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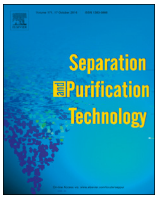

Trichloronitromethane formation from amino acids by preozonation-chlorination: The effects of ozone dosage, reaction time, pH, and nitrite

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ABSTRACT

The formation potentials of trichloronitromethane (TCNMFPs) of four natural amino acids (glycine, threonine, lysine and tryptophane) were investigated during chlorination and preozonation-chlorination. The effects of initial ozone dosage, reaction time, pH, and nitrite concentration on the TCNMFP of selected amino acid (AA) solutions were carried out in detail. During preozonation-chlorination, TCNMFPs of glycine- and lysine-containing solutions were more significant than that containing the other two AAs. Increasing the initial ozone concentration resulted in a considerable increase of TCNMFPs from glycine, lysine, and tryptophane. The concentration of trichloronitromethane (TCNM) of glycine, threonine, and lysine solutions increased during preozonation-chlorination with the ozonation time extended. The effect of pH on TCNMFPs of amino acid by preozonation was compound-specific. In addition, the presence of nitrite ions contributes greatly to TCNMFP for all four types of amino acids. However, as the concentration of NO_2^- increased to higher levels, there was no significant further enhancement of TCNMFP. For chlorination alone, TCNM formed in all four amino acid solutions, with tryptophane solution having the highest TCNMFP.

1. Introduction

Nitrogenous disinfection by-products (N-DBPs) have received increasing attention in recent years [1,2]. Halonitromethanes (HNMs) constitute one group of halogenated N-DBPs. It has been identified as high priority DBPs by USEPA due to its higher cytotoxicity and genotoxicity compared to other DBPs like trihalomethanes (THMs), haloacetic acids (HAAs) and bromate [3–8]. In 12 American water treatment utilities that employed advanced treatment to treat waters with high total organic carbon (TOC) and bromide concentrations, the formation of trichloronitromethane (TCNM) in the 2006–2007 survey was higher than the sum of HNMs recorded during the 2000–2002 survey [9]. Since TCNM is the major HNM species in both water treatment plant (WTP) and general water bodies [10,11], most of previous researches focused on TCNM and it is often regarded as a representative compound by researchers for studying the formation potential of HNMs (HNMFP, HNMs formation under excessive amount of free chlorine for a sufficiently long period).

Some nitrogen containing substances, such as amino acids, amino sugars, nitromethane, nitro phenols, algae and so on, are the major precursors of TCNM in drinking water [12–14]. Amino acids (AAs), which are widespread in surface water, are one group of the most extensively studied precursors of TCNM [15,16]. Several groups have done researches on TCNM formation potential (TCNMFP, TCNM formation under excessive amount of free chlorine for a sufficiently long period) of different AAs and some assumptions of TCNM formation pathway were proposed. TCNMFP during the chlorination of 20 elementary amino acids were studied by Wang et al. [17]. The results showed that threonine and tryptophane had high formation potential of TCNM. Chen et al. [18] found that the formation of TCNM in chlorination and chloramination of aspartic acid was dependent on the chlorine dosage and showed a trend of first increasing and then decreasing with contact time during the chlorination of aspartic acid. When the Cl_2/aspartic acid molar ratio increased from 5 to 30, the yield of TCNM increased. But TCNM was not produced when the ratio was less than 5. On the other hand, higher pH, higher temperature and longer free chlorine contact time during chloramination all lead to elevated the formation of TCNM. Hu et al. [3] proposed a pathway of

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TCNM formation during chlorination of aspartic acid. Amino group is firstly chlorinated, resulting in the formation of C=N double bond, followed by the dehydrogenation of N-hydroxyl groups and the formation of TCNM.

The conventional processes used in drinking water treatment plants such as coagulation, sedimentation and filtration have little effect on the removal of TCNM precursors [13,19] because of their hydrophilic characteristics [3,10,12]. Some of specific pretreatment and post-treatment processes could improve the removal of TCNM precursors, including physical (e.g., adsorption by powdered activated carbon [PAC]), chemical (e.g., persulfate [PS] or permanganate oxidation) and combined chemical and biological processes (e.g., ozone and biological activated carbon [O_3-BAC]). Chu et al. [20,21] found that PS pre-oxidation could reduce the formation of TCNM from chloramphenicols (CAPs) during chlorination but had no significant effect on TCNM formation during chloramination, whereas UV/PS could possibly minimize the formation of TCNM. However, the removal rates of the precursors of TCNM are still limited.

It is well known that preozonation can reduce THM formation potential (THMFP) and HAA formation potential (HAAFP) because it can break the aromatic rings or C=C double bonds that exist in the structure of natural organic matter (NOM) prior to chlorination [22,23]. However, ozonation-chlorination process can enhance HNM formation dramatically. Hoigne and Bader [24] treated lake water by preozonation-chlorination and reported 4–5 times increase of TCNM. In another study, when preozonation was used before chlorination and chloramination, it was found to cause an increase of TCNMFP by 226% and 133%, respectively [25]. There have been several hypotheses regarding the mechanism of ozone in enhancing HNM formation [11,26,27]. One of the hypotheses is that ozonation increased the formation of aldehydes in natural waters and aldehydes may participate in the formation of TCNM during subsequent chlorination [28]. Chu et al. [29] found that the subsequent biological activated carbon (BAC) is one of the most effective methods of reducing the TCNMFP after preozonation. The mechanism of removing TCNM in BAC was associated with the adsorption of aldehydes and other low molecular TCNM precursors by BAC filter.

Until now, there have been only a few studies investigating operation parameters that could affect HNMFP during preozonation-chlorination. Hu et al. [30] observed that the concentration of HNM increased with pH increasing during ozonation–chlorination of natural waters. Yang et al. [31] reported that the increases in TCNM concentrations were positively related to the increases in initial ozone dose during ozonation-chlorination of China's Pearl River water. Shan et al. [15] examined the formation of HNMs from eight amino acids at different pH, and in the presence or absence of bromide, and nitrite anions during chlorination and preozonation-chlorination processes. However, the influences of contact time and ozone dosage on HNMFP from AAs have not been investigated. Also, no quantitative information has been obtained regarding the influences of bromide and nitrite concentrations on TCNMFP. It is still unclear how the pH changes and nitrite concentrations can influence TCNMFP during preozonation of AAs.

This work is to investigate the formation potential of TCNM of four natural amino acid (glycine, threonine, lysine and tryptophane) solutions during chlorination and preozonation-chlorination. The effects of initial ozone dosage, reaction time, pH, and nitrite concentration on the TCNMFP of selected AA solutions are further studied in detail.

2. Materials and methods

2.1. AAs

Glycine (nonpolar), threonine (polar), lysine (basic), tryptophane (aromatic), were selected for the TCNMFP examination. Table 1 listed the chemical structures of the four compounds.

The amino acid (AA) concentration is 0.5 mmol/L for all four types and was prepared with deionized (DI) water. For experiments on pH effect, the pH of the prepared AA solutions were adjusted to be 4, 6, 8 and 10 with 1 M H_2SO_4 or NaOH. To examine the effect of NO_2^-, the amounts of sodium nitrite were precalculated and then added to the AA solutions to ensure the target concentrations of NO_2^- were 0.5, 1.0, 2.0, 3.0 mg/L, which are concentrations commonly found in drinking waters.

2.2. Preozonation procedure and TCNMFP tests

Ozone solution was prepared by introducing gaseous ozone into DI water maintained using a 2 L gas washing bottle. Ozone was produced from dried oxygen by an ozone generator (3S-A, Tonglin Technology). The temperature of ozone solution was maintained at 16 °C using circulated cooling water. The ozone concentration in the water increased over time and stabilized after 10 min of ozonation. The steady concentration of ozone in solutions depends on the electric current of ozone generator. For most experiments, the ozone concentration was adjusted to be 4.0 mg/L. 200 mL of ozone-bearing water was injected into 200 mL of AA stock solution in a conical flask with ground-glass stopper. Immediately after mixing, the conical flask was sealed and stirred magnetically at a constant temperature of 16 °C, which was maintained by circulated cooling water. Thus, the initial ozone concentration in the working solution was approximately 2.0 ± 0.2 mg/L. In some experiments, the effect of ozone dosage was examined. The ozone concentrations in working solutions ranged from 1.1 to 4.5 mg/L. Throughout the preozonation process, the residual ozone concentrations were measured at regular time intervals. Unreacted ozone was stripped off by bubbling the solution with nitrogen gas for 10 min to quench the reaction before other analysis. For the experiments in which there was no preozonation, 200 mL of AA stock solutions were mixed with 200 mL DI water before chlorination. The starting concentration of AAs and corresponding concentrations of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) of the working solutions are listed in Table 2.

TCNMFP, a measure of the amount of TCNM precursors in a sample, was used to gauge the degree of TCNM formation. The experiments were conducted under excessive amount of free chlorine for a sufficiently long period. According to standard methods for the examination of water and wastewater (Section 5710B) [32], 200 mL of AA working solutions, preozonated or unpreozonated, were drawn from the conical flask. The pH of the working solution was buffered at pH = 7.0 ± 0.2 by a phosphate solution and the temperature was maintained at 25 ± 2 °C. Then predetermined amount of NaClO stock solutions were added so that the molar ratio of Cl to DOC was 5:1 in order to ensure that residual concentration of free chlorine is 3–5 mg/L. After 72 h of chlorination in dark, chlorination was quenched by adding enough ascorbic acid and the pH was adjusted to 4.8–5.5 with 0.1 M H_2SO_4 for subsequent reactions.

2.3. Analytical methods

TCNM was analyzed using the standard method of EPA 551.1 with minor modifications. The detection limit of the method for TCNM is 0.7 μg/L. Indigo method by Bader and Hoigne was used to measure the concentration of ozone in water [33]. The residual concentrations of free chlorine and combined chlorine were measured by DPD/FAS titration [34]. Concentrations of ammonia, nitrite and nitrate were determined by spectrophotometry. Dissolved organic carbon (DOC) and dissolved nitrogen (DN) were measured using a TOC Analyzer (Multi N/C 3100, analytikjena, Germany). DON was determined by subtracting NO_2^-, NO_3^- and NH_4^+ from DN.