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Formation potential of N-nitrosamines from soluble microbial products (SMPs) exposed to chlorine, chloramine and ozone

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Abstract

Soluble microbial products (SMPs) are an important component of effluent organic matter in wastewater treatment. This study investigated the N-nitrosamines formation potential (NAsFP) from chlorination, chloramination and ozonation of SMPs. The results show that more NAs were formed in chloramination than chlorination and ozonation. Specially, the formation of NAs showed a good linear relationship with disinfectant dosage and bromide level, and increased with reaction time, but decreased at high temperature during chlorination, chloramination and ozonation. The effects of pH on the NAsFP were different for different disinfection methods. The pH values showed negative effects on the NAsFP in chlorination and positive effects on the NAsFP in ozonation. Yet in chloramination study, the NAsFP showed a first increasing and then a decreasing trend. Regression procedure revealed that bromide level was the most important factor for NAs formation whether for chlorination, chloramination or ozonation. The NAsFP of SMPs in the three disinfection methods

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was compared between synthetic and real wastewater. Five NAs were detected, and NDMA was the most NAs accounting for more than 50%. As for reducing NAs in the effluent, ozonation was the best alternative to chlorination and chloramination, and the bromide removal was the most important for chlorination, chloramination and ozonation.

Keywords

Soluble microbial products (SMPs); N-nitrosamines (NAs); disinfection methods; influence factors

1. Introduction

Nowadays, wastewater reuse has gained more and more attention to alleviate the problem of freshwater resources shortage. As a cheap and effective disinfection method, chlorine has been widely used to inactivate the pathogenic microorganisms in water treatment. However, due to the strong oxidation of chlorine, it can also react with some organic matters to form disinfection by-products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), halonitromethanes (HNMs), etc.[1,2] Organic matters from wastewater effluent are generated by microbial metabolism and the main components are called soluble microbial products (SMPs),[3] which consist of macromolecules and cellular debris including proteins, polysaccharides, humic acids, and DNA.[4] According to previous studies, SMPs can undergo both carbonaceous DBPs (C-DBPs) and nitrogenous DBPs (N-DBPs) formation when subjected to chlorination, such as THMs, HAAs and dichloroacetonitrile (DCAN), and could increase the DBPs formation in both wastewater effluent and surface water supply after chlorination.[5-7]

With the great efforts of researchers,[8] DBPs were associated with the teratogenic, carcinogenic and mutagenic risks, and could also increase the ecotoxicity of the receiving water body. In order to reduce the amount of regulated DBPs, chloramine and ozone are chosen as the alternative disinfectant. However, some N-DBPs, which were more toxic than C-DBPs may be formed by these alternative disinfectants. For example, chloramine could decrease the amount of regulated DBPs, but more N-DBPs, such as HNMs and N-nitrosamines (NAs), may be formed.[9,10] Ozone can significantly reduce or eliminate the formation of THMs and HAAs, however, it can result in the formation of bromate and NAs.[11] In general, N-DBPs, especially NAs are present in relatively low concentrations (ng/L) but actually more toxic than C-DBPs,[12] therefore, more and more attentions are paying to the formation of N-DBPs.

The concentration and speciation of N-DBPs during disinfection were significantly affected by water quality parameters and operating conditions. In the chlorination process, increasing pH decreased the formation of DCAN but increased the formation of HNMs, however, the opposite trend of DCAN and HNMs may occur during the chloramination process.[13,14] The higher disinfectant dose and bromide level had a positive effect on haloacetonitriles (HANs) yields during chloramination but not during chlorination.[13] For both chlorination and chloramination, high disinfectant dose, long reaction time and high bromide level increased the formation of HNMs. [2,14,15] Chloramination generated more NAs than chlorination and ozonation, and the formation of NAs increased with an increase of bromide level.[11,16,17] However, in the most of these previous studies, drinking water or surface water disinfection were studied, and thus natural organic matter (NOM) was the main organic precursor which generated the studied DBPs. Up to now, limited studies have been carried out to investigate the formation of NAs formed by SMPs during disinfection,[7] and the influence factors on the formation of NAs in chlorination, chloramination and ozonaion of SMPs is even fewer. Since wastewater reuse has become a growing portion of water supplies, chloramine and ozone have gained more and more popularity in water disinfection, and NAs are of potentially greater health concern than THMs, HAAs, HANs and HNMs, it is quite necessary to compare the formation of NAs from SMPs under chlorination, chloramination and ozonation with various conditions, and thus provide more information for the disinfection of reuse water.

The objectives of the study were, therefore, to investigate the effects of disinfection methods (chlorination, chloramination and ozonation) and various factors (temperature, pH, bromide level, disinfectant dosage and reaction time) on the formation of NAs from SMPs, and to evaluate the main factors affecting the formation of NAs from SMPs. The SMPs are chosen because almost all the soluble organic matters of wastewater effluent are SMPs.

2. Material and methods

2.1. Chemicals and reagents

Sodium hypochlorite solution (NaClO, 5%), standard solutions of nine NAs (NDMA, N-nitrosodimethylamine; NMEA, N-nitrosomethylethylamine; NDEA, N-nitrosodiethylamine; NPyr, N-nitrosopyrrolidine; NMor, N-nitrosomorpholine; NDPA, N-nitrosodipropylamine; NPip, N-nitrosopiperidine; NDBA, N-nitrosodibutylamine; NDPhA, N-nitrosodiphenylamine) were supplied from Sigma-Aldrich. Isotopically labelled standards [6-^{2}H] N-nitrosodimethylamine (NDMA-d_6, 98%) and [14-^{2}H] N-nitrosodipropylamine (NDPA-d_{14}, 98%) were obtained from Cambridge Isotope Laboratories (Andover, MA) and used as surrogate and internal standard for NAs, respectively. All other reagents were reagent grade.

2.2. SMPs collection

Activated sludge was collected from an aeration tank in a Municipal Wastewater Treatment Plant, and used as inoculums for the laboratory-scale Sequencing Batch Reactor (SBR). The seed activated sludge was added into the synthetic wastewater to a final biomass concentration of about 2000 mg/L. Glucose (800 mg/L) was selected as the only carbon and energy source, as it can be biodegraded completely leaving only SMPs as the remaining organics in the solution.[7] The other substances were as following according to our previous study (in mg per L): $(NH_4)_2SO_4$ (189), KH_2PO_4 (35), $CaCl_2$ (0.37), $MgSO_4$ (5.07), $MnCl_2$ (0.27), $ZnSO_4$ (0.44), $FeCl_3$ (1.45), $CuSO_4$ (0.39), $CoCl_2$ (0.42), Na_2MoO_4 (1.26).[18] The reactor was incubated for 6 h at 25°C followed by a precipitation time of 30 min. Supernatant was then collected and filtered through a 0.45 μm filter paper. The filtrate was defined as SMPs. [18,19]

The characteristics of SMPs were determined. Dissolved organic carbon (DOC) was measured with a TOC analyzer (TOC-VCH, Shimadzu, Japan). Glucose (measured as chemical oxygen demand (COD)), Total nitrogen (TN), ammonia nitrogen (NH_4^+-N), nitrite nitrogen (NO_2^--N), and nitrate nitrogen (NO_3^--N) were determined by HACH methods (www.hach.com/wah) using a DR2800 (HACH, USA). Dissolved organic nitrogen (DON) was calculated by subtracting values of NO_2^--N, NO_3^--N and NH_4^+-N from the TN value. UV_{254} absorption was analyzed with a visible spectrophotometer (UV7595, Shanghai). Bromide was measured with an ion chromatography (Dionex DX-600, German). The parameters of the obtained SMPs were as follows: Glucose (measured as COD) = none, DOC = 20.4 - 25.2 mg/L,

UV_{254} = 0.042 - 0.058 cm^{-1}, TN = 12.4 - 15.0 mg/L, NH_4^+-N = 2.9 – 3.3 mg/L, NO_2^--N = 0.117 - 0.133 mg/L, NO_3^--N = 1.9 - 2.6 mg/L, DON = 6.3 – 8.9 mg/L. These parameters of SMPs were generally constant in different batches.

In addition, SMPs were also collected from the real wastewater effluent from two domestic wastewater treatment plants of Nanjing. The parameters of SMPs were as follows: DOC = 21.5 – 23.2 mg/L, UV_{254} = 0.137 – 0.179cm^{-1}, TN = 10.4 – 11.6 mg/L, NH_4^+-N = 3.8 – 4.3 mg/L, NO_2^--N = 0.176 – 0.246 mg/L, NO_3^--N = 2.2 – 3.1 mg/L, Br^- = 108.4 – 112.6 μg/L, DON = 3.3 – 4.9 mg/L, respectively.

2.3. Disinfection of SMPs

Chlorination, chloramination and ozonation were conducted as previously describe.[20,21] Briefly, SMPs from synthetic and real wastewater were chlorinated by NaClO. Monochloramine was prepared daily by slowly adding sodium hypochlorite into ammonium chloride solution at a Cl/N molar ratio of 0.7:1 with continuous stirring. To minimize the disproportionation of monochloramine to dichloramine, phosphate buffer (10 mmol/L) was used to maintain the pH above 8.5. After 30 min of stirring, monochloramine solution was aged in the dark for at least 1 h. Both chlorine and monochloramine solutions were standardized using the N, N-diethylphenylene-1,4-diamine (DPD) colorimetric method before disinfection.[22] Ozone was produced from extra dry grade oxygen (with a minimum purity of 99.99%) using a WH-H-Y10 ozone-generator (WAOHUANG, China). The ozone concentration was determined using spectrophotometric methods.[21]

Chlorination, chloramination and ozonation were conducted in glass bottles with Teflon inner plugs. Temperature was kept by a thermostatic reactor and pH was adjusted with phosphate buffer. After disinfection, the residual chlorine, chloramine and ozone were quenched using $Na_2S_2O_3$.

In order to compare and understand the formation of NAs from SMPs under different conditions, except for the formation of NAs under different disinfectant dosage and reaction time conditions, NAs formation potential (NAsFP), which was conducted with relatively high disinfectant dosage for a long reaction time was used in this study. The details of the prepared samples are shown in Table 1. All samples were conducted in duplicate.

2.4. Analysis of NAs

NAs were measured using a gas chromatography-mass spectrometer (GC-MS) (Thermo Polaris Q, USA), with a modified version of EPA method 521 reported by Pozzi et al.[23] The recoveries of nine NAs ranged from 78% to 109%. The detection limits of nine NAs ranged from 0.8 – 4.3 ng/L.

2.5. Statistical analysis

The linear relationship was carried out by Origin software (Version 8.0). A multivariate regression procedure (stepwise) was used to investigate the key factors influencing the formation of NAs in disinfection of SMPs, and this statistical analysis was conducted with SPSS software (Version 17.0) reported by Hong et al.[15] Briefly, the individual NAs and total NAs were respectively designated as the dependent variable, and the influence factors (temperature, pH, bromide level, disinfectant dosage and reaction time) were defined as independent variables. The regression placed independent variables into the equation in the order of their partial correlation coefficients with the dependent variable. Thus, the key factors were identified using this process.

3. Results and discussions

3.1. Factors affecting NAsFP

3.1.1. Effect of temperature

Five NAs were detected including NDMA, NDEA, NMEA, NMor and NPip when SMPs reacted with the three disinfectants, sodium hypochlorite, chloramine and ozone, respectively. Fig.1 shows NAsFP levels at three different temperatures (25, 30 and 40 °C). The formation potential of NDMA was the highest among these five detected NAs. The total NAsFP in chlorination and chloramination was much more than that in ozonation in these temperature conditions. The total NAsFP decreased slightly with temperature increased from 25 to 40 °C in the three different disinfection methods, but no significant difference except in chloramination. The previous study indicated that temperature had a significant effect on the stability of sodium hypochlorite, monochloramine and ozone, and the higher temperature, the more unstable of them.[14] Although increasing temperature accelerates the reaction rate, it may also increase the decomposition rate of chlorine, chloramine and ozone, thus reducing the amount of effective disinfectant and the formation of NAs.

3.1.2. Effect of pH

Fig. 2 illustrates the effect of pH values on the formation of NAs. During chlorination, increasing pH significantly decreased the total NAsFP. While sodium hypochlorite was used as a disinfectant, the concentration of effective chlorine decreased with the increasing of pH.[24] Therefore, acidic condition could accelerate the formation of NAs in chlorination.

For chloramination, the different trends of total NAsFP were observed in different pH values (Fig. 2). The total NAsFP is the highest in pH = 8, and followed in pH = 6 and pH = 10. The previous study had indicated that pH affected the speciation of chloramines and the hydrolysis of monochloramine to form free chlorine, which had been suggested to play a significant role in DBPs formation.[25] Under alkaline condition (pH = 10), monochloramine was the only species and its hydrolysis to free chlorine was reduced, which resulted in the decreasing formation of total NAsFP in spite of the promotion of some intermediate products, such as asymmetric secondary hydrazine.[26] However in pH = 8, monochloramine can generate dichloramine by disproportionation, so that monochloramine and dichloramine could coexist in the reaction solution. Schreiber and Mitch had proved that the amount of NDMA generated by dichloramine was 1 - 2 orders of magnitude more than that of monochloramine.[27] Under pH = 6, the amount of dichloramine increased and became the dominant species, and the concentration of NAs precursors decreased (mostly in the protonated form) at this pH, which resulted in fewer NAs generated. [27]

For ozonation, the total NAsFP increased with the pH increased from 5 - 9, and showed significantly difference between pH = 7 and pH = 9 (Fig. 2). The results were difficult to be explained with formaldehyde catalytic theory by Keefer et al,[28] but could be explained with hydroxylamine way by Yang et al.[29] Under pH = 9, hydroxide ions can accelerate the decomposition of ozone to generate hydroxyl radical and thus generated more hydroxylamine.

3.1.3. Effect of bromide level

The effect of bromide level on NAsFP was studied by performing experiments at four bromide levels (0, 0.2, 0.5, 1.0 mg/L, Fig. 3). Similar to previous reports that bromide can catalyze the formation of NAs, the NAsFP improved as the bromide level increased during chlorination, chloramination and ozonation.[11,17,30] The linear relationships were observed between the total NAsFP and bromide level ($R^2 > 0.98$). The bromide significantly accelerate the formation of NAs in chloramination (slope = 3.4) more than that in chlorination (slope = 1.9) and ozonation (slope = 0.3) (Fig. 3). For chlorination, when the water contains ammonia and bromide ions, HOCl will first react with ammonia to form chloramine. Chloramine is unstable and degrades rapidly when mixed with an excess of bromide, and could react with bromide ions to form dibromamine and bromochloramine.[17] Because of the higher nucleophilic and reactivity of dibromamine and bromochloramine, more NAs could be generated. For ozonation, bromide ions could be oxidized by ozone or hydroxyl radical to hypobromous acid (HOBr), a more effective halogen-substituting agent, thus resulting in increased levels of NAs. [11,31]

The effect of bromide level on the species fraction of NAs was also investigated in this study (Fig. 4). For chlorination, chloramination and ozonation, bromide hardly affected on the species of NAs, and NDMA was always the most abundant NAs species accounting for more than 40% of total NAsFP, even more than 50% in ozonation. The proportions of both NMor and NPip were about 20-30%, but that of NMEA and NDEA were less than 5%. The proportions of different NAs species were influenced by bromide level (Fig. 4). NDMA and NMEA decreased but NDEA and NPip increased as the increasing bromide level in chlorination. NDMA decreased with the increasing bromide levels in chloramination but slightly increased in ozonation.

3.1.4. Effect of disinfectant dosage

Fig. 5 illustrates the NAs levels with different disinfectant dosage. The formation of the total NAs increased as disinfectant dosage rising. Moreover, there was a good linear relationship between the concentration of total NAs and disinfectant dosage ($R^2 > 0.98$), implying that disinfectant dosage was an important factor for the formation of NAs in the range of our study. The effects of the disinfectant dosage on total NAs levels in chlorination (slope = 40.8) were more than that in chloramination (slope = 28.2).

3.1.5. Effect of reaction time

Fig. 6 shows the effect of reaction time on the formation of NAs. The concentrations of NAs increased with increasing reaction time for the three disinfection methods. During chlorination and ozonation, the total NAs levels first significantly increased (chlorination: 1-5 d; ozonation: 0.5-2 h) and then slightly increased as the reaction time continuously prolonged (chlorination: 5-7 d; ozonation: 2-12 h). While during chloramination, the total NAs levels showed an obvious ($p < 0.05$) enhancement as the reaction time grew from 1-7 d. The results were consistent with the stability of disinfectant that chloramine can be long-term presence in the water supply network due to its strong stability.[32] If the precursors of NAs were not removed during water treatment, they would react with chloramine to form more NAs during water distribution.

3.2. Key factors affecting NAs formation

Key factors affecting NAs formation from SMPs in chlorination, chloramination and ozonation were searched using a multivariate regression procedure and the results were shown in Table 2. The regression coefficients ranged from 0.701 to 0.979, and all terms were significant ($p < 0.05$).

Generally, the higher the partial correlations coefficients, the more important the factor is. Among these factors, bromide level was generally more significant than other factors during chlorination, chloramination and ozonation. Disinfectant dosage was also an important influence on the formation of the total NAs and individual NAs during chlorination and ozonation, but only on the formation of the total NAs during chloramination. Additionally, temperature and pH showed some effect on the total NAs during chlorination, however, these factors showed little effect during chloramination and ozonation. These results indicated that reducing bromide level and lowering the disinfectant dosage will be effective strategies to control the total NAs formation whether for chlorination, chloramination or ozonation.

3.3. NAsFP of real wastewater

SMPs from two real wastewater treatment plants (A and B) were treated by chlorination, chloramination and ozonation, respectively. The NAs species and formation potential were almost the same for the two wastewater treatment plants (Fig. 7A-B). During chlorination and chloramination, the NAs species included NDMA, NMor, NPip, NMEA and NDEA. During ozonation, there were only NDMA, NMor, NPip and NMEA generated. The total NAsFP formed by chloramination (14.6 and 16.7 ng/mg DOC) were twice more than that by chlorination (6.3 and 7.0 ng/mg DOC) and one order of magnitude more than that by ozonation (0.7 and 0.8 ng/mg DOC). The proportions of different NAsFP from wastewater A and B were also almost the same with that from synthetic wastewater. These results might be owing to their similar water quality parameters including DOC and TN between the real wastewater and synthetic wastewater despite of higher UV_{254} and bromide but lower DON in real wastewater.

3.4. NAs speciation and formation from SMPs under different disinfection

methods

Through the analysis of the concentrations of NAs in the chlorinated/chloraminated/ozonated SMPs samples with different treatments (Figs. 1-7), the NAsFP during disinfection of SMPs was about twice more than that from disinfection of NOM,[16,33] probably due to the higher portion of low molecular weight (MW) hydrophobic acids and higher DON content in SMPs, which were associated with NAs formation.[14,18,34,35]

Furthermore, chloramination was induced to produce more NAs than chlorination and ozonation. The most important NAs formation pathways during chloramination were unsymmetrical dimethylhydrazine (UDMH) and chlorinated UDMH (Cl-UDMH).[27,36] Chloramine oxidized the precursors of NAs to form UDMH or Cl-UDMH, and then UDMH or Cl-UDMH oxidation again by chloramine formed NAs. For chlorination, there are two possible pathways: first, HOCl oxidized the nitrite and nitrate to form dinitrogen tetroxide (N_2O_4), a nitrosation reagent with a high reaction activity, and then N_2O_4 reacted with the precursors to form NAs.[26] Second, HOCl could react with ammonia to form chloramine, and then NAs was produced through the UDMH and Cl-UDMH pathways.[37] However, HOCl could react faster with the precursors of NAs (such as dimethylamine (DMA), the precursor of NDMA) to form organic chloramines (such as chlorinated- dimethylamine (CDMA)), which were stable substances and could not be continuously oxidized. Therefore, the NAs produced from chlorination were less than that from chloramination. As to ozonation, besides formaldehyde catalytic nitration and N_2O_4 nitration,[28] hydroxylamine mechanism was also an important pathway to generate NAs.[29] Ozone oxidized the precursor to hydroxylamine, and then hydroxylamine reacted with the precursor again to form NAs. The precursor consumed in this process was two times of others, thus resulting less NAs formation during ozonation. Combining these results, it could be concluded that chloramination may be a good alternative to chlorination in terms of reducing C-DBPs in wastewater disinfection,[14] but not a better choice to control the formation of NAs.

Additionally, NDMA was always the major NAs in the three disinfection methods. This may be related to the species and formation yields of the precursors. For example, the formation yield of the precursor was NDMA > NMEA > NDEA during chloramination of DMA, methylethylamine (MEA) and diethylamine (DEA).[29]

4. Conclusions

Overall, five NAs were investigated during chlorination, chloramination and ozonation of SMPs from synthetic and real wastewater. NDMA was the major NAs, and the formation potential of NDMA accounted for more than 50% of total NAsFP. Compared with chlorine and ozone, chloramine as the disinfectant generally resulted in higher NAsFP. Ozonation was the best choice to reduce the formation of NAs in wastewater disinfection. Bromide level and disinfectant dosage were two key factors to affect the total NAsFP of SMPs from wastewater. NDMA, as the most important NAs in SMPs disinfection, should be paid more attention on the precursor and formation mechanism.

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Table 1 Experimental design

Factors	Chlorination	Chloramination	Ozonation
Temperature (°C)	25, 30, 40	25, 30, 40	25, 30, 40
pH	5.0, 7.0, 9.0	6.0, 8.0, 10.0	5.0, 7.0, 9.0
Reaction time	1, 3,5, 7 (d)	1, 3, 5, 7 (d)	0.5, 2, 12 (h)
Disinfectant dosage	0.2, 0.5, 1.0, 2.0*	0.2, 0.5, 1.0, 2.0*	1, 2, 3, 4 (mg/L)
Bromide (mg/L)	0, 0.2, 0.5, 1.0	0, 0.2, 0.5, 1.0	0, 0.2, 0.5, 1.0
Baseline conditions	25°C, pH=7, 7d	25°C, pH=8, 7d	25°C, pH=7, 12h
	2.0*, Bromide =none	2.0*, Bromide= none	4 mg/L, Bromide=none

*molar ratio of disinfectant (chlorine or chloramine)/dissolved organic carbon (DOC)

Table 2 Results of regression procedure for NAs

		partial correlations coefficients						
disinfectant	DBPs	Temperature	pH	disinfectant dosage	reaction time	bromide level	regression coefficients	p values
chlorine	NDMA		-0.853	0.938	0.798	0.951	0.949	<0.01
	NMEA	-0.701	-0.955	0.976	0.962	0.948	0.975	<0.05
	NDEA					0.938	0.870	<0.01
	NMor		-0.896	0.961	0.918	0.980	0.976	<0.01
	NPip			0.554		0.920	0.851	<0.05
	NAs	-0.643	-0.893	0.959	0.894	0.975	0.971	<0.05
chloramine	NDMA					0.883	0.761	<0.01
	NMEA					0.912	0.817	<0.01
	NDEA					0.974	0.945	<0.01
	NMor					0.851	0.701	<0.01
	NPip					0.863	0.724	<0.01
	NAs			0.822		0.885	0.855	<0.01
ozone	NDMA			0.911	0.737	0.985	0.975	<0.01
	NMEA		0.827	0.765		0.991	0.979	<0.01
	NMor		0.635	0.908	0.725	0.958	0.940	<0.05
	NPip			0.732		0.952	0.914	<0.01
	NAs			0.891	0.689	0.977	0.963	<0.05

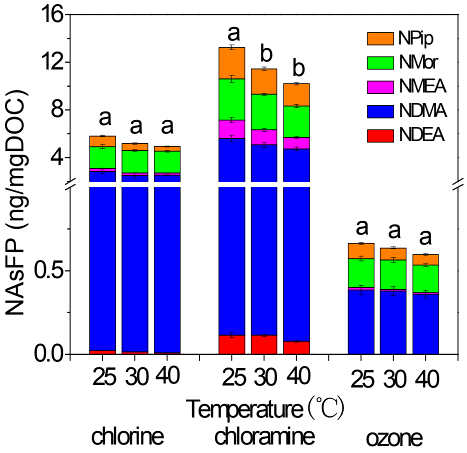


Fig. 1 NAsFP as a function of temperature after chlorination (pH=7, bromide=none, molar ratio of chlorine/DOC=2.0, reaction time=7d), chloramination (pH=8, bromide=none, molar ratio of chloramine/DOC=2.0, reaction time=7d) and ozonation (pH=7, bromide=none, ozone=4mg/L, reaction time=12h). Means with the same letter were not significantly different ($p>0.05$) according to One Way Anova test (Duncan)

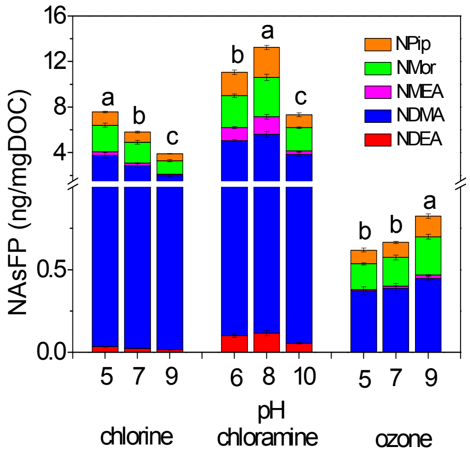


Fig. 2 NAsFP as a function of pH after chlorination (temperature =25 °C, bromide=none, molar ratio of chlorine/DOC=2.0, reaction time=7d), chloramination (temperature =25 °C, bromide=none, molar ratio of chloramine/DOC=2.0, reaction time=7d) and ozonation (temperature =25 °C, bromide=none, ozone=4mg/L, reaction time=12h). Means with the same letter were not significantly different (p>0.05) according to One Way Anova test (Duncan)

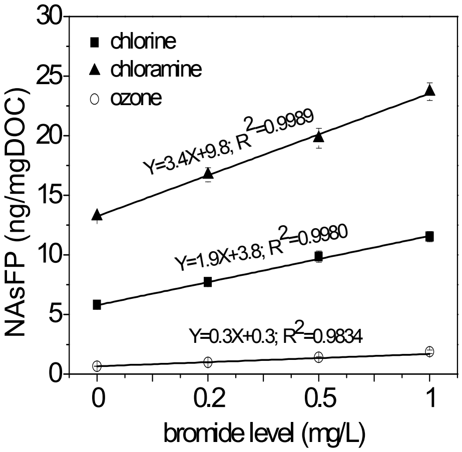


Fig. 3 NAsFP as a function of bromide level after chlorination (temperature =25 °C, pH=7, molar ratio of chlorine/DOC=2.0, reaction time=7d), chloramination (temperature =25 °C, pH=8, molar ratio of chloramine/DOC=2.0, reaction time=7d) and ozonation (temperature =25 °C, pH=7, ozone=4mg/L, reaction time=12h). Means with the same letter were not significantly different (p>0.05) according to One Way Anova test (Duncan)

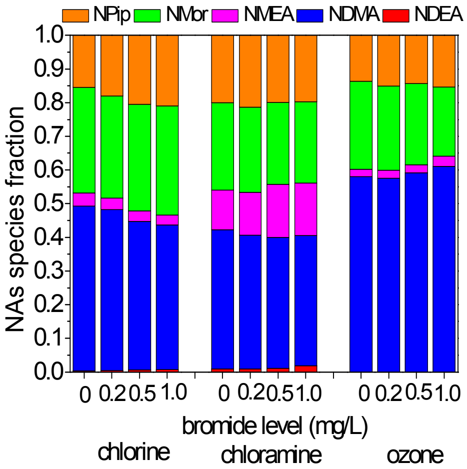


Fig. 4 NAs species fraction as a function of bromide level after chlorination (temperature =25 °C, pH=7, molar ratio of chlorine/DOC=2.0, reaction time=7d), chloramination (temperature =25 °C, pH=8, molar ratio of chloramine/DOC=2.0, reaction time=7d) and ozonation (temperature =25 °C, pH=7, ozone=4mg/L, reaction time=12h). Means with the same letter were not significantly different (p>0.05) according to One Way Anova test (Duncan)

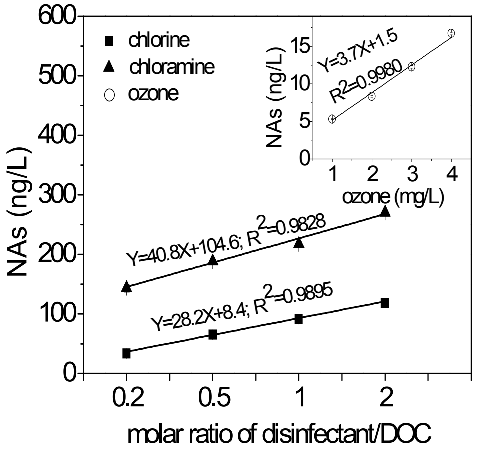


Fig. 5 NAs levels as a function of disinfectant dosage after chlorination (temperature =25 °C, pH=7, bromide level=none, reaction time=7d), chloramination (temperature =25 °C, pH=8, bromide level=none, reaction time=7d) and ozonation (temperature =25 °C, pH=7, bromide level=none, reaction time=12h). Means with the same letter were not significantly different (p>0.05) according to One Way Anova test (Duncan)

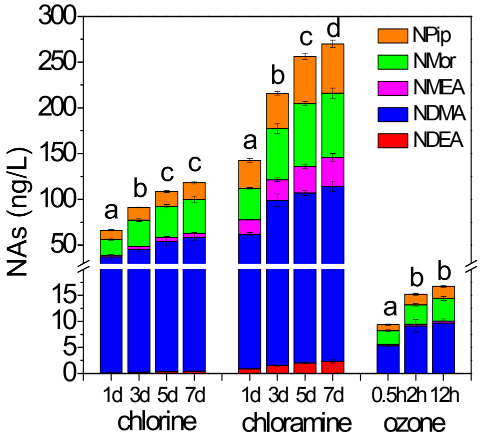


Fig. 6 NAs levels as a function of reaction time from chlorination (temperature =25 °C, pH=7, bromide level=none, molar ratio of chlorine/DOC=2.0), chloramination (temperature =25 °C, pH=8, bromide level=none, molar ratio of chloramine/DOC=2.0) and ozonation (temperature =25 °C, pH=7, bromide level=none, ozone=4mg/L). Means with the same letter were not significantly different (p>0.05) according to One Way Anova test (Duncan)

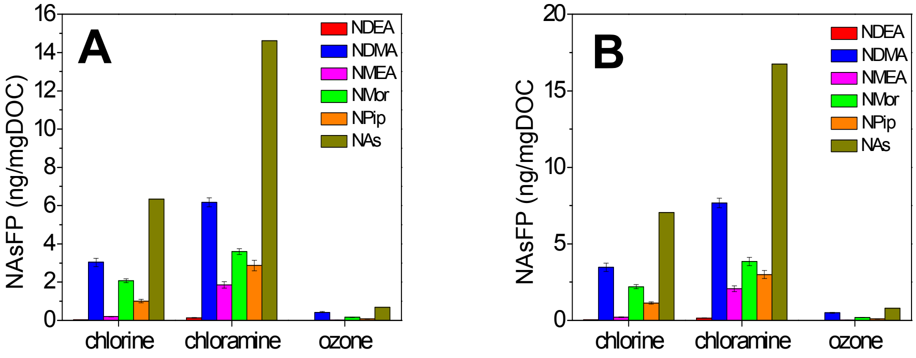
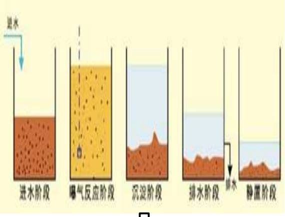


Fig. 7 NAsFP of two real domestic wastewater treatment plants (A and B) upon chlorination (temperature =25 °C, pH=7, bromide level=none, molar ratio of chlorine/DOC=2.0, reaction time=7d), chloramination (temperature =25 °C, pH=8, bromide level=none, molar ratio of chloramine/DOC=2.0, reaction time=7d) and ozonation (temperature =25 °C, pH=7, bromide level=none, ozone=4mg/L, reaction time=12h)

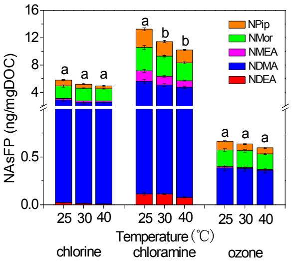
synthetic wastewater



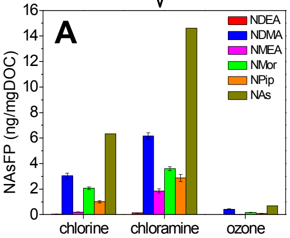
SBR treatment

SMPs

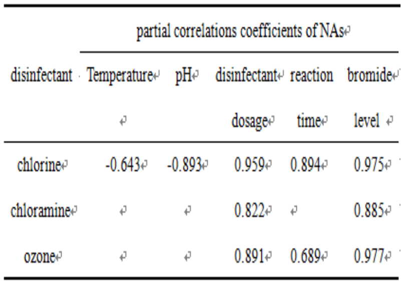
disinfect



NAsFP under different disinfection methods and factors



NAsFP of the real domestic wastewater treatment plants



	partial correlations coefficients of NAs				
disinfectant	Temperature	pH	disinfectant dosage	reaction time	bromide level
chlorine	-0.643	-0.893	0.959	0.894	0.975
chloramine			0.822		0.885
ozone			0.891	0.689	0.977

Key factors affecting DBPs faormation