



Degradation of azole fungicide fluconazole in aqueous solution by thermally activated persulfate

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HIGHLIGHTS

- The azole fungicide FLC in aqueous phase can be efficiently removed by heat-activated persulfate.
- Operating conditions can significantly affect the decomposition of FLC.
- Natural water constituents can inhibit the degradation rate of FLC in thermally activated persulfate system.
- The carbon in the benzene ring of FLC was identified as the predominant reactive site.
- Intermediate products during FLC oxidation were identified and a primary reaction mechanism was proposed.

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ABSTRACT

The azole fungicide fluconazole (FLC) is persistent in conventional wastewater treatment plants, thus posing potential threats to human and ecosystem health. This study investigated the oxidation of FLC in aqueous solution by thermally activated persulfate (TAP) under different operation conditions. Higher temperature greatly improved the removal rate of FLC (0.057 h^{-1} for $30\text{ }^{\circ}\text{C}$ and 0.223 h^{-1} for $60\text{ }^{\circ}\text{C}$) and the relationship between pseudo-first-order rate constant (k_{obs}) and temperature fit the Arrhenius equation, with a comparatively low activation energy of 37.8 kJ mol^{-1} . The degradation rate constants were enhanced with the increase of PS concentration during FLC oxidation (0.072 h^{-1} for 1.0 mM PS and 0.50 h^{-1} for 20 mM PS). Solution pH influenced the k_{obs} of FLC degradation and the highest and lowest degradation rates were obtained at pH 3 (0.51 h^{-1}) and pH 5 (0.23 h^{-1}), respectively. Increasing the level of natural water constituents (HCO_3^- , Cl^- , and humic acid) significantly inhibited FLC degradation. Geometry optimization of FLC was performed using density functional theory (DFT) and the data indicated that the C3 atom in the benzene ring was the most reactive site. SPE-HPLC/MS/MS analysis showed that intermediate products could form during FLC oxidation by PS and the total organic carbon (TOC) results indicated that FLC could be mineralized into CO_2 and H_2O . Accordingly, a plausible pathway for the degradation of FLC by the thermally activated PS could be proposed. The results of this study suggested that TAP is an applicable approach for the removal of azole fungicides in water.

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1. Introduction

Azole fungicides are applied in many products including drugs and personal care products due to their excellent antifungal prop-

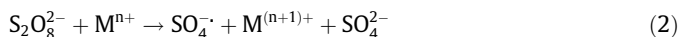
erties. The activities of these compounds derive from the inhibition of cytochrome *P*-450 enzyme activity affecting sterol biosynthesis [1], which eventually decreases the principal sterol ergosterol in the fungal cell membrane to alter membrane functions and permeability [2]. Because traditional biochemical treatment cannot completely remove azole fungicides, they can enter the aquatic environment as treated wastewater effluent and enter the terrestrial environment by wastewater irrigation and the land use of sludge [3–6]. Unfortunately, there are many reports that azole

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fungicides may cause harmful biological effects on organisms (including algae, fish, and microorganisms) [7–14]. Azole fungicides are considered a group of emerging contaminants and it is urgent to develop alternative methods to remove these contaminants in wastewater to decrease the associated risks.

Advanced oxidation processes (AOPs) are of growing interest because they are able to transform and even mineralize organic pollutants, thus minimizing their potential harm to the environment and human health. AOPs including Fenton, electron-Fenton, and UV/H₂O₂ have been widely applied for drug wastewater treatment due to the presence of hydroxyl radicals (HO·) with high reactivity [15–17]. In recent years, sulfate radical (SO₄^{·-})-based AOPs have been proposed as an alternative method for the removal of organic pollutants. Activating persulfate (PS) can generate SO₄^{·-} by various methods like transit-metals, heat, and sonolysis (Eqs. (1) and (2)). Similar to HO· (*E*⁰ = 2.7V), SO₄^{·-} is a radical of relatively high standard reduction potential (2.5–3.1 V) [18] and can act as a powerful oxidant to diminish many organic pollutants in water. In addition, SO₄^{·-} is relatively more stable and selective during treatment processes compared to HO· (i.e., 300 μs vs. 40 μs for lifetime) [19]. Due to its moderate cost, relatively high stability, solubility, and redox potential, SO₄^{·-}-based AOPs have become increasingly used for the treatment of polluted soil and water in situ [20,21]. Additionally, thermally activated persulfate (TAP) is an important method of activation due to high efficiency and is increasingly utilized in remediation efforts for the treatment of hazardous organic chemical-contaminated water or soil [22–25]. However, to date, there are no reports of the use of SO₄^{·-}-based AOPs for the degradation of azole fungicides in aqueous solution.



The present study aimed to explore the practical possibility of using TAP to degrade azole fungicides in aqueous solution. Using the azole fungicide fluconazole (FLC) as a model chemical, we studied the influence of various factors including temperature, pH, oxidant concentration, and natural water constituents (humic acid (HA), Cl⁻, and HCO₃⁻) on the oxidation process by determining the kinetic parameters of degradation. The oxidation products were also identified, and the reaction pathways were proposed.

2. Materials and methods

2.1. Materials

FLC (≥99.5%) was supplied by Genebest Pharmaceutical Co., Ltd (Zhejiang, China) (Fig. 1). Sodium persulfate (≥99.99%) was purchased from Aladdin (Shanghai, China) and used as source of SO₄^{·-}. Methanol (HPLC grade) was obtained from Honeywell (Guangzhou, China) and used as a mobile phase and radical scavenger. Humic acid sodium salt (technical grade) (HA) was purchased from Aldrich (Guangzhou, China) for a model of organic matter. All other reagents were analytical grade and purchased from the Damao Chemical Reagent Factory (Tianjing, China).

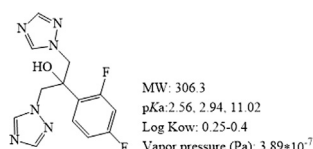


Fig. 1. Structure of the azole fungicide fluconazole.

2.2. Experimental procedures

All batch kinetic experiments were performed in 100-mL conical glass flasks placed in a constant temperature oscillator (Jiangnan Instrument Co., Ltd, Ningbo, China) at a predetermined temperature and at a speed of 200 rpm. Stock solutions of FLC and sodium persulfate were prepared using ultrapure water and then diluted using ultrapure water to predetermined concentrations as needed. To reduce interference from other ions, the reaction solution pH was adjusted by addition of 0.01 M H₂SO₄ or NaOH. The final volume of the reaction solution was 20 mL. The effects of water constituents on the degradation of FLC were investigated using chloride ion, bicarbonate ion, and HA. At various time points, 0.5 mL of aliquots of the reaction solution were withdrawn and transferred to vials containing methanol to terminate the reaction before analysis. Control experiments without the oxidant were also conducted under the same conditions and the results indicated the FLC cannot hydrolyze or thermally decompose. All the experiments were performed in triplicate and the average values of the data are presented.

2.3. Analytical methods

The FLC concentrations in aqueous solution were measured by high performance liquid chromatography (HPLC; Agilent1260, Agilent Technologies, USA) equipped with a diode array detector. The separation of FLC was carried out on an XDB-C₁₈ analytical reversed-phase column (4.6 mm × 150 mm, 5 μm) and the detection wavelength was set at 310 nm. The injection volume and the column temperature were 20 μL and 25 °C, respectively. The mobile phase was a mixture consisting of methanol and water (70:30, v/v) and was eluted at a flow rate of 0.8 mL/min. The products of FLC degradation were concentrated by solid phase extraction (SPE) and identified by LC-MS/MS. The detailed methods are provided in the [Supplementary materials](#). The total organic carbon (TOC) in reaction solution were measured by TOC analyzer (TOC-L CPH, Shimadzu, Japan). Persulfate anion concentration was determined by an UV-vis spectrophotometer (UV-2600, Shimadzu, Japan) and the absorbance wavelength of the PS complex was set at 352 nm. PS calibration curve were conducted with a range of concentration of 0.2–30 mM.

2.4. Frontier orbitals and electron densities

All calculations were conducted using the 2009 version of the Gaussian suite program. The geometrical parameters of FLC were optimized using the Becke, three parameters, Lee–Yang–Parr (B3LYP) level of theory implementing the 6-31+G(d, p) basis set. In order to guarantee that the molecule was at the minimal potential energy surface, a frequency calculation was also performed. The frontier molecular orbital (FMO) and frontier electron density (FED) were calculated at the mentioned level. The Mulliken charge distribution was also calculated for the optimized structure on the B3LYP/6-31-G(d, p) level of theory.

3. Results and discussions

3.1. Effect of reaction temperature

Fig. 2 shows the degradation of FLC at different temperatures (30–60 °C) at pH 5. The degradation rate of FLC increased within the TAP system as the temperature increased from 30 °C to 60 °C and the removal rate of FLC increased from 41% to 80% within 8 h. The increase of the reaction temperature improved the formation of SO₄^{·-} due to more decomposed PS [23–25]. Additionally,

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