Factors affecting the formation of nitrogenous disinfection by-products during chlorination of aspartic acid in drinking water

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Abstract: The formation of emerging nitrogenous disinfection by-products (N-DBPs) from the chlorination of aspartic acid (Asp) was investigated. The yield of dichloroacetonitrile (DCAN) was higher than other N-DBPs, such as dichloroacetamide(DCAcAm) and chloropicrin (TCNM) during the chlorination of Asp. The formation of DCAN, DCAcAm, and TCNM all showed a trend of first increasing and then decreasing during the chlorination of Asp with increasing contact time. The dosage of chlorine had an impact on the formation of DCAN, DCAcAm, and TCNM. The highest yields of DCAN and DCAcAm appeared when the Cl₂/Asp molar ratio was about 20, the yield of TCNM increased with increasing the Cl₂/Asp molar ratio from 5 to 30 and TCNM was not produced when the ratio was less than 5. Cyanogen chloride (CNCl) was detected when the Cl₂/Asp molar ratio was lower than 5. N-DBPs formation was influenced by pH. DCAN formation increased with increasing pH from 5 to 6 and then decreased with increasing pH from 6 to 9, but DCAcAm and TCNM increased with increasing pH from 5 to 8 and then decreased. Higher temperatures reduced the formation of DCAN and DCAcAm, but increased TCNM formation. DCAN and DCAcAm formation decreased, and relatively stable TCNM formation increased, with increasing free chlorine contact time during chloramination. N-nitrosodimethylamine (NDMA) was produced during chloramination of Asp and increased with prolonged chloramination contact time. The presence of bromide ions enhanced the yields of haloacetonitriles and shifted N-DBPs to more brominated species.

Keywords: Drinking water; Dichloroacetonitrile; Chloropicrin; Dichloroacetamide; N-nitrosodimethylamine; Cyanogen chloride

1. Introduction

As its low cost and high disinfection efficiency in inactivating pathogenic microorganisms, chlorine has been widely used to deliver major public health improvements worldwide by preventing the spread of waterborne diseases. However, the formation of hazardous disinfection by-products (DBPs), such as trihalomethanes, haloacetic acids, nitrosamines, cyanogen halides, haloacetonitriles (HANs), haloacetamides, halonitromethanes and so on, through reactions between precursor materials and chlorine has been reported (Ma et al. 2014; Muellner et al. 2007; Stalter et al. 2016; West et al. 2016).

In recent years, the number of reports on nitrogenous disinfection by-products (N-DBPs) has increased rapidly (Bond et al. 2011; Krasner et al. 2013). These species typically occur in drinking water at low concentrations, but have high cytotoxicity and genotoxicity (Frank et al. 1988; Muellner et al. 2007). Collectively, dichloroacetonitrile (DCAN), chloropicrin (TCNM), dichloroacetamide (DCAcAm), N-nitrosodimethylamine (NDMA) and cyanogen chloride (CNCl) are the most important DBPs that are often identified in chlorinated water (Chu et al. 2016; Richardson et al. 1999; Shah and Mitch 2012; Yang et al. 2010).

The presence of dissolved organic nitrogen (DON) in surface water has a negative effect on drinking water security as it is an important precursor of N-DBPs (Krasner et al. 2009; Lee et al. 2007). Amino acids are the most extensively studied precursors of DON. They are widespread in surface water and are difficult to remove by conventional drinking water treatment (Jia et al. 2016). Aspartic acid (Asp) is a naturally present amino acid in DON and is an important component of peptides, proteins and algae organic compounds (Chu et al. 2012; Liu et al. 2015). Studies have indicated that Asp had one of the highest N-DBPs yields among 20 free amino acids tested (Chu et al. 2012; Yang et al. 2012a). The DCAcAm yield from Asp was 0.231 mmol/mol (Asp=0.05mM, Cl₂=0.2mM, pH=7.5) and its source was the Qingcaosha Reservoir in China (Chu et al. 2010). Asp produced TCNM and DCAN during chlorination (Asp=0.1mM, Cl₂=3mM, pH=7.2) (Yang et al. 2012a).

Chloramination is often preformed on the laboratory scale, but ammonia and chlorine are added separately in practical processes. The free chlorine contact time may impact N-DBPs formation especially NDMA during post-chloramination (Schreiber and Mitch 2005). Most brominated DBPs are more cytotoxic and genotoxic than their chlorinated analogues, the distribution can be shifted from DCAN to bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) by increasing the bromide ion concentrations (Guanghui and David A 2008; Plewa et al. 2002). In addition, the influence of chlorination on the formation of N-DBPs from Asp added into the effluent of filters is currently unknown.

A better understanding of the comprehensive formation mechanism of N-DBPs during chlorination disinfection may improve the accuracy of N-DBP occurrence prediction and disinfection practice processes could be optimized to minimize the formation of N-DBPs. The main objectives of this study were to assess the role of Asp in the formation of the most common N-DBPs, namely, DCAN, TCNM, DCAcAm, NDMA and CNCl, and investigate the influence of operational parameters, such as contact time, chlorine dosage, pH, temperature, chloramination and bromide ion concentration on these N-DBPs formation.

2. Materials and methods

2.1. Materials and chemicals

Table 1 shows the water quality used in this study, collected from the V-type clarifying filtration in a drinking water treatment plant of Ningbo city, Zhejiang Province, China. DCAN, TCNM, DCAcAm, NDMA, CNCl, BCAN and DBAN were not detected in the collected water used for the experiments. Except where noted in the text, all reagents used in the experiments were of analytical purity. Asp was

obtained from Wako (Osaka, Japan), Four HANs, including DCAN, trichloroacetonitrile (TCAN), BCAN and DBAN, TCNM and NDMA were purchased from Sigma-Aldrich (St. Louis, Missouri, USA), DCACAm and CNCl were obtained from Alfa Aesar (Karlsruhe, Germany). All solutions were prepared using ultrapure water and all bottles were prewashed at 105°C for 24h. A stock of free chlorine solution was prepared from 5% sodium hypochlorite (NaOCl) (from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), diluted to 1000 mg/L as chlorine and stored in an aluminum foil-covered, glass stoppered flask. Bromide ion solutions were prepared using the dilution of sodium bromide solution (NaBr, GR grade). Buffer solutions at different pH values were prepared by phosphate salts.

Table 1

Water quality collected from filtration.

<i>pH</i>	<i>Temperature(°C)</i>	<i>Turbidity(NTU)</i>	<i>COD_{Mn}(mg/L)</i>	<i>NH₃ – N(mg/L)</i>	<i>Br⁻(μg/L)</i>
6.9	21	0.07	0.72	0.06	5.2

2.2. Experimental procedures

For all experiments during chlorination/chloramination, the concentration of Asp solutions was 0.1mM and the disinfectant to Asp molar ratio was 30:1, providing an excess of disinfectant. All chlorinated/chloraminated samples were stored headspace-free in the dark at room temperature (22 ± 1 °C). After reaction for a certain time, the samples were quenched and extracted immediately with methyl tert-butyl ether, based on US EPA Method 551.1. In order to study the influence of operation parameters on N-DBP formation, an orthogonal matrix experimental was designed. In this design, chlorine dosages to Asp molar ratios were 1-30, pH were 5-9, temperatures were 10-30 °C, adding times of post-chloramination were 0-24 h and bromide ion concentrations were 0-5mg/L.

2.3. Analytical methods

Residual and total chlorine concentrations were detected by a portable spectrophotometer (HACH DR1900) based on HACH method 8021. HANs, and TCNM were analyzed by purge and trap (OI Analytical, Eclipse 4660, College Station, Texas, USA) and gas chromatography/mass spectrometry (GC/MS, Shimadzu-QP-2010 Ultra, Japan), DCACAm was measured by liquid-liquid extraction and GC/MS (Shimadzu-QP2010) (Chu et al. 2012). The detection limits for them were below 1μg/L, and recovery of them were 81.5%-118.7%. For the analysis of NDMA, a sample was used for solid phase extraction using procedures described by the US EPA 521 (Munch and Bassett 2006). NDMA was determined by following the method described by Zhang et al. (Zhang et al. 2014). The method detection limit for NDMA was 4 ng/L. The recovery of NDMA was $82\% \pm 5\%$. The analytical technique to monitor CNCl was in-line membrane introduction mass spectrometry (MIMS). A detailed description of the reactor and MIMS detection system can be found in an earlier publication (Na and Olson 2004). An HPLC pump (Acuflo Series I, Lab Alliance Inc.), a membrane inlet probe, and a quadrupole mass spectrometer with electron impact ionization (Hewlett-Packet 5972) were used in MIMS detection system. The analysis of CNCl concentration was virtually nondestructive and the

detection limit was about 4.5 $\mu\text{g/L}$.

3. Results and discussion

3.1. N-DBPs formation

Figure.1 shows the formation of N-DBPs in different reaction time during chlorination of Asp. It was found that the concentrations of N-DBPs including DCAN, TCNM and DCACAm increased quickly with increasing time at the beginning and slowly continued to reach maximum, then decreased with increasing time. However, the yields of TCNM and DCACAm were lower than DCAN. Besides, the speeds of increase and decrease of different N-DBPs were not the same. The maximum concentration of DCAN (128.5 $\mu\text{g/L}$) occurred in 4h, but TCNM (24.8 $\mu\text{g/L}$) and DCACAm (34.9 $\mu\text{g/L}$) appeared in 8h.

Yang et al. proposed a scheme for DCAN and TCNM formation by chlorination of amino acid (Yang et al. 2012a), as shown in scheme 1a and 1b. When N-terminal amino group was dichlorinated, decarboxylation coupled with chloride loss, a chlorinated imine was formed. Further elimination of hydrochloric acid formed a nitrile. Lastly, chlorination of nitrile by HOCl might lead to the formation of DCAN. “R” side chain could be withdrawn easily, in other words, a carboxyl in Asp was electron-withdrawing functions groups and might be broken during chlorination.

The formation pathway of TCNM was also proposed, as shown in scheme 1b. A critical branching point appeared where the C=N double bond in chlorinated imine was oxidized by HOCl. Elimination of hydrochloric acid, followed by further oxidation of HOCl and elimination of H₂O and aldehyde, formed CHCl₂-N(OH)Cl. TCNM formed after a reaction series of elimination, oxidation, and deprotonation. A release of the RCHO group was proposed as a step leading to TCNM formation. In addition, functional groups of “R” easily withdrawn tended to make the C-C bond break easily, leading to the formation of TCNM.

The variation of DCAN and DCACAm concentrations could be explained by the hydrolysis, DCAN could be hydrolyzed to form DCACAm (Chu et al. 2010; ICTOR et al. 1999). Scheme 1c shows the formation of DCACAm from the hydrolysis of DCAN (ICTOR et al. 1999).

Besides, CNCl and NDMA were not detected, the reason for this would be discussed later in the contents of effect of Cl₂ dosage and effect of chloramination.

Fig.1. Formation of N-DBPs during chlorination of Asp at different contact times

(a)

3.2. Effect of Cl_2 dosage

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concentration of chlorination could increase the formation of DCAN and DCACAm, but excess chlorine accelerated the decomposition rate of DCAN and DCACAm. Until at ratios of Cl_2/Asp above 5, TCNM was detected and then began to increase with the increasing molar ratios of Cl_2/Asp up to 30. The outcome was similar to the formation during chlorination of other amino acids (Chu et al. 2012; Jia et al. 2016). CNCl was detected at $\text{Cl}_2/\text{Asp}=1, 2$ and 5, but the level of CNCl was very low (no more than $7\mu\text{g/L}$) compared with other N-DBPs and there was no obvious change of CNCl concentrations. When the molar ratios of Cl_2/Asp reached over 10, CNCl was not detected. CNCl formation was independent of the free chlorine concentration, while excess chlorination promoted its hydrolysis (Na and Olson 2006; Weng and Blatchley 2013).

Fig.2. Formation of N-DBPs during chlorination of Asp at different Cl_2/Asp molar ratios (Asp=0.1 mM, $\text{pH}=7\pm0.2$, reaction time for chlorination=1 day and room temperature= $22\pm1^\circ\text{C}$). The bars represent the standard deviation of replicate measurements ($n=3$).

3.3. Effect of pH

The yields of N-DBPs after 1 day chlorination of Asp at different pH levels are summarized in Fig. 3. As shown, the concentration of DCAN increased with increasing pH from 5 to 6, and then decreased with increasing pH from 6 to 9. The yields of DCAN reached a maximum at pH 6, $115.7\mu\text{g/L}$. The variation trend of DCACAm and TCNM were similar to DCAN. But the highest formation of DCACAm appeared at pH 8, $41.3\mu\text{g/L}$. The yields of TCNM reached highest concentration at pH 8, $26.2\mu\text{g/L}$. NDMA and CNCl were not detected at all. The pH potentially influenced the stability of DCAN, which could be easily hydrolyzed under alkaline conditions (Chu et al. 2009). Furthermore, when the solution was acidic, the existing form of free chlorine was mainly hypochlorous acid (HOCl). With the increase of pH, the HOCl concentration was gradually reduced and hypochlorite ion (OCl^-) concentration was gradually increased. HOCl was a stronger oxidizing agent than OCl^- , which increased the reaction yield of DCAN (Jia et al. 2016). As the pH ranged from 5 to 8, the formation rate of DCACAm from DCAN hydrolysis was higher than the hydrolysis rate of DCACAm. As the pH ranged from 8 to 9, the result was opposite. The yield of

DCAcAm reached highest at pH 8. The yields of TCNM increased slowly with increasing pH from 5 to 8, and then decreased, in accordance with the earlier results. The reason was that halogenation of nitroalkane intermediates was enhanced at high pH, which promoted the formation of TCNM with increasing pH, but too high alkaline conditions might increase its instability (Yang et al. 2012b).

Fig.3. Formation of N-DBPs during chlorination of Asp at different pH (Asp=0.1mM, Cl_2 =3mM, reaction time for chlorination=1 day and room temperature= $22\pm 1^\circ\text{C}$). The bars represent the standard deviation of replicate measurements (n=3).

3.4. Effect of temperature

Fig. 4 displays the formation of N-DBPs during chlorination of Asp solutions at different temperatures. DCAN and DCAcAm decreased with increasing temperature from 10°C to 30°C . However, the formation of TCNM increased with increasing temperature from 10°C to 30°C . Increasing water temperature could enhance the formation rates of N-DBPs and the decomposition rates (Zhang et al. 2013). With the increase of temperature, the rate of formation and decomposition of N-DBPs all increased. Therefore, the concentration of N-DBPs detected in the solution was the formation minus decomposition. The yields of DCAN and DCAcAm decreased with increasing temperature, so the decomposition rates were relatively higher than the formation rates at higher temperatures; the decomposition rate of TCNM was relatively lower than the formation rate at higher temperatures.

Fig.4. Formation of N-DBPs during chlorination of Asp at different temperatures (Asp=0.1mM, Cl₂=3mM, pH=7±0.2 and reaction time for chlorination=1 day). The bars represent the standard deviation of replicate measurements (n=3).

3.5. Effect of chloramination

Fig. 5 shows the formation of N-DBPs during chlorination of Asp at chloramination schemes. As shown, with increasing free chlorine contact time, DCAN and DCACAm decreased, and relatively stable TCNM increased. In addition, it was noted that NDMA could be detected when chloramination existed in the solutions. The yield of DCAN by chlorine was lower than by chloramines, which was consistent with earlier study (Jia et al. 2016). DCAN was relatively more stable in monochloramine solutions than in free chlorine solutions, but it could still hydrolyze to DCACAm during chloramination, the hydrolysis rate of DCACAm in monochloramine solutions was much lower than that in chlorine solutions (Chu et al. 2012), thus DCACAm decreased with increasing free chlorine contact time. TCNM was not detected in monochloramine solutions, which illustrated that the reaction between Asp and monochloramine could not generate TCNM. On the contrary, NDMA could be produced during chloramination of Asp, and the concentration increased with increasing chloramination time.

Fig.5. Formation of N-DBPs during chlorination of Asp at chloramination schemes (Asp=0.1mM, Cl₂=3mM, pH=7±0.2, reaction time for chlorination=1 day and room temperature=22±1°C). The bars represent the standard deviation of replicate measurements (n=3).

3.6. Effect of bromide

The formation of brominated N-DBPs in drinking water is a very noticeable issue, because they present higher frequency of cytotoxicity and genotoxicity than their chlorinated N-DBPs (RICHARDSON et al. 2007). Fig. 6 illustrates the formation of N-DBPs during chlorination of Asp at different Br⁻ concentrations. Four HANs, including DCAN, TCAN, BCAN, and DBAN were detected. Increasing bromide concentrations enhanced the yields of HANs, but reduced the yields of TCNM and DCACAm. The reason for this might be that their brominated substitutions were not detected. The concentrations of DCAN and TCAN decreased with increasing bromide

concentrations, yet concentrations of BCAN and DBAN increased. BCAN was generated, but DBAN was not detected when the concentration of Br^- was 0.1mg/L. The yields of BCAN and DBAN were very similar when Br^- was 1mg/L, then the yields of DBAN were much greater than of BCAN with increasing the concentration of Br^- . The presence of bromide increased the total HANs concentrations and shifted HANs to more brominated species (Fig. 7). Bromine species (HOBr/OBr^-) were known to be more effective substitution agents than the corresponding chlorine species, so increasing bromide concentrations shifted the distribution of di-HANs, including DCAN, BCAN, and DBAN, from DCAN to BCAN and then to DBAN (Bond et al. 2011; Hu et al. 2016).

Fig.6. Formation of N-DBPs during chlorination of Asp at different Br^- concentrations (Asp=0.1mM, Cl_2 =3mM, $\text{pH}=7\pm0.2$ and reaction time for chlorination=1 day and room temperature= $22\pm1^\circ\text{C}$). The bars represent the standard deviation of replicate measurements (n=3).

Fig.7. Formation of total yield of HANs during chlorination of Asp at different Br^- concentration (Asp=0.1mM, Cl_2 =3mM, $\text{pH}=7\pm0.2$ and reaction time for chlorination=1 day and room temperature= $22\pm1^\circ\text{C}$).

4. Conclusions

In this study, it was found that the yields of DCAN were higher than of DCACAm and TCNM during chlorination of Asp. DCAN, DCACAm, and TCNM formation showed

the trend of first increasing and then decreasing during chlorination of Asp with prolonged contact time. Chlorine dosages impacted on the formation of DCAN, DCaAm, and TCNM. CNCl was detected when the Cl_2/Asp molar ratio was below 5. Influenced by pH, N-DBPs formation was different. Higher temperatures reduced the formation of DCAN and DCaAm, while increased TCNM formation. DCAN and DCaAm decreased, while relatively stable TCNM increased with increasing free chlorine contact time during chloramination. NDMA could be produced during chloramination of Asp, and its concentration increased with increasing chloramination time. The presence of bromide ions enhanced the yields of HANs and shifted N-DBPs to more brominated species.

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