



Establishment of a pretreatment method for tetracycline production wastewater using enhanced hydrolysis



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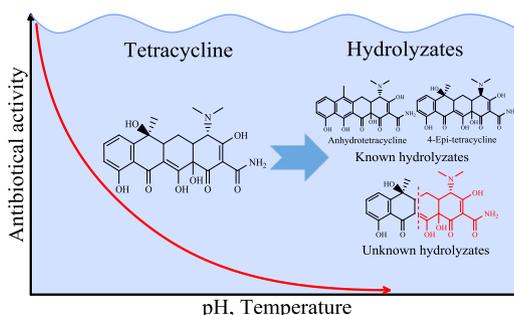
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HIGHLIGHTS

- The hydrolysis half-life of tetracycline was shortened by condition optimization.
- The antibacterial activity was reduced to a negligible level after hydrolysis.
- No anaerobic inhibition was found after enhanced hydrolysis pretreatment.

GRAPHICAL ABSTRACT



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ABSTRACT

High concentrations of antibiotics in wastewater may inhibit the functions of biological treatment systems. Herein, we established a pretreatment method for tetracycline production wastewater using an enhanced hydrolysis process with the optimization of temperature and pH conditions. An increase of 10 °C accelerated the tetracycline hydrolysis rate by 2.22–2.74-fold, and the hydrolysis half-life of tetracycline was shortened by 3.23-fold when the pH value was increased from 3 to 11 at 85 °C. The tetracycline solution lost 80.3–97.8% of its antibacterial activity after 6 h hydrolysis at 85 °C in the pH range 3–11. The correlation factor between the antibacterial activity and the tetracycline concentration was 0.941, indicating that the antibacterial activity of the hydrolyzed tetracycline solutions was mainly attributed to tetracycline. The average specific methanogenic activity (SMA) of acetoclastic methanogens in the anaerobic inhibition test was decreased by 100% when treating either tetracycline solution (tetracycline concentration of 1000 mg L⁻¹) or tetracycline production wastewater (tetracycline concentration: 800–1000 mg L⁻¹). After enhanced hydrolysis pretreatment (pH 9, temperature 85 °C and hydrolysis for 6 h), no suppression phenomenon was found under the same conditions. The results of this study demonstrated that the proposed approach was effective in enhancing the hydrolysis of antibiotics, and may be effective as a pretreatment technology for antibiotic production wastewater.

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1. Introduction

Antibiotic production wastewater (APW) contains high concentrations of residual antibiotics, and treated wastewater has been identified as an important point source of antibiotic

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pollution in the environment [1–3]. Our previous study shown that oxytetracycline mother liquor samples contained extremely high levels of oxytetracycline residues (844–1077 mg L⁻¹), and even after dilution, the oxytetracycline concentrations in the wastewater treatment plants were several to several 10 mg L⁻¹ [4]. The APW is normally treated with biological processes in China, and the presence of high concentrations of antibiotics in APW could disturb the stability of biological wastewater treatment systems due to the strong bacteriostatic effects of antibiotics [1,2]. As the same time, precursors, intermediates and byproducts can also accompany the production of objective antibiotics, and these substances can also possess antibacterial activity. Thus the best way to ensure the stability of wastewater treatment systems during APW treatment is to remove antibiotics from APW and destroy the antibacterial activity of antibiotics before biological treatment.

Ozone, Fenton's reagent, etc., have been found to effectively decompose antibiotics [4–7]. However, antibiotics only account for a small part of the organic pollutants in APW. When these chemical oxidation agents are used for the pretreatment of APW, most of them will be consumed by the coexisting pollutants, resulting in high treatment cost. On the other hand, hydrolysis is known to be one of the principal chemical transformation pathways of pharmaceutical degradation in the environment [8]. Many antibiotics, such as tetracyclines, penicillins, erythromycins and sulfonamides, have poor stability in aqueous solutions, and are susceptible to hydrolysis to form epimers and dehydrated products [9–11]. Although numerous studies have been carried out on the antibiotic hydrolysis process because hydrolysis is a major degradation route for antibiotics in water environments [12], few reports are available regarding APW treatment using hydrolysis technology. This is probably because the hydrolysis half-lives of antibiotics range from days to weeks under normal conditions [10], which is too long for practical application with large volume of APW in limited space of reactors. It has been reported that hydrolysis of many organic compounds can be enhanced by increasing temperature and acid- and base-catalytic reactions [13,14]. This made it possible to enhance the hydrolysis process by reducing the hydrolysis half-lives of antibiotics and accordingly develop a hydrolysis pretreatment technology for improving APW treatment.

Tetracycline was selected as the target antibiotic because tetracycline constitutes one of the most important antibiotic families for human therapy, animal husbandry and aquaculture, ranking second in production and usage worldwide [15,16], and also ranked first in China [17]. This study aimed to explore the feasibility of enhanced hydrolysis pretreatment for tetracycline in APW to reduce its antibacterial activity. The hydrolysis kinetics of tetracycline was investigated under different temperature and pH conditions to optimize the process and determine practical conditions for hydrolysis pretreatment. The hydrolysis products were identified using high performance liquid chromatography (HPLC) and liquid chromatography-time of flight mass spectrometry (HPLC/TOF/MS) analysis. Since some hydrolysis products of antibiotics may inherit the antibacterial activity of the parent pharmacophores, the antibacterial activities of the hydrolyzed solutions obtained under hydrolysis conditions were assessed using a microbial assay developed previously [18]. Furthermore, an anaerobic inhibition test using simulated tetracycline wastewater and actual tetracycline production water with/without enhanced hydrolysis pretreatment was carried out to verify the effects of the hydrolysis process. The results of this study will provide a novel approach for improving APW treatment.

2. Materials and methods

2.1. Chemicals and materials

Tetracycline hydrochloride (98.0%, analytical standard) was purchased from Dr. Ehrenstorfer (Germany), while 4-epitetracycline (ETC) hydrochloride (98.6%, analytical standard) and anhydrotetracycline (ATC) (98.0%, analytical standard) were purchased from Sigma–Aldrich (USA). Acetonitrile and formic acid of HPLC grade were purchased from Thermo Fisher (USA). Ultrapure water was purified to 18.2 M Ω -cm using a Milli-Q Synthesis (Milli-Q System, Millipore, Billerica, MA, USA).

2.2. Experimental conditions

The hydrolysis study of tetracycline was conducted according to Mabey [13]. Acetate buffer solution of 10 mM was used for achieving pH 3 and 5 with 10 mM HCl and 10 mM NaOH solutions, and sodium borate buffer solution of 10 mM was used for achieving pH 7, 9 and 11. The initial reaction concentration of tetracycline hydrochloride was 100 mg L⁻¹ unless otherwise specified. All reactions were conducted in amber glass bottles (500 mL) in a temperature-controlled water bath in the absence of light. During the hydrolysis process, samples were put on ice cooling at designated time intervals and transferred to a freezer (–20 °C) immediately, then analyzed as soon as possible. All experiments were conducted at least in duplicate and average values were reported.

2.3. Analysis

2.3.1. HPLC analysis

Tetracycline, ETC and ATC were quantified by an HPLC (Waters, America) fitted with a reversed-phase C18 analytical column (4.6 mm \times 250 mm, 5 μ m; ZORBAX SB-C18, Agilent, USA) [19]. Solvents A and B were 0.3% formic acid in ultrapure water and acetonitrile, respectively. A linear solvent gradient was used with a flow rate of 1 mL min⁻¹ with a gradient of 10% B (0–5.0 min), 10–60% B (5–40.0 min), 60–90% B (40.0–48.0 min), 90–10% B (48.0–55.0 min), 10% B (55.0–60.0 min). The sample injection volume was 20 μ L. Tetracycline and ETC were detected at a wavelength of 365 nm, and ATC was detected at 254 nm by a Photodiode Array Detector (Waters 2996, Waters, USA).

2.3.2. UPLC/TOF/MS analysis

The identification of hydrolysis products was conducted on a Waters Acquity™ Ultra Performance Liquid Chromatography (UPLC) system (Milford, MA, USA) equipped with a Waters Xevo™ G2 qTOF MS and an ESI source. The separation of analytes was carried out on an Agilent Zorbax SB-C18 column under the same conditions as the HPLC analysis except for the flow rate (0.2 ml min⁻¹, total flow rate 1.0 ml min⁻¹, inlet split flow rate 1:4). The HPLC/TOF/MS was operated under the following conditions: source temperature 100 °C, desolvation temperature 250 °C, cone voltage 30 V, capillary voltage 3.5 kV; the gas flows of cone and desolvation were 50 and 600 L h⁻¹, respectively. The ion source was operated in both positive and negative ion scan mode to detect tetracycline hydrolysis products. HPLC/TOF/MS accurate mass spectra were recorded across the range of 100–1000 *m/z*. The instrument performed internal mass calibration automatically using a dual-nebulizer ion source combined with an automated calibrant delivery system, which introduces the internal reference masses (121.0509 and 922.0098 in positive ion mode; 112.9856 and 1033.9881 in negative ion mode) at approximately 600 μ L h⁻¹.

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