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Degradation of acrylamide during chlorination as a precursor of haloacetonitriles and haloacetamides

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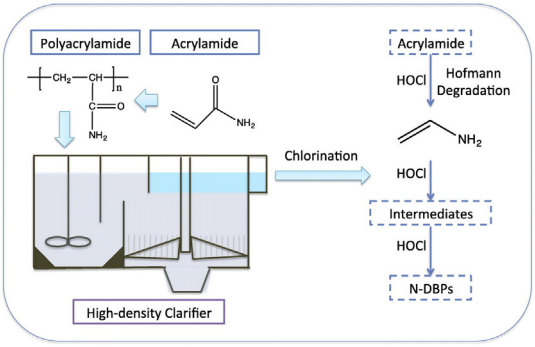
HIGHLIGHTS

- The kinetics of acrylamide chlorination can be well described by a second-order model.
- The degradation of acrylamide during chlorination is favorable at basic pHs.
- Hofmann degradation between acrylamide and ClO^- was the dominant degradation pathway.
- High concentration of DCAN was generated during acrylamide chlorination.
- HAcAm formation favors basic pHs during acrylamide chlorination.

GRAPHICAL ABSTRACT



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ABSTRACT

Acrylamide is a monomer of polyacrylamide, which is widely used in the water treatment process as a flocculant. The degradation kinetics and formation of disinfection by-products (DBPs) during acrylamide chlorination were investigated in this study. The reaction between chlorine and acrylamide followed a pseudo-first-order kinetics. A kinetic model regarding acrylamide chlorination was established and the rate constants of each predominant elementary reaction (i.e., the base-catalyzed reaction of acrylamide with ClO^- as well as the reactions of acrylamide with HOCl and ClO^-) were calculated as $7.89 \times 10^7\ M^{-2}\ h^{-1}$, $7.72 \times 10^1\ M^{-1}\ h^{-1}$, and $1.65 \times 10^3\ M^{-1}\ h^{-1}$, respectively. The presence of Br^- in water led to the formation of HOBr and accelerated the rate of acrylamide degradation by chlorine. The reaction rate constant of acrylamide with HOBr was calculated as $1.33 \times 10^3\ M^{-1}\ h^{-1}$. The degradation pathways of acrylamide chlorination were proposed according to the intermediates identified using ultra-performance liquid chromatography and electrospray ionization-quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF/MS). Five chlorinated DBPs including chloroform (CF), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), dichloroacetamide (DCAcAm), and trichloroacetamide (TCAcAm) were identified during acrylamide chlorination. The formation of CF, DCAN, DCAcAm, and TCAcAm kept increasing, while that of TCAN increased and then decreased with increasing reaction time. As the chlorine dosage increased from 0.75 to 4.5 mM, DCAN became the dominant DBP. Large amounts of CF, DCAN, and TCAN were formed at basic pHs. The hydrolysis of DCAN and TCAN led to the formation of DCAcAm

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and TCAcAm, respectively. The results of this study elucidated that acrylamide can be a precursor for the formation of haloacetonitriles (HANs) and haloacetamides (HAcAms) during drinking water treatment.

1. Introduction

Acrylamide is widely found in biscuits and starchy foods, which has raised people's attention lately because toxicological studies have shown that acrylamide is neurotoxic and genotoxic to animals, and can damage the nervous system and male reproductive organs at high doses (LoPachin and Gavin, 2008; European Food Safety Authority, 2012). Thus, the International Agency for Research on Cancer (IARC) classifies acrylamide as a "probable human carcinogen" (IARC, 2004). The World Health Organization (WHO), the European Union (EU) and the US Environment Protection Agency (USEPA) regulate the maximum concentrations of acrylamide as 0.5, 0.1, and 0.5 μg L^{-1}, respectively, in drinking water for human consumption (European Council, 1998; USEPA, 2002; WHO, 2003).

In drinking water treatment processes, polyacrylamide is the most frequently used flocculant worldwide (Li et al., 2016; Zhu et al., 2016). However, small amounts of residual acrylamide may be present as an impurity in polyacrylamide with concentration as high as 5% (W/W) (Croll et al., 1974). In Shanghai, China, water treatment plants often use polyacrylamide as a polymer coagulant aid in the high-density clarifier process, which is also an important source of acrylamide impurities in drinking water. In 1979, the concentration of acrylamide in drinking water samples in Plymouth, UK was up to 4.5 μg L^{-1} (Brown and Rhead, 1979). More recently, acrylamide was measured in Iranian and American drinking water at concentrations of 0.26 and 0.046 μg L^{-1}, respectively (Yamini et al., 2012; Backe et al., 2014).

Chlorine has been worldwide used for drinking water disinfection. However, it can react with dissolved organic matter (DOM) to form a variety of disinfection by-products (DBPs) in drinking water, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and haloacetamides (HAcAms), which has become a major concern (Krasner et al., 1989; Sohn et al., 2004; Richardson et al., 2007; Bond et al., 2011). Recently, nitrogenated DBPs (N-DBPs) such as HANs and HAcAms have raised concern due to their higher carcinogenicity and mutagenicity than the regulated ones (Muellner et al., 2007; Plewa, 2008). For example, HAcAms could be 142 times more cytotoxic and 12 times more genotoxic in vitro mammalian cell assays than the regulated HAAs (Plewa et al., 2007).

Previously, Bolto (2005) has reported that acrylamide can react with chlorine to form chloroform (CF) (2 μg L^{-1}) under realistic drinking water treatment conditions. However, the reaction kinetics and the formation of N-DBPs such as HANs and HAcAms during acrylamide chlorination have barely been reported. Therefore, the objectives of this paper were (1) to investigate the degradation kinetics of relevant elementary reactions during acrylamide chlorination, (2) to identify the intermediates so as to propose the degradation pathways of acrylamide during chlorination, and (3) to assess the formation of CF and N-DBPs during acrylamide chlorination as a function of reaction time, chlorine dosage, pH and real water background.

2. Materials and methods

2.1. Reagents and chemicals

Acrylamide (≥99.8%), NaOH (≥98%), KH_2PO_4 (≥99.0%), and standard solutions for volatile DBPs including CF, dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), dichloroacetamide (DCAcAm), and trichloroacetamide (TCAcAm) were purchased from Sigma-Aldrich (St. Louis, MO, USA). $Na_2S_2O_3$ and H_2SO_4 were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol of high performance liquid chromatography (HPLC) grade and the extraction solvent, methyl tert-butyl ether (MTBE), were obtained from J.T. Baker (USA). All solutions and samples were prepared using ultra-pure water produced from a Milli-Q water purification system (Millipore, USA).

Free chlorine stock solutions were prepared using sodium hypochlorite (NaOCl) solution (available chlorine 4.00–4.99%, Sinopharm Chemical Reagent Co., Ltd., China). All other chemicals were at least analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless otherwise stated. Two real water samples were collected from the tap water (TW) and raw water of Huangpu River (HPR) in Shanghai, and were filtered through 0.45 μm cellulose acetate membranes (Anpel Co. Led, Shanghai, China) immediately. The water samples were stored at 4 °C in dark until usage. The characteristics of the two collected water samples were shown in Table S1 of Supplementary Material.

2.2. Experimental procedures

Kinetic studies of acrylamide and chlorine were carried out in a 250 mL batch reactor equipped with a dispenser, which was fixed in a thermostatic culture oscillator with controlled temperature (25 ± 1 °C) and oscillation rate (200 rpm). The stock solution of acrylamide was prepared by dissolving 1000 mg acrylamide crystals into 1.0 L Milli-Q water and was stored at 4 °C for up to 6 months. The acrylamide stock solution was diluted to 15 μM for the experiments using Milli-Q water with the addition of 10 mM buffer and concentrated chlorine solution with pH being controlled between 4 and 9 (acetate buffer for pH 4–5, phosphate buffer for pH 5–8 and carbonate buffer for pH 8–9). Small volumes of H_2SO_4 and NaOH were used to quickly adjust pH to the desired values. To explore the influence of molar ratio of bromide (Br^-) to Cl_2 (0–0.1) on acrylamide degradation during chlorination, an aliquot of concentrated KBr solution was added into the solutions before the dose of chlorine to 750 μM. At different reaction time, 1.0-mL solution was rapidly transferred into an HPLC vial with the residual chlorine being quenched with 20 mM $Na_2S_2O_3$. The kinetic

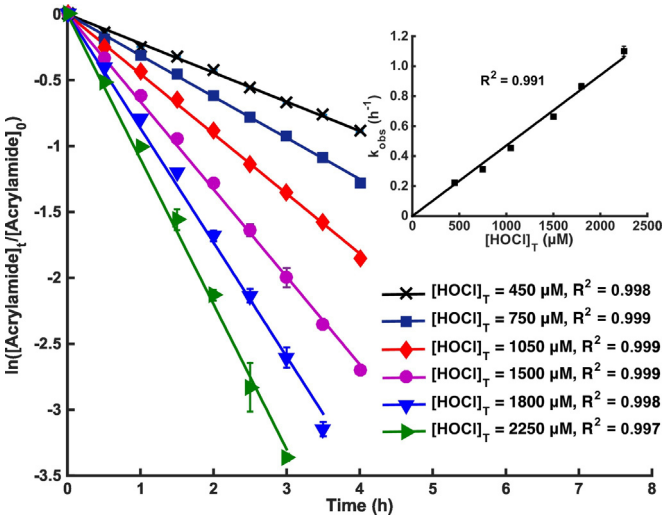

Fig. 1. Pseudo-first-order kinetics plot of acrylamide chlorination at 25 ± 1 °C, pH 7, $[Acrylamide]_0$ = 15 μM and six different chlorine dosages. Error bars represent one standard deviation of triplicate experiments.