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Influencing factors and degradation behavior of propyphenazone and aminopyrine by free chlorine oxidation

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HIGHLIGHTS

- Free chlorine can effectively remove PRP and AMP in the order: PRP > AMP.
- Chlorine dosage was favorable to the removal of two pharmaceuticals by free chlorine.
- Higher removal efficiencies of PRP and AMP were observed with neutral and slightly acidic pH, respectively.
- PRP and AMP were not mineralized by free chlorine, but were transformed to other byproducts.
- The substitution of Cl, dealkylation and ring-opening were the main transformation pathways.

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ABSTRACT

Chlorine is widely used in drinking water treatment plants as a common disinfectant, and it also can effectively remove many pharmaceuticals and personal care products in water and wastewater. Two pyrazolone compounds (propyphenazone and aminopyrine) that have been frequently detected in aquatic environments were selected for investigation into their removal during free chlorine disinfection. The influencing factors on the removal of the pharmaceuticals were explored at initial pharmaceutical concentrations ranging from 0.1 to 1.25 μM, chlorine dosages ranging from 14.08 to 28.17 μM and pH values ranging from 3.0 to 9.0. The results showed high removal efficiencies of the two pharmaceuticals by free chlorine in the order of propyphenazone > aminopyrine. Their removal and reaction rate constants (k_{obs}) were clearly dependent on the chlorine dosage and pH. High chlorine dosages accelerated the removal rates of both compounds. The highest removal efficiencies and the highest k_{obs} were observed at neutral pH for propyphenazone (>90% for 24 s reaction) and slightly acidic pH for aminopyrine (>85% for 110 s reaction). In addition, the degradation of the two compounds by free chlorine and the structure characteristics of the oxidation byproducts were estimated by non-purgeable organic carbon (NPOC), ultraviolet (UV-Vis) spectroscopy and Fourier transform infrared spectroscopy (FT-IR) analysis. The results of the NPOC analysis indicated that chlorine cannot completely mineralize propyphenazone or aminopyrine. Chlorine atom substitution, dealkylations and ring-opening reactions may occur during propyphenazone or aminopyrine chlorination according to the UV-Vis and FT-IR analysis.

1. Introduction

The occurrence and fate of pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) has received widespread concern and has been confirmed in various environmental samples around the world at concentrations that range from ng/L to μg/L throughout the last few decades [1,2]. The potential risks of these compounds to the ecosystem and to human health cannot be ignored, considering the increasing of PPCPs species, their usage and their persistence in aquatic environments.

Many studies have demonstrated that conventional drinking water treatment methods, such as coagulation and filtration, are not effective with regard to the removal of most PPCPs and EDCs, in which removal rates of less than 25% are typically observed [3–7]. Disinfection with free chlorine or sodium hypochlorite has a broad range of uses in most drinking water treatment plants (DWTPs), as a low-cost water treatment technology [8–12], and it shows selective elimination of most pharmaceuticals, including

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acetaminophen, naproxen, diclofenac, antipyrine, sulfamethoxazole and 17β-estradiol [12–19]. It should be noted that PPCPs and EDCs are difficult to be completely removed in DWTPs in most cases. During water treatment, certain compounds, such as acetaminophen and naproxen, can transform into other uncharacterized chlorinated byproducts that possess higher toxicities than the parent compounds [20,21]. Compared with other conventional water treatments, studies on the removal of pharmaceuticals during disinfection processes should receive more attention.

Pyrazolone compounds, including propyphenazone (PRP) and aminopyrine (AMP), have been used as analgesic, antipyretic and anti-inflammatory drugs since the end of the 1990s [22]. They also belong to the most popular over-the-counter drugs. Previous studies have found these two pharmaceuticals in the effluents and influents of wastewater treatment plants (WWTPs) and DWTPs and ground water in Germany and Greece at concentrations that range from 0.01 to 1.2 μg/L [23–28]. Relatively low removal rates of PRP (44%) and AMP (38%) have been observed in WWTPs, and these poor removal rates indicated that a significant fraction of these compounds may enter the receiving natural waters and subsequently threaten human health [23,29]. The removal rates of PRP and AMP were found to be as high as 90% and 95%, respectively, following aeration and multi-media filtration treatments at DWTPs [25]. Nevertheless, despite their high eliminations at DWTPs, PRP has still been detected in the effluents of DWTPs at concentrations as high as 0.16 μg/L [25,27,28]. Obviously, these pyrazolone compounds may widely exist throughout the environment and are not completely removed during general water and wastewater treatments.

Given the low removal efficiencies of pharmaceuticals by coagulation and filtration, the elimination of PRP and AMP in DWTPs may be largely attributed to the disinfection process. Recent investigations concerning the chlorination of antipyrine-type drugs indicated that pyrazolone compounds (e.g., antipyrine) can be removed and transformed into chlorinated byproducts by free chlorine in as little as several seconds [12,18,19]. Some strong oxidants, including ClO_2, O_3 and Fe (VI), exhibit appreciable reactivity toward PRP and AMP [30–32]. However, the removal and degradation behaviors of these compounds during the disinfection process have not yet been fully investigated and require more research. The aim of this study was to investigate the removal of PRP and AMP by free chlorine oxidation and to illustrate the influence of initial pharmaceutical concentration, initial chlorine dosage and pH on their removal. Furthermore, their degradation behaviors during chlorination were identified by non-purgeable organic carbon (NPOC), ultraviolet–visible (UV-Vis) spectroscopy and Fourier transform infrared spectroscopy (FT-IR) analysis to explore the degree of oxidation of these compounds from free chlorine and the structure characteristic of the oxidation byproducts. The transformations of the compounds during chlorination were then preliminarily conjectured.

2. Materials and methods

2.1. Chemicals and reagents

PRP (>99.0%) and AMP (>98%) were obtained from WAKO (Japan) and Sigma–Aldrich (USA), respectively. Stock solutions (2.5 mM) of PRP and AMP were prepared with ultrapure water after dissolution in 1 mL methanol, and then protected from light and stored at 4 °C. Sodium hypochlorite solution (NaOCl) with ~13% available chlorine was obtained from Sigma–Aldrich. Methanol was HPLC grade (Fisher Scientific). All other reagents ($Na_2S_2O_3$, NaOH, HNO_3, phosphate, etc.) were analytical grade or above and were used without further purification. Ultrapure water (18 MΩ cm) was used to prepare the reagent solutions and was produced from a Water Purification System (Elga Purelab Classic, Veolia).

2.2. Analytical methods

A free chlorine stock solution was prepared by diluting the NaOCl solution to yield ~100 mg/L (≈1.4 mM) Cl_2 and was standardized by the DPD (N, N-diethyl-p-phenylenediamine, Sigma–Aldrich, >99%) colorimetric method [33]. In kinetic experiments, residual chlorine was also analyzed by the DPD colorimetric method [33]. PRP and AMP were analyzed by a Rapid Resolution Liquid Chromatography system (RRLC 1260, Agilent, USA) equipped with a variable wavelength UV detector. A 5 μL sample volume was injected onto a Poroshell 120 EC-C18 column (4.6 × 50 mm, 2.7 μm, Agilent, USA). The column was maintained at 30 °C with a flow rate of 0.5 mL/min. The mobile phases consisted of methanol and ultrapure water. Isocratic elution consisting of 55% methanol and 45% methanol was performed for PRP and AMP determinations, respectively. PRP and AMP were detected at 266 and 262 nm. The limits of quantitation (LOQs) at a signal/noise ratio of 10 were approximately 10 μg/L (0.043 μM) for both compounds.

2.3. Chlorination experiments in ultrapure water

The PRP and AMP solutions (10 mg/L, ≈43 μM) were prepared by diluting a stock solution (2.5 mM) using ultrapure water. Amber borosilicate bottles with glass stoppers (30 mL) were used for batch experiments. The batch experiments were conducted with continuous magnetic stirring at room temperature (25 ± 1 °C). The concentration of methanol during each experiment was less than 0.02‰ (v/v, ≈0.5 mM), and the impact of the methanol on the oxidation of PRP and AMP was negligible [34]. Acetate (pH 3.0–5.0), phosphate (pH 5.5–8.0) and borate (pH 8.5–9.0) buffer solutions were used to control the pH, and NaOH and HNO_3 were used to adjust the final desired pH values. The solution pH did not vary by more than 0.1 unit at the initial and final point of each experiment. The reaction volume for each experiment was controlled at 25 mL. Chlorination experiments were initiated by spiking the free chlorine stock solution (≈1.4 mM) into the reactor bottles. Each sample (1 mL) was obtained at constant time intervals and immediately quenched with 10 μL sodium thiosulfate (31.64 mM). Supplementary experiments were conducted to confirm that sodium thiosulfate exhibited negligible effect on the PRP and AMP chlorination in the oxidant-free controls and in the experiments dosed with chlorine. The residual concentrations of PRP and AMP were analyzed by RRLC/UV. Moreover, experiments without oxidant were conducted over a pH range of 2.84–8.91 which resulted in less than a 6.7% loss of PRP over a period of 312 h (14 days) and an 11.2% loss of AMP over a period of 289 h (13 days). Therefore, the hydrolysis of the two pharmaceuticals was extraordinarily weak and was considered negligible.

The effects of the initial target compounds concentrations (0.1–1.25 μM), chlorine dosages (14.08–28.17 μM) and pH values (3.0–9.0) on the removal efficiencies of PRP and AMP were investigated. All experiments were conducted in duplicate or in triplicate, and the averaged data are presented.

2.4. NPOC, UV-Vis and FT-IR analysis of PRP and AMP degradation during chlorination

NPOC, UV-Vis and FT-IR analyses were employed to reveal the degradation behaviors and the structural changes of PRP and AMP during the chlorine oxidation process.

A stock solution of PRP or AMP (2.5 mM) was added to the reactors to achieve an initial concentration of 0.05 mM. Without using