



The photocatalytic degradation and modeling of 2,4-Dichlorophenoxyacetic acid by bismuth tungstate/peroxide



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HIGHLIGHTS

- Bismuth tungstate was synthesized through a hydrothermal process.
- Photocatalytic degradation of 2,4-D by bismuth tungstate were optimized at pH = 5.
- The involvement of H₂O₂ doubled the 2,4-D photocatalytic decay rate.
- Kinetic models were derived to describe the degradation of 2,4-D.

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ABSTRACT

The photodegradation of herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) by bismuth tungstate with or without hydrogen peroxide by visible light was investigated. The photocatalytic reactions were studied under various conditions including the examination of the effects of initial pH, 2,4-D concentrations, light intensities, and hydrogen peroxide. Photocatalytic reactions were optimized at pH 5, higher or lower pH levels will reduce the decay rate due to the phase change of 2,4-D molecules and/or bismuth tungstate. The increase of catalyst/[2,4-D] ratio and light intensity were found to improve the 2,4-D decay rates, due to the increment of number of active sites and electron–holes on the Bi₂WO₆ surface, respectively. The involvement of H₂O₂ in the Bi₂WO₆ photocatalytic process can effectively double the 2,4-D decay rate, however, this was observed within a narrow gap of H₂O₂ dosages and easily overdosed, a precise control of H₂O₂ dosing is critical for a successful application. Kinetic models were derived successfully, so that the process performance is predictable by incorporating initial pH level, 2,4-D concentration, light intensities, and hydrogen peroxide.

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1. Introduction

Semiconductor photocatalysts have attracted great interests for their application in the detoxification of water and wastewater [1–5]. TiO₂ is by far the most popular one for its high photocatalytic activity, good photostability, non-toxicity, and low cost. However, the large bandgap of TiO₂ (3.2 eV) makes its excitation only feasible by UV light with wavelengths below 387 nm, which greatly limits its usage of free solar energy (only less than 5% of the full spectrum is within this range) and hinders its commercialization. Therefore, in order to eliminate the drawback, broadening the visible light response region has received considerable attention, such as the modification of TiO₂ by doping transition metals [6], doping non-metallic elements [7], and forming composite photocatalysts from different semiconductors [8]. Bismuth tungstate (Bi₂WO₆), as one of the simplest members of the Aurivillius oxide family

(having a crystal structure composed of accumulated layers of alternating bismuth oxide (Bi₂O₂)²⁺ layers and octahedral (WO₄)²⁻ sheets), has received great interest. Shang et al. have reported that Bi₂WO₆ can degrade both CHCl₃ and CH₃CHO under visible-light irradiation [9], which revealed a potential application of Bi₂WO₆ in environmental purification. The synthesis of Bi₂WO₆ from the hydrothermal method has been widely reported in recent researches [10–13].

2,4-Dichlorophenoxyacetic acid (2,4-D) is a popular herbicide which is used globally because of its low cost and effectiveness on broadleaf plants. The 2,4-D controls broadleaf weeds selectively in cereals such as wheat, barley, oats, and raps crops and is typically applied to cereals at a rate (active ingredient) of 0.5 kg/ha [14–16]. It is often formulated as amine salts or low volatile esters through various manufacturing processes, and exists in many commercial products [17,18]. 2,4-D is an environmental concern because of its high solubility in water (i.e., 900 mg/L at 25 °C). It would not be easily absorbed in coarse-grained sandy soils (with a low fraction of organic carbon) or basic soils, but it can leach

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down into groundwater and contaminate the natural water resources. The 2,4-D is detectable in surface water and ground water not only during the application of the herbicide, but also after a long period of usage. When released into fresh water, 2,4-D is readily degraded by microorganisms at a rate that depends on factors such as water type, level of nutrients, temperature, oxygen availability, sediment load, and dissolved organic content.

Bi_2WO_6 exhibits promising photocatalytic activities in degrading organics. The removal efficiency of herbicide 2,4-D by Bi_2WO_6 using visible light is investigated in this study.

2. Experimental

2.1. Synthesis of photocatalyst and characterization

All the chemicals used in the experiments were analytical grade without further purification. The water used in the preparation of all the solutions was obtained from a Barnstead Nonopure water purification system with conductivity of 18 Ω m. In this work, the catalyst Bi_2WO_6 was synthesized through a hydrothermal process, in which 10 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was first dissolved in a 6 mL 15% nitric acid solution. A white precipitate was formed when the above solution was added into 30 mL of 5 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ solution. The pH level was adjusted to 6 by adding KOH solution. After being magnetic stirred at room temperature for 1 h, the resulting precursor suspension was added to a 50 mL Teflon lined autoclave, which was sealed in a stainless steel tank and heated at 180 °C for 24 h. Subsequently, the reactor was cool down to room temperature by natural ventilation. The resulting samples were washed with deionized water several times and dried at 100 °C in an oven. X-ray diffractometry patterns (XRD) of the powders were recorded at room temperature by a Bruker D8 Advance X-ray diffractometer using the Cu K α radiation and a 2θ scan rate of 0.04°/s.

2.2. Dark adsorption test

For all dark reactions (i.e. without the involvement of any light irradiation), the reactor was 200 mL quartz beaker wrapped externally with aluminum foil. The Bi_2WO_6 catalyst and probe compound were mixed in a pre-determined volume of solution for 15 min to ensure a homogeneous solution. The dark reactions were normally initiated by adding diluted hydrogen peroxide. If hydrogen peroxide was not involved, the experiments were initiated by turning on the magnetic stirrer. Samples were taken out from the reaction vessel at a prefixed time for further HPLC analysis.

2.3. Photochemical reaction

The photodegradation process was conducted in a computerized Luzchem CCP-4V photochemical reactor. The Bi_2WO_6 and probe compound were prepared as described before. A quartz reactor was used and placed inside the photochemical reactor covered with aluminum foil to minimize volatilization. The light sources of 420 nm lamps (LZC-420, the emission spectra were shown in the insert of Fig. 6) were symmetrically placed in the reactor. The light intensity to which the reactor was exposed was determined from a light meter (Extech). A magnetic stirrer was located at the reactor's base such that a homogenous Bi_2WO_6 suspension could be maintained in the quartz vessel throughout the reaction.

The initial concentration of the probe compound at time zero was determined from an unexposed sample. The illuminated samples were removed from the photoreactor at predetermined time intervals and analyzed by high-performance liquid chromatography (HPLC) with an Alltech Elite solvent degasser, a Waters 515

HPLC pump with a 10 μL injection loop, and a Waters 2487 dual λ absorbance detector. The compounds in the sample were separated by a RESTEK column packed with Pinnacle™ Octyl Amine (5 μm , 250 \times 4.6 mm). The mobile phase was a mixture of 0.15% acetic acid and ACN (using a ratio of 40:60 with a pH value around 4) at a flow rate of 1.0 mL/min for the quantification of 2,4-D. The wavelengths of the UV detector were set at 283 nm as the intensities of the absorption peaks at this wavelength were dominant.

3. Results and discussions

3.1. Characterization of synthetic catalyst

Fig. 1 shows the representative XRD pattern of synthetic catalyst. Peaks in the diffraction pattern can be indexed as the orthorhombic Bi_2WO_6 with the calculated lattice constants ($a = 5.457 \text{ \AA}$, $b = 5.436 \text{ \AA}$, and $c = 16.427 \text{ \AA}$), which are consistent with the value of JCPDS card 73-1126. No redundant peaks of any other phase are indexed, suggesting the purity of the synthetic catalyst is high.

3.2. Photocatalytical efficiency

3.2.1. Effects of initial pH

The direct photolysis of 2,4-D by 420 nm light irradiation was negligible ($k = 2 \times 10^{-5}$). The effect of different initial pH levels on the photocatalytic degradation rates of 2,4-D was investigated. In general, the photocatalytic degradations rate was found to strongly depend on pH. The decay of 2,4-D basically follows pseudo first-order kinetics. The decay rate increased as the pH levels increased from 2.11 to 4.91. However, further increase of the pH (up to 8.98 in this study) will retard the rate gradually. The optimal pH level for 2,4-D decay was determined around 5.0, as shown in Fig. 2.

For a heterogeneous media, the active sites on the surface of most semiconductors are dependent on the concentration of hydrogen ion (H^+) or hydroxide ion (OH^-) in aqueous solution. As a result, pH of the reaction solution may significantly affect the adsorption property and catalytic activity of the photocatalyst. It was reported that Bi_2WO_6 is unstable in acidic solution, and it can be transformed to H_2WO_4 and Bi_2O_3 [19], leading to a poor photocatalytic activity of Bi_2WO_6 at low pH levels. The redox potential of Bi_2WO_6 theoretically could be affected by the pH of solution, just similar to that of TiO_2 as reported by Turchi and Ollis [20]. When pH is higher than 5, bisphenolate anion of 2,4-D becomes

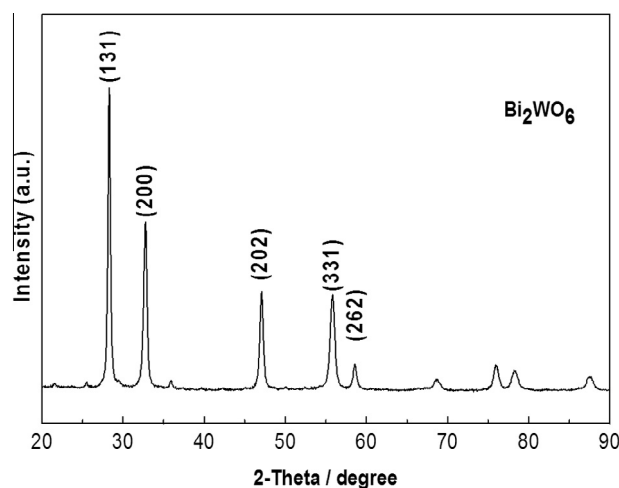


Fig. 1. XRD patterns of Bi_2WO_6 samples prepared at 180 °C for 24 h with pH 6.

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