Degradation of boscalid by nitrogen-doped/undoped TiO$_2$ and persulfate ions using different activation conditions and the identification of its main degradation products using LC/MS/MS

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H I G H L I G H T S

- N-doped TiO$_2$ catalyst has a higher photocatalytic activity under sunlight than undoped TiO$_2$.
- The addition of persulfate increases the performance of photocatalysis based TiO$_2$.
- A MRM method for qualitative analysis of Bd and its identified DPds was developed.
- DPds with structures that resulted from ring opening of Bd have not been observed in the previous studies.

A R T I C L E   I N F O

A B S T R A C T

The degradation of boscalid (Bd) in an aqueous solution was studied using different oxidation systems, including the persulfate ion (PS), TiO$_2$ (UT), N-TiO$_2$ (NT) and mixtures of UT/PS and NT/PS under sunlight irradiation, in addition to using heat-activated (50 or 80 °C) PS ions. NT exhibited a higher percent Bd degradation than UT, which was explained by a higher surface area and a higher amount of anatase for NT. However, the NT/PS or UT/PS systems did not degrade Bd as much as PS alone under sunlight, which may be a result of interactions between the produced hydroxyl and sulfate radicals. Eventually, the highest Bd degradation was obtained by the activation of PS at 80 °C. However, the degradation of Bd by NT or UT in an aqueous solution containing MeOH was completely inhibited. MeOH is a scavenger for hydroxyl radicals, OH· and the positive holes of activated catalysts. In addition, the PS system was influenced more than the UT/PS and NT/PS systems were in the presence of MeOH. This result can be explained by the facts that (i) MeOH scavenged more OH· than SO$_4^-$, and (ii) more SO$_4^-$ was present for the UT/PS and NT/PS systems than for the PS. Therefore, the NT/PS and UT/PS systems showed a higher percent Bd degradation in an aqueous solution containing MeOH than the PS system did. Eventually, an analysis of the Bd residues was carried out using LC/MS/MS, and the seven basic intermediates were identified.

1. Introduction

Boscalid (Bd) is one of the most commonly used fungicides [1] because it can effectively inhibit spore germination [2] and can be used for a variety of agricultural products [3–5]. However, Bd has a relatively high stability during hydrolytic and photolytic

degradation [6,7]. Recently, a study on Bd photodegradation demonstrated that the cyclized photoproducts can be more toxic than Bd itself [8]. Hence, Bd might present an environmental risk when intensive fungicide usage is carried out. Reilly et al. [9] showed that Bd was the most frequently detected pesticide in surface and ground waters located close to potato fields in the United States; the Bd concentration reached 2120 ng/L in some places. This situation may be worse in low-income countries, which already have high pesticide contamination levels in their limited water sources [10–14] as a result of uncontrolled pesticide practices [15].

Water that is contaminated by Bd can be effectively treated by its adsorption onto activated biochar [16] and activated clinoptilolite [17].
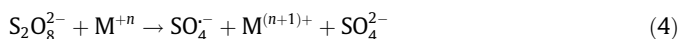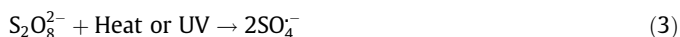
However, these treatment processes do not provide a complete solution because they still require the safe disposal of spent adsorbent. The complete removal of different organic pollutants from water can also be achieved by their oxidation with hydroxyl radicals (OH·) in advanced oxidation processes (AOP) [18–20]. TiO$_2$ is one of the most utilized photocatalysts in AOP because it has a high stability and a high photocatalytic degradation efficiency, and it is a non-toxic and low-cost material [21–25]. When the surface of TiO$_2$ is exposed to UV light, its valence band (VB) electrons excite and generate electron/hole (e$^-$/h$^+$) pairs, which then promote the formation of OH· (Eqs. (1) and (2)), which is responsible for organic compound degradation.

$$TiO_2 + h\nu \ (\lambda < 387 \ nm) \rightarrow e^- + h^+ \tag{1}$$

$$h^+ + H_2O \rightarrow OH^· + H^+ \tag{2}$$
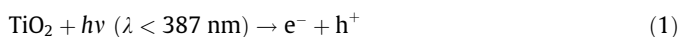
The photocatalytic degradation of Bd by UV/TiO$_2$ has been previously investigated; mono- and di-hydroxylated Bd were identified as the main photoproducts, which can be easily degraded via the rupture of the N–C bond [26].

Despite extensive photocatalysis research conducted over recent years, no waste water treatment plants using UV/TiO$_2$ were developed, which may be due to the high costs of UV lamps and electrical energy. There are also some limitations in using TiO$_2$ as a photocatalyst such as the rapid e$^-$/h$^+$ recombination [20]. However, this recombination can be minimized with the use of electron scavengers, such as persulfate ions (PS) [27], or by adding a small amount of Fe^{+3} [28]. Another limitation lies in the fact that TiO$_2$ is not efficiently activated under visible light; only 5% of the solar spectrum that reaches the Earth's surface is absorbed by the catalyst. Consequently, most of the photocatalytic degradation studies were performed under UV irradiation. Recently, in the literature, different approaches have been proposed for the improvement of the visible-light photocatalytic activities of various semiconductors. Among them, doping TiO$_2$ with nitrogen atoms leads to great enhancements in its photocatalytic properties under visible light [29].

To avoid the problems linked with the utilization of TiO$_2$, other AOPs using oxidants such as PS or peroxymonosulfate have recently attracted increasing attention. PS can be activated thermally, by UV irradiation and by mixing with transition metals to produce sulfate radicals, which are stronger oxidants than PS itself (Eqs. (3)–(5)) [30–39].

$$S_2O_8^{2-} + Heat \ or \ UV \rightarrow 2SO_4^{·-} \tag{3}$$

$$S_2O_8^{2-} + M^{+n} \rightarrow SO_4^{·-} + M^{(n+1)+} + SO_4^{2-} \tag{4}$$

$$SO_4^{·-} + e^- \rightarrow SO_4^{2-} \tag{5}$$

However, in the PS/metal system, the excess concentration of an oxidized metal ion can react with the produced sulfate radicals [40].

For example, Ahmed et al. [41] showed that a UV–Vis/peroxymonosulfate/Fe (II) system could perform ten times faster than a UV–Vis/TiO$_2$ system for pesticide and pharmaceutical removal from domestic wastewater, which was attributed to the higher selectivity in the reactions of SO$_4^{·-}$ with respect to HO· in organic rich matrices.

In this context, the main objectives of this work were to study the photocatalytic degradation of Bd under sunlight using an N-doped TiO$_2$ catalyst, which was expected to have a higher activity under sunlight than undoped TiO$_2$. To limit the electron–hole

recombination and improve Bd degradation, the influence of PS as an electron scavenger was investigated. Because TiO$_2$ suffers from some limitations, Bd degradation was also investigated using PS as an oxidant, which was subsequently thermally activated. All of these investigated systems are discussed and compared taking into account the role played by radicals.

Efforts were also directed toward the analysis of the Bd residues and the identification of as many degradation products (DPds) as possible using high-performance liquid chromatography with tandem mass spectrometry (LC/MS/MS).

A MRM method for the qualitative analysis of Bd and its identified DPds was developed to confirm the proposed structures of the DPds and to propose a complete pathway of the Bd degradation. The main DPds are compared with those previously obtained by the photocatalytic degradation of Bd using UV/TiO$_2$ [25] and with results obtained from the online electrochemistry liquid chromatography mass spectrometry (EC/LC/MS) analysis of Bd, where Bd was used for the simulation of pesticide metabolism [42].

2. Experimental section

2.1. Materials

Methanol and titanium isopropoxide were purchased from Merck Chemicals. Diethyl amine was obtained from the OXFORD Laboratory. Ethanol was purchased from Sigma–Aldrich. All other chemicals were of high analytical grade. Deionized water (DIW) (18.2 M ohm/cm, 3 ppb Total Organic Content) was supplied by a Millipore water purification system (Milli-Q). Bd was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

2.2. Preparation of undoped and N-doped TiO$_2$

The preparation of TiO$_2$ (UT) and N-doped TiO$_2$ (NT) was carried out mainly as reported by Senthilnathan and Philip [43]. Briefly, 24 mL of titanium isopropoxide was dissolved in 200 mL of ethyl alcohol, and 24 ml of diethyl amine was added for the NT preparation. Diethylamine N-doped TiO$_2$ has the largest pore volume among the following N-dopants: methylamine, ethylamine, diethylamine, ethylenediamine, triethylamine, triethanolamine and ammonia [44]. Then, 200 mL of HCl (0.1 M) was added to the above solution, upon which a white creamy solution immediately formed; this solution was stirred for 3 h and aged overnight. The prepared solution was autoclaved at 80 °C for 4 h and then dried at 80 °C for 24 h. The dried powders were collected and washed with ethanol (200 ml × 2) and 100 ml of DIW (with fast filtration) and finally rinsed with ethanol (200 ml × 2). These samples were then calcinated at 550 °C for 4 h. The prepared UT and NT were gently ground using a mortar and pestle, sieved through a test sieve with an aperture size of 160 mm and placed in brown vials.

2.3. Characterization of undoped and N-doped TiO$_2$

The X-ray diffraction (XRD) measurements for the UT and NT were carried out using an Empyrean diffractometer equipped with Cu radiation CuKα (λ = 1.54056 Å) at the National Research Centre; the scanning range was 5–80° (2θ) with step size of 0.2 (2θ). The surface area characteristics of the UT and NT were studied at the Central Metallurgical Research Institute by liquid nitrogen adsorption at 77 K using a Nova 2000 Quantachrome with an automatic adsorption gas system (0.15% accuracy). The surface areas (S_{BET}, m^2/g) and the BET–C constants were evaluated from the BET plots. The total pore volumes (V_P, ml/g) were obtained from the amount of nitrogen adsorbed near the saturation vapor pressure (P/P^o = 1) of the adsorbate (N$_2$ gas).