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Destruction of phenicol antibiotics using the UV/H_2O_2 process: Kinetics, byproducts, toxicity evaluation and trichloromethane formation potential

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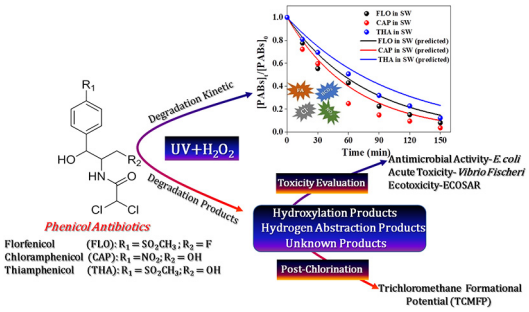
HIGHLIGHTS

- A pseudo-steady-state model was established to predict PABs degradation.
- A degradation pathway via HO·-triggering was proposed.
- Antimicrobial property, acute toxicity and ecotoxicity were evaluated.
- Extending irradiation time for UV/H_2O_2 process was favor of reducing TCMFP due to low DOC.

GRAPHICAL ABSTRACT



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ABSTRACT

Phenicol antibiotics (PABs) degradation by UV/H_2O_2 is important because we need to determine the reduction in toxicity and disinfection byproducts for post-chlorine. In this study, the degradation of PABs, including florfenicol (FLO), chloramphenicol (CAP) and thiamphenicol (THA), was examined. The pseudo-first order degradation rate constants of PABs were 3 times higher in ultrapure water (UW) than that in synthetic wastewater (SW) for these conditions: $[PABs]_0$ = 1 μM, $[H_2O_2]$ = 0.1 mM, and $I_0 = 1.985 \times 10^{-6}$ E L^{-1} s^{-1}. Fulvic acid (FA) and HCO_3^- inhibited PABs degradation, Cl^- and NO_3^- concentrations of up to 5 mM and 10 mM had a negligible impact. The impact of water matrix on PABs degradation was successfully predicted using pseudo-steady-state kinetic model. The degradation of PABs was triggered via hydroxylation and/or hydrogen abstraction. The treatment of PABs via UV/H_2O_2 could decrease their antimicrobial properties, while the byproducts of FLO and THA showed higher acute toxicity in *Vibrio fischeri*. In addition, two identification products (TP-276 and TP-354) of FLO had higher ecotoxicity toxicity (using ECOSAR) in fish, daphnid and green algae. The trichloromethane formation potential (TCMFP) for PABs with post-chlorination in UW and SW can be reduced after UV/H_2O_2 compared to UV, and is related to the corresponding decrease of dissolved organic carbon (DOC).

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1. Introduction

Phenicol antibiotics (PABs), including florfenicol (FLO), chloramphenicol (CAP) and thiamphenicol (THA), are widely used to inhibit disease in both human and livestock aquaculture [1,2]. The overuse of antimicrobial agents has created the risk of transferring antibiotic resistance to pathogenic microbes [3–5]. Meanwhile, PABs have been frequently detected in various aquatic environments and may eventually be present in drinking water sources [6,7]. PABs are very stable [8], and difficult to degrade by conventional water treatment technologies, such as biological processes, filtration, coagulation, flocculation and sedimentation [9–11]. Thus, it is urgent to remove PABs from wastewater before being discharged into aquatic environments.

Advanced oxidation processes (AOPs) are an attractive and promising technology to eliminate organic contaminants. In particular, the combination of ultraviolet light with hydrogen peroxide (UV/H_2O_2) has been frequently utilized to destruct organic pollutants in water by creating highly reactive hydroxyl radical (HO·) [12–15]. Even so, it remains difficult to completely mineralize pollutants over the typical operation time, and a number of byproducts may persist in water [15,16]. The byproducts may have much lower activity [13,17] or retain the properties of the parent compounds (e.g., antimicrobial nature) and potentially become biologically active [18,19]. Furthermore, the toxicity of byproducts may exceed the parent compounds [20]. Therefore, identifying the reaction mechanism and measuring the toxicity of products are an indispensable part of evaluating the UV/H_2O_2 process. However, the current toxicity evaluation of byproducts and parent molecules has focused mainly on a single bioassay (e.g., antimicrobial property, acute toxicity or ecotoxicity). This is inadequate to obtain a comprehensive understanding of the change in toxicity and provide practical guidelines. Additionally, undesirable disinfection by-products (DBPs), including trichloromethane (TCM) can be formed during post-chlorination of PABs after UV/H_2O_2 treatment and this need to be considered [21,22]. Meanwhile, theoretical calculations (e.g., density functional theory) can identify whether target organic pollutants can be efficiently degraded by oxidizing species [23]. To the best of our knowledge, there has no been theoretical calculation on the reactivity of PABs by radical attack or direct photolysis using UV/H_2O_2 process. Water constituents in actual wastewater could affect the efficacy of UV/H_2O_2 process, thus establishing a suitable mathematical model to predict their impact is highly valuable [15,24,25]. Therefore, a comprehensive understanding of the UV/H_2O_2 process is needed that determined the (1) degradation kinetics, (2) byproducts and pathways, (3) change to toxicity and (4) TCM formation potential (TCMFP).

In this study, we examined the impacts of operational variables, such as PABs concentration, H_2O_2 dose, and matrix species (including fulvic acid (FA), HCO_3^-, Cl^- and NO_3^-), on PABs degradation. The relationship between the degradation efficiency and electronic structure of PABs was confirmed by density functional theory (DFT). A pseudo-steady-state kinetic model was established to predict the impact of water constituents on PABs degradation. Meanwhile, the initial fate of PABs via UV/H_2O_2 process was investigated to uncover their destruction pathways. The toxicity of the parent compounds and their byproducts was comprehensively evaluated by antimicrobial property, acute toxicity and ecotoxicity. The TCMFP in post-chlorination was investigated on PABs after UV and UV/H_2O_2 pretreatment.

2. Materials and methods

2.1. Chemicals

FLO, CAP, THA and *p*-chlorobenzoic acid (*p*CBA) were purchased from Aladdin (Shanghai, China). The structures and chemical properties of the antibiotics are shown in Table S1 in the Supporting Information. Ultrapure water (18.2 MΩ·cm) was obtained from a Ulupure water purification system. Hydrogen peroxide solutions were prepared by diluting H_2O_2 (30% w/w) with ultrapure water, which was standardized by the I_3^- method [26]. Other chemical reagents were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The stock solutions (0.1 mM) of FLO, CAP and THA were separately prepared with ultrapure water. Prior to the tests, the stock solution was diluted to a desired concentration.

2.2. Experimental procedure

A collimated beam apparatus (Fig. S1), consisting of one 15 W low-pressure mercury lamp above a quartz reactor, was employed for the batch UV/H_2O_2 studies. Water samples were irradiated and withdrawn at a scheduled interval. A minimum of one hour of warm-up time ensured a stabilized UV emission output. The oxidation was initiated after adding appropriate volumes of H_2O_2 stock solution by stirring (250 r min^{-1}) at room temperature (approximately 25 °C) under UV irradiation. The treatment process with UV alone was conducted as a control under similar conditions.

After the PAB solution was treated by UV/H_2O_2 or UV (initial concentration of PABs = 3 μM, H_2O_2 = 0.3 mM), the PAB reaction solution was further treated with enough chlorination for 24 h in the dark (Cl_2 dose = 1.0 mM). After the chlorination, the disinfectant residual was quenched with ascorbic acid (2.0 mM) [27,28]. The disinfection by-product TCM was analyzed with a static headspace and gas chromatography/mass spectrometry (GC/MS) (Trace2000 Polaris Q). TCM yield was determined according to Eq. (1).

$$\text{TCM yield} = \frac{\text{Formed TCM molar concentration}}{\text{Initial PAB molar concentration}} \times 100\% \quad (1)$$

2.3. Analytical methods

A determination method was used, which included solid-phase extraction (SPE), high-performance liquid chromatography (HPLC), and triple quadrupole mass spectrography (tqMS) (Agilent Technology 1290/6460) with electron spray ionization (ESI) using multiple reaction monitoring (MRM) in the negative mode. The detection limits for FLO, CAP, THA, and TCM were all below 0.1 μg/L. Detailed information about the operation procedures, conditions and parameters is provided in Text S1 and Table S2.

2.4. Calculation of frontier electron densities (FEDs)

All the calculations based on DFT were performed using the DMol3 package with the Perdew-Burke-Ernzerhof/Double-Numerical Dasis 4.4 set. All computations converged upon a true energy minimum, which was confirmed by the absence of imaginary frequencies. The cutoff radius was 4 Å.

2.5. Toxicity tests

The antimicrobial property of the PABs and their byproducts were tested using the *Escherichia coli* bacteria. Because standards of byproducts are not commercially available, it is difficult to assess the toxicity of the products individually. Instead, a sample aliquot was taken from the reaction mixture of PABs in UW via UV/H_2O_2 at each selected time interval. Luria Bertani (LB) broth was used for activation and culturing. After mixing the LB broth with the samples containing parent PABs or byproducts, *Escherichia coli* was incubated in an incubator rotating under 160 rpm at 37 °C for 7 h. OD_{600} (optical density at 600 nm wavelength) was used as an indication of bacterial growth. The acute toxicity assay was carried out against marine luminescent bacterium *Vibrio fischeri*. Quantitative structure-activity relationship (QSAR) analysis, as calculated by the Ecological Structure-Activity Relationship Model (ECOSAR) program, was employed to assess the acute and chronic toxicity for fish, daphnid and green algae.