Photochemical fate and advanced oxidation of Pyrimethanil in waters and wastewater

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Abstract

Commonly used fungicide pyrimethanil (PYR) has been detected in various aquatic environments, presenting persistence, adverse effects on ecology and resistance to conventional degrading methods[1,2]. In this study, the abiotic phototransformation of PYR was investigated under simulated solar irradiation (SSI). The results indicated that photolysis was the principal degradation process, following pseudo – first order kinetics in the following order: ultra-pure < sea < lake < river water. The impact of prevalent water components such as humic acid, Fe^{3+}, NO$_3^-$, and Cl$^-$ was examined. Furthermore, sulfate radical-based advanced oxidation processes (SR-AOPs) activated by SSI were explored for its removal from both ultra-pure water and wastewater. SSI/persulfate (PS) exhibited the best degradation efficiency, achieving 100% PYR removal in 240 min, compared to PMS and H_2O_2. Wastewater experiments significantly affected the degradation efficiency, leading to a 55% decrease in first-order reaction rate constant. Scavenging studies assessed the role of reactive species revealing •OH as the dominant contributor concerning SSI/PS process. Major phototransformation routes include C–N bond cleavage, hydroxylation, and oxidative ring opening as indicated by liquid chromatography-high-resolution mass spectrometry (LC-HRMS). Potential environmental implications of photoproducts were evaluated using *in vitro* (Microtox assay) and *in silico* (ECOSAR) ecotoxicity tools.

Keywords: pyrimethanil; liquid chromatography-high resolution mass spectrometry; pesticides; phototransformation products; toxicity assessment

1. Introduction

The widespread use of pesticides, particularly organic pollutants like fungicides, has raised growing environmental and public health concerns due to their persistence and accumulation in natural ecosystems[3]. Among these, residues of fungicides are frequently detected in aquatic environments such as surface waters and wastewater[4]. Pyrimethanil (PYR) is an anilino-pyrimidine fungicide that is widely applied in agriculture and has been consistently detected in surface waters[5] and wastewater streams[6]. The chemical stability of PYR allows it to withstand natural degradation mechanisms, including photodegradation, hence enabling it to remain in the environment long after application[7]. Consequently, important research topics now include efficient treatment techniques for its elimination[8]. Although advanced oxidation processes (AOPs), particularly TiO_2-based photocatalysis, have been thoroughly investigated for pesticide degradation[9], sulfate radical-based AOPs (SR-AOPs) have yet to be adequately examined for PYR. These processes provide significant benefits, since sulfate radicals ($SO_4^{\cdot -}$) exhibit a superior oxidation potential (E^o = 2.5–3.1 V) and function well across a wider pH spectrum compared to hydroxyl radicals($\cdot$OH)[10]. PS may be activated using UV radiation, heat, or transition metals, leading to the production of several reactive species such as $\cdot$OH, $SO_4^{\cdot -}$, and $^1O_2$[11].

2. Methods

A Suntest CPS+ apparatus from Heraus (Hanau, Germany) was used to simulate sun irradiation. A 1100 W xenon arc lamp, functioning at 500 W m^{-2}, equipped with glass filters to obstruct wavelengths below 290 nm. Distilled water samples were fortified with 5 mg L^{-1} PYR. PS, PMS, and H_2O_2 were selected as potential oxidants. 1 mM of each oxidant was introduced into a 50 mL reaction solution containing 5 mg L^{-1} PYR and was maintained at a steady temperature in a Pyrex UV reactor equipped with a tap-water cooling circuit. SSI/PS was identified as the most efficacious procedure, and the impact of PS dose was studied. A solution of 5 mg L^{-1} PYR and 1 mM PS was subjected to the SSI procedure to detect the degradation products of PYR.

3. Results

Among the studied systems, SSI/PS exhibited the greatest removal efficiency (96.4% in 240 minutes, k_{obs} = 0.0136 min^{-1}), outperforming SSI/H_2O_2 (84%) and SSI/PMS (52%). Elevating PS concentration from 0.2 to 1.0 mM markedly improved degradation, indicating a proportionate correlation up to 0.8 mM and a substantial escalation at 1.0 mM. The composition of the water matrix significantly affected degradation rates. Although 2 mM HCO_3^- marginally improved PYR removal by 11.7%, Cl^- and NO_3^- hindered it by 48% and 70%, respectively, owing to radical scavenging and competition for UV light. Humic acids (10 mg L^{-1}) reduced efficiency, presumably owing to light absorption and radical scavenging.

Experiments on reactive species quenching demonstrated that ·OH and $^1O_2$ were the principal agents in PYR degradation, whereas $SO_4^{\cdot-}$ served a minor function. L-histidine exhibited the most significant inhibition (97.8%), underscoring the significance of $^1O_2$. In real wastewater, PYR degradation was markedly reduced (~55% lower k_{obs}) in relation to purified water, highlighting the influence of natural organic matter and competing chemicals on the efficacy of AOPs. LC-HRMS revealed key transformation pathways including C–N bond cleavage, hydroxylation, and oxidative ring-opening. Ecotoxicity was monitored via the Microtox bioassay, showing initial high toxicity that increased during the first 90 minutes, likely due to reactive transformation products. However, toxicity declined thereafter, returning to near-initial levels after 240 minutes of irradiation, indicating that extended photoactivation enhances detoxification.

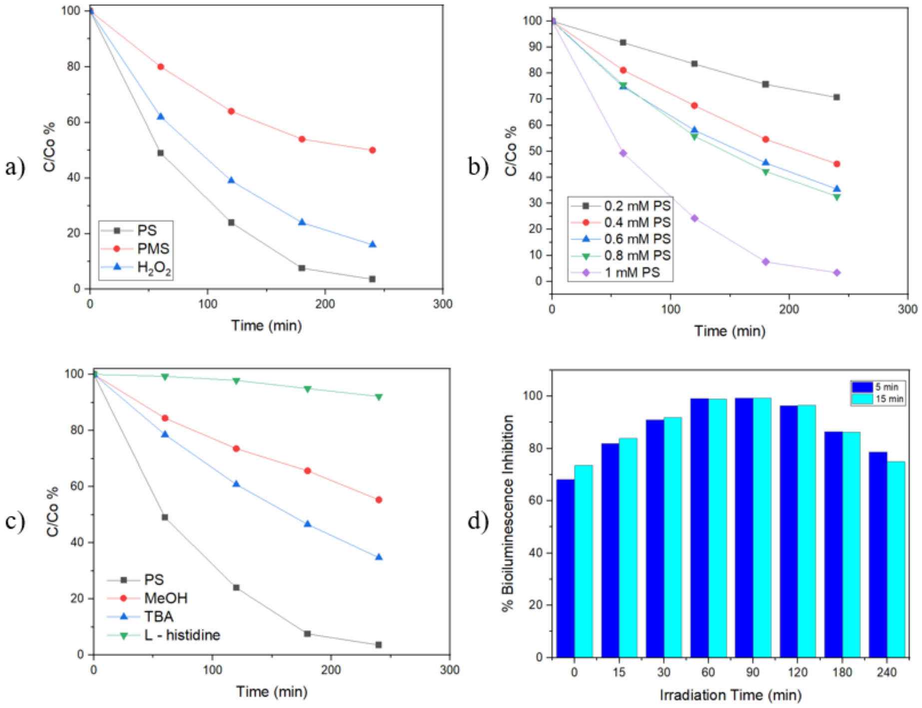

Figure 1. a) Degradation kinetics, b) PS dosage, c) reactive species contributions and d) in vitro ecotoxicity.

4. References

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