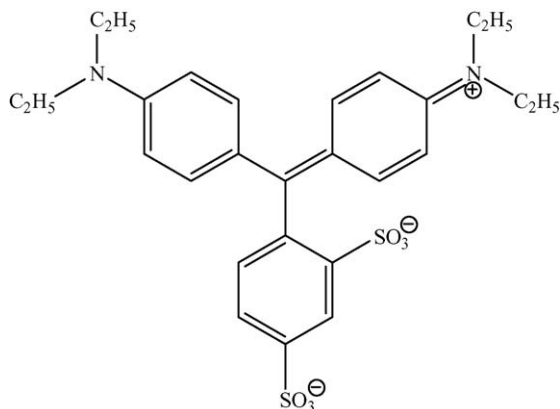


Fig. 1. Chemical structure of sulfan blue.

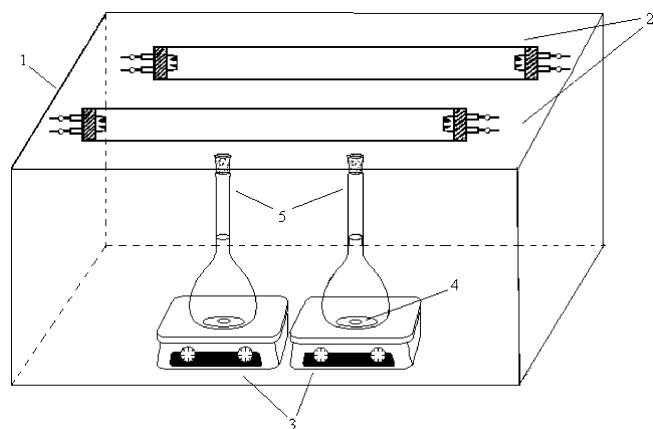


Fig. 2. Experimental apparatus: (1) C-75 Chromato-Vue cabinet of UVP, (2) UV-lamp, (3) magnetic stir, (4) stir bar, (5) 100 mL flask reactor.

De-ionized water was used throughout this study. The water was then purified with a Milli-Q water ion-exchange system (Millipore Co.) to give a resistivity of $1.8 \times 10^7 \Omega \text{ cm}$.

2.2. Apparatus and instruments

The schematic of diagram of experimental apparatus was shown in Fig. 2. The C-75 Chromato-Vue cabinet of UVP provides a wide area of illumination from the 15-W UV-365 nm tubes positioned on two sides of the cabinet interior.

Waters ZQ LC/MS system, equipped with a binary pump, a photodiode array detector, an autosampler and a micromass detector, was used for separation and identification.

2.3. Procedures and analysis

An aqueous TiO₂ dispersion was prepared by adding 50 mg of TiO₂ powder to a 100 mL solution containing the SB dye at appropriate concentrations. For reactions in different pH media, the initial pH of the suspensions was adjusted by addition of either NaOH or HNO₃ solutions. Prior to irradiation, the dispersions were magnetically stirred in the dark for ca. 30 min to ensure the establishment of the adsorption/desorption equilibrium. Irradiations were carried out using two UV-365 nm lamps (15 W). At any given irradiation time interval, the dispersion was continued stirred, sampled (5 mL), centrifuged, and subsequently filtered through a Millipore filter (pore size, 0.22 μm) to separate the TiO₂ particles.

After each irradiation cycle, the amount of the residual dye was thus determined by HPLC-PDA. The analysis of organic intermediates was accomplished by HPLC-ESI-MS after the readjustment of the chromatographic conditions in order to make the mobile phase compatible with the working conditions of the mass spectrometer. Two different kinds of solvents were prepared in this study. Solvent A was 25 mM aqueous ammonium acetate buffer (pH 6.9) while solvent B was methanol instead of ammonium acetate. LC was carried out on an AtlantisTM dC18 column (250 mm × 4.6 mm i.d., dp = 5 μm). The flow rate of the mobile phase was set at 1.0 mL/min. A linear gradient was set as follows: $t = 0$, $A = 95$, $B = 5$; $t = 20$, $A = 50$, $B = 50$;

Download English Version:

<https://daneshyari.com/en/article/585125>

Download Persian Version:

<https://daneshyari.com/article/585125>

[Daneshyari.com](https://daneshyari.com)