Chemical Engineering Journal 317 (2017) 112–118

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Impact of pre-oxidation using H_2O_2 and ultraviolet/H_2O_2 on disinfection byproducts generated from chlor(am)ination of chloramphenicol

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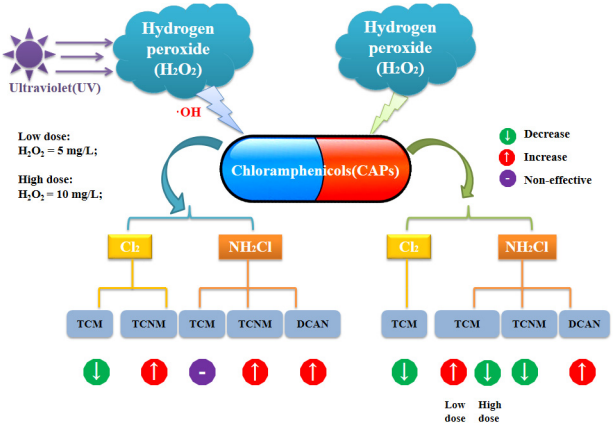
HIGHLIGHTS

- Chloramphenicol (CAP) in chloramine forms DCAN and TCNM, but not in chlorine.
- H_2O_2 pre-oxidation reduced TCNM formation but formed DCAN during chloramination.
- UV/H_2O_2 pre-oxidation resulted in unexpected formation of TCNM during chlorination.
- UV/H_2O_2 (low dosage)-Cl_2 showed a lower estimated toxicity than other scenarios.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 October 2016
Received in revised form 28 January 2017
Accepted 30 January 2017
Available online 1 February 2017

Keywords:
Drinking water
Disinfection by-products
Chloramphenicols
Toxicity
Oxidation
Control

ABSTRACT

Hydrogen peroxide with and without activation by ultraviolet irradiation (UV/H_2O_2 and H_2O_2, respectively) has been investigated to degrade emerging contaminants in drinking water. The antibiotic chloramphenicol (CAP) and its analogues (thiamphenicol and florfenicol), referred to collectively as CAPs, can produce a range of disinfection by-products (DBPs) during chlorination or chloramination (chlor(am)ination). The impact of unactivated and activated H_2O_2 pre-oxidation on the formation of nitrogenous and carbonaceous DBPs from the chlor(am)ination of CAP model precursors was investigated. A theoretical estimated toxicity evaluation was also carried out based on the DBPs that formed. H_2O_2 pretreatment alone did not affect organic carbon and nitrogen concentrations, but significantly reduced the formation of trichloromethane (TCM) during chlorination and trichloronitromethane (TCNM) during chloramination, and enhanced dichloroacetonitrile (DCAN) yields during chloramination. These significant changes in DBP yields caused by H_2O_2 pre-oxidation are attributable to the transformation of the three CAPs into more reactive precursor structures. The three CAPs did not form DCAN and TCNM during chlorination, regardless of whether H_2O_2 pre-oxidation was used. However, UV/H_2O_2 pretreatment resulted in the unexpected formation of TCNM during chlorination. Furthermore, UV/H_2O_2 pre-oxidation increased the formation of DCAN and TCNM, whereas it had little effect on TCM formation during chloramination. A preliminary estimated toxicity evaluation demonstrated that UV/H_2O_2 pre-

Abbreviations: AOP, advanced oxidation process; C-DBPs, carbonaceous disinfection by-products; CAP, chloramphenicol; CF, chloroform; DBPs, disinfection by-products; DWTPs, drinking water treatment plants; DCAN, dichloroacetonitrile; DCAcAm, dichloroacetamide; DON, dissolved organic nitrogen; DOC, dissolved organic carbon; FLO, florfenicol; HAN, haloacetonitrile; HNM, halonitromethane; HAcAm, haloacetamide; N-DBPs, nitrogenous disinfection by-products; THM, trihalomethane; THA, thiamphenicol; TCM, trichloromethane; TCNM, trichloronitromethane; TCAN, trichloroacetonitrile; TDN, total dissolved nitrogen; UV/H_2O_2, ultraviolet/hydrogen peroxide.

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http://dx.doi.org/10.1016/j.cej.2017.01.119

oxidation at low doses, followed by chlorination, resulted in the lowest estimated toxicity from a range of DBPs. Conversely, the estimated toxicity evaluation showed that unactivated H_2O_2 (high dose) was preferable to UV activated H_2O_2 for overall control of these investigated DBPs during chloramination.

1. Introduction

Because of rising water demand and rapid population growth, source waters are increasingly being affected by algal blooms, wastewater effluents, and agricultural pollution [1,2]. These pollution sources are characterized by high levels of dissolved organic nitrogen (DON) that can react with commonly used disinfectants (e.g., chlorine, chloramines) to form undesirable nitrogenous disinfection by-products (N-DBPs) in drinking water treatment plants (DWTPs) [3]. In recent years, the presence of halogenated N-DBPs (haloacetonitriles, HANs; halonitromethanes, HNMs; haloacetamides, HAcAms) at μg/L concentrations in drinking water has gained much attention because these compounds are significantly more genotoxic and cytotoxic than the currently regulated carbonaceous DBPs (C-DBPs), such as trihalomethanes (THMs) [4–6].

Pharmaceuticals are significant contaminants in environmental waters, due to their ubiquity (generally attributed to incomplete removal during wastewater treatment), and concerns about possible estrogenic and other adverse effects (e.g., antibiotic resistance of microbes), both to wildlife and humans [6,7]. Another concern is related to the possibility of formation of N-DBPs from pharmaceutical precursors during chlorination or chloramination (chlor(am)ination) disinfection [8,9]. A recent study found that the antibiotic chloramphenicol (CAP) and two of its analogues (thiamphenicol, THA; florfenicol, FLO), referred to collectively as CAPs (Fig. SM1), which commonly occur in natural waters (sub-ng/L-19 μg/L) and wastewaters (sub-ng/L-47 μg/L) [10–16], significantly contributed to the formation of dichloroacetamide (DCAcAm, the most commonly detected HAcAm in drinking water) during chlorination of heavily wastewater-impacted natural waters [17]. Moreover, another recent study found CAP could form HNMs, and all three CAPs (CAP, THA, and FLO) formed HANs and THMs, during chlorination or chloramination [18]. Because very few pharmaceuticals were found able to form all three classes of typical halogenated N-DBPs (HAcAm, HANs, and HNMs) during chlor(am)ination [19], the CAPs are regarded as an important class of N-DBP precursors.

Many DBPs can be reduced substantially in drinking water by removing dissolved organic matter (the main precursors of DBPs) via physical-chemical treatment processes, such as enhanced coagulation and filtration, upstream of the disinfection process. However, halogenated N-DBP precursors were removed relatively poorly using coagulation-sedimentation-filtration in DWTPs [20–22]. The advanced oxidation process (AOP) of ultraviolet (UV) radiation in combination with hydrogen peroxide (UV/H_2O_2) is a promising drinking water technology for the reduction of a broad spectrum of synthetic organic micropollutants (e.g., pharmaceuticals) [23–29]. A recent study reported that UV/H_2O_2 pre-oxidation may reduce the formation of DCAcAm effectively during the subsequent chlorination of CAP, but unactivated H_2O_2 pre-oxidation did not significantly change DCAcAm formation [17]. Additionally, previous studies found that UV/H_2O_2 pre-oxidation can potentially increase the formation of THMs (chloroform) from the subsequent chlorination of natural waters [30,31]. However, it is still unknown how unactivated or activated H_2O_2 pre-oxidation affect the formation of typical C-DBPs (THMs) and N-DBPs (HANs and HNMs) during subsequent chlor(am)ination of the CAPs. Therefore, the objective of this study was to explore the impact of H_2O_2 pre-oxidation and UV/H_2O_2 advanced pre-oxidation on the formation of THMs (representing C-DBPs,) and HANs and HNMs (representing N-DBPs) from three CAPs (representing antibiotic model compounds) during chlor(am)ination. The results will be useful in suggesting treatment techniques for simultaneous control of C- and N-DBPs and antibiotics in drinking water.

2. Materials and methods

2.1. Materials

Trichloromethane (TCM), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), and trichloronitromethane (TCNM) chemical standards were supplied from Sigma–Aldrich (St. Louis, USA). Three model precursors, including CAP (⩾99.5%), THA (98.5%), and FLO (98.5%), were purchased from Aladdin (Shanghai, China). H_2O_2 solution (35% v/v, stab.) was supplied from Alfa Aesar (MA, USA,) and standardized via the colorimetric method using *N, N*-diethyl-p-phenylenediamine (DPD) prior to use [32]. A sodium hypochlorite solution (active chlorine >5%, guaranteed reagent), obtained from Sinopharm Chemical Reagent Co., Ltd., China, was used to prepare free chlorine (Cl_2) stock solutions. Preformed monochloramine (NH_2Cl) solutions were prepared daily by dissolving ammonium chloride (99.6%, Acros Organics) in ultrapure water adjusted to pH 8.5 with sodium hydroxide. Sodium hypochlorite solution was then slowly added into the rapidly stirred ammonium chloride solution at the N: Cl (ammonium chloride: sodium hypochlorite) molar ratio of 1.2:1 [33]. Milli-Q ultrapure water (18 MΩ·cm) produced by a water purification system (Millipore, USA) was used for all experiments. Other materials were at least analytical grade or higher and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), except as otherwise noted.

2.2. Experimental procedure

2.2.1. UV/H_2O_2 and H_2O_2 pre-oxidation

Oxidation pretreatment was performed in a bench scale collimated beam apparatus (Fig. SM2), composed of a 40 W low-pressure UV mercury lamp (254 nm) above quiescently stirred Petri dishes that was employed in a batch mode [34]. Appropriate amounts of antibiotic stock solutions were dosed into the Petri dishes. The UV/H_2O_2 pre-oxidation was activated once the Petri dishes were moved under the low-pressure UV lamps, and a certain dose of H_2O_2 (H_2O_2 = 5 and 10 mg/L) was dosed into the Petri dishes. Water samples were irradiated for calculated durations to achieve different incident UV fluences, including a relatively low UV fluence (19.5 mJ/cm^2) and a relatively high UV fluence (292.5 mJ/cm^2), to match with a low H_2O_2 dose (H_2O_2 = 5 mg/L) and a high H_2O_2 dose (H_2O_2 = 10 mg/L). The selection of the low and high UV and H_2O_2 doses took into account the practical conditions and the oxidation potential of the H_2O_2 and UV/H_2O_2 processes, as found in previous studies [35,36]. Additionally, the low and high UV and H_2O_2 doses may result in low antibiotic removal and high antibiotic removal during UV/H_2O_2 oxidation pretreatment (Table SM1), which were selected to reflect the impact of UV/H_2O_2 pre-oxidation on DBP formation under different appli-