



# Degradation of sunscreen agent 2-phenylbenzimidazole-5-sulfonic acid by TiO<sub>2</sub> photocatalysis: Kinetics, photoproducts and comparison to structurally related compounds

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## ABSTRACT

The wide occurrence of sunscreen agent micropollutants in natural environment received extensive attention in recent years due to their potential endocrine disrupting effect. The present study focuses on the kinetics and mechanism of photocatalytic degradation of sunscreen agent 2-phenylbenzimidazole-5-sulfonic acid (PBSA) in illuminated TiO<sub>2</sub> suspensions. Photocatalysis of PBSA was systematically investigated under different process conditions and water matrices. Experimental results demonstrated that PBSA photocatalytic reactions followed pseudo-first-order kinetics. Radical scavenging experiments indicated that hydroxyl radical (HO<sup>•</sup>) is the predominant reactive species responsible for an appreciable degradation of PBSA. Second-order rate constant of PBSA-HO<sup>•</sup> reaction was determined to be  $5.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  by competition kinetics method. Major intermediates included hydroxylated products, benzamide, hydroxylated benzimidine, hydroxylated 2-phenyl-1H-benzimidazole as well as phenylimidazolecarboxylic derivatives which were elucidated by means of high performance liquid chromatograph–mass spectrometry (HPLC–MS) technique. Four carboxylic acids, oxalic, malonic, acetic and maleic acids, were detected during PBSA photocatalysis by HPLC–UV analysis. Ion chromatography (IC) results revealed that the sulfonic group of PBSA was primarily converted to sulfate ion while nitrogen atoms were released predominantly as ammonium and to a lesser extent as nitrate. The reduction of TOC processed much more slowly compared to PBSA degradation, however, approximately 80% TOC was removed after 720 min irradiation. A comparison of photocatalytic degradation of PBSA and structurally related compounds revealed that the 5-sulfonic moiety in PBSA had negligible effect on the photocatalysis of 2-phenyl-1H-benzimidazole while 2-phenyl substituent stabilized the benzimidazole ring system to photocatalytic degradation.

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## 1. Introduction

Sunscreens are widely used in personal care products (PCPs) in recent years due to the public awareness of protection against ultraviolet (UV) irradiation and skin cancer [1]. Sunscreens enter the aquatic environment directly as consequence of recreational water activities (e.g., bathing and swimming) or indirectly via wastewater treatment plants (WWTPs) as result of the use of cosmetics, showering, washing, rubbing off and excretion after dermal application

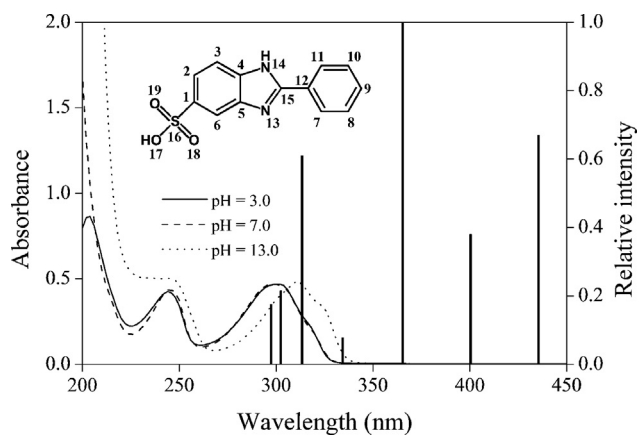
[2,3]. The extensive use of sunscreens already led to frequent detection in many aquatic ecosystems with a considerably high concentration [2–4]. Indeed, sunscreens are regarded as a new kind of environmental contaminants according to the US Environmental Protection Agency [5]. Recent studies have provided evidence that organic sunscreens possess estrogenic properties and behavior as endocrine disrupting chemicals (EDCs) in the environment [6–12]. Furthermore, photo-induced transformation products of some kinds of sunscreens under natural solar irradiation were found to be more toxic than their parent species, which could be a further danger to the biota in environment [9]. Therefore, the long-term and extensive use of sunscreens may cause irreversible adversity on the ecology system.

2-Phenylbenzimidazole-5-sulfonic acid (PBSA), as one kind of sunscreen, is widely used in sunscreen formulations and cosmetics

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**Fig. 1.** UV-vis absorption spectra of 2-phenylbenzimidazole-5-sulfonic acid (PBSA) at different pH values and emission spectrum of HPK lamp. [PBSA] = 45  $\mu$ M. Note that wavelength with  $\lambda < 340$  nm was filtered by a 340 nm cut-off filter (0–52 Corning) to avoid direct photolysis of PBSA. The insert figure shows the chemical structure of PBSA,  $C_{13}H_{10}O_3N_2S$ . The atoms in PBSA molecular were labeled with numbers for the purpose of frontier electron density (FED) calculation.

because of its strong absorption in the UVB region (see Fig. 1). It has also been approved by the U.S. Food and Drug Administration as an effective sunscreen ingredient based on its ability to prevent erythema [1]. Due to its high polarity and continued input into the environment through personal care applications and incomplete elimination during wastewater treatment, PBSA was frequently detected in natural surface waters with a concentration ranging from 109 to 2679  $ng L^{-1}$  [10]. PBSA has been known to photochemically generate reactive oxygen species (i.e.,  $^1O_2$  and  $O_2^{\bullet-}$ ) under UV irradiation and cause DNA damage. For example, Johnson Inbaraj et al. reported that PBSA showed strong oxidizing properties when UV irradiated in neutral aqueous solution in the presence of cysteine, glutathione and azide [13]. Zhang et al. developed a computational method based on the density functional theory (DFT) to predict and evaluate the photodegradation behavior of PBSA and found that energy and electron transfer reactions of excited state PBSA (PBSA\*) could photogenerate  $^1O_2$  and  $O_2^{\bullet-}$  [14,15]. Therefore, it is essential to develop advanced treatment technologies for eliminating PBSA in aqueous solutions for the sake of reducing potential risk to ecological system.

During the past years, various advanced oxidation processes (AOPs) have been reported for the decomposition of organic pollutants in aqueous matrices. Among them, heterogeneous semiconductor photocatalysis using  $TiO_2$  as the photocatalyst has been found to be a promising treatment technology for eliminating organic pollutants, including sunscreens and other PCPs. When irradiating with photons of energy equal to or exceeding the band gap energy of  $TiO_2$  (for anatase, 3.2 eV band gap), valence band holes ( $h_{vb}^+$ ) and reductive conduction band electrons ( $e_{cb}^-$ ) are generated [16,17]. The photogenerated holes can: (i) directly oxidize the adsorbed chemical substance; or (ii) produce adsorbed hydroxyl radical ( $HO^{\bullet}$ ) via the surface-bound  $OH^-$  and/or the adsorbed water molecules. As a highly reactive oxidant,  $HO^{\bullet}$  is capable of unselectively reacting with most recalcitrant organic contaminants at near-diffusion-controlled rates in water ( $10^8$ – $10^{10} M^{-1} s^{-1}$ ). Therefore,  $TiO_2$  is considered to be the most suitable semiconductor for widespread environmental photocatalytic applications because it is photoactive, non-toxic, inexpensive, and relatively biologically and chemically stable [16,17].

This study reports on the photocatalytic degradation of PBSA in aqueous suspensions of  $TiO_2$ . The main purpose of this study is to (i) study the influence of process condition and water matrix on photocatalytic degradation; (ii) clarify the dominant reactive species

involved in photocatalysis process; (iii) characterize intermediates and photoproducts; (iv) elucidate the mechanism and transformation pathways leading to PBSA mineralization; (v) compare with structurally related compounds in photocatalytic degradation. To the authors' knowledge, this is the first study that includes a systematic exploration of kinetics, intermediates and degradation pathways of PBSA photocatalytic degradation.

## 2. Experimental

### 2.1. Chemicals and materials

PBSA, 2-phenyl-1H-benzimidazole and benzimidazole were purchased from Sigma-Aldrich and used as received. Commercial humic acid (sodium salt) was purchased from Aldrich. HPLC grade methanol and acetonitrile were obtained from Fisher Scientific. Other reagents were at least of analytical grade and used as received without further purification. Non-porous titanium dioxide (Degussa P25  $TiO_2$ , Germany) with primary particle diameter of 30 nm, specific surface area of 50  $m^2 g^{-1}$  and crystal distribution of 80% anatase and 20% rutile was used as the photocatalyst for most of the experiments. Hombikat UV100 (100% anatase, 5 nm, 250  $m^2 g^{-1}$ ) and Aldrich rutile (100% rutile, 750 nm, 3  $m^2 g^{-1}$ ) were also used as photocatalysts in the preliminary experiment. Syringes (Injekt-F, 1 mL) were purchased from B. Braun. Millex-HV syringe filters (PVDF, 0.45  $\mu$ m) were purchased from Millipore Corporation. All the solutions were prepared with 18  $M\Omega$  cm water from a Milli-Q water purification system.

### 2.2. Photocatalysis procedures

The photocatalytic experiments were performed in an open Pyrex glass cell with approximately 60 mL volume containing the aqueous suspension of  $TiO_2$  powder and PBSA. The irradiation source was a high pressure mercury lamp (HPK 125W, Heraeus) with maximum emission wavelength mainly around 365 nm. Infrared radiation (IR) was well filtered by water circulation in the reactor jacket which maintained the temperature at  $20 \pm 1^\circ C$ . Direct photolysis caused by UV irradiation was avoided by using a 340 nm cut-off filter (0–52 Corning). The radiant flux entering the reactor was measured directly by a VLX-3W radiometer with a CX-365 detector (UV-A) and was found to be approximately 3.32  $mW cm^{-2}$ . A volume of 25 mL aqueous solution containing PBSA and  $TiO_2$  powder with required concentration was introduced in the reactor. Before irradiation, the suspension was magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium. During irradiation, aliquots of samples ( $\sim 300 \mu$ L) were withdrawn with the help of syringe at various intervals and filtered through syringe filters to remove  $TiO_2$  particles before analysis. The adsorption of PBSA on filters was found to be negligible based on a preliminary test. Total volume of the samples withdrawn from each experiment was less than 10% (by volume) of the reaction solution. The pH of the reaction solution was adjusted by adding 0.1 M  $HClO_4$  or 0.1 M NaOH.

### 2.3. Analytical procedures

A Shimadzu 10A series high performance liquid chromatography (Shimadzu, Japan) with a SPD-M10A DAD was employed to analyze the concentration of PBSA, 2-phenyl-1H-benzimidazole, benzimidazole and benzoic acid, as well as the abundance of the photocatalytic degradation intermediates. The intermediates generated during photocatalysis of PBSA were analyzed by a HP 1100 series HPLC system equipped with a API 3000 triple quadrupole mass spectrometer (Applied Biosystems/MDS Analytical Technologies, Foster City, CA, USA) and coupled with a TurbolonSpray source

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