Potential enhanced *N*-nitrosodimethylamine (NDMA) formation under water treatment conditions

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Abstract

This study investigates two aspects of NDMA formation reactions: (i) evaluation of the potential effect of formaldehyde on NDMA formation, particularly in reactions of dimethylamine (DMA) and nitrite, and (ii) assessment of potential NDMA formation from a range of polymeric coagulants and flocculants upon exposure to disinfection oxidants. The results show that the presence of formaldehyde can enhance NDMA formation in reactions of DMA and nitrite; however, this effect is dependent on the concentrations of DMA and nitrite and is significant only when either concentration was above 5 mM under the employed experimental conditions. Experiments have been conducted at relatively high polymer (0.8-19 mg/L active) and oxidant (8-20 mg/L) concentrations to screen for NDMA formation potentials from four types of polymers and oxidants, respectively. Results show that aminomethylated polyacrylamide (Mannich) yielded significantly higher levels of NDMA than poly(diallyldimethylammonium chloride) (polyDADMAC), polyamine and cationic polyacrylamide in reactions with monochloramine and nitrite. Much lower levels of NDMA were formed with free chlorine and chlorine dioxide.

1 Introduction

N-Nitrosodimethylamine (NDMA) is a probable human carcinogen, as classified by the US Environmental Protection Agency (USEPA) with 10^{-6} cancer risk level of 0.7 ng/L. Recently NDMA has been identified as a drinking water contaminant after several water utilities in Canada and the U.S. reported the occurrence of NDMA in drinking water supplies (MOE, [13]; DHS, [5]). Studies later recognized that NDMA is generated in water treatment facilities, particularly in chlorine-based disinfection processes. Currently, the Ontario Ministry of Environment has set an interim maximum allowable concentration for NDMA at 9 ng/L (MOE, [14]), and the State of California has established an action level of 10 ng/L (DHS, 2002).

A range of studies has been conducted in the effort to identify NDMA formation mechanisms and its precursors in potable water and wastewater treatment plants. A widely accepted mechanism is that dimethylamine or organic compounds with dimethylamine functional groups can react with monochloramine to generate an unsymmetrical dimethylhydrazine (UDMH) intermediate. The UDMH intermediate is then further oxidized to yield NDMA and other products (Mitch and Sedlak, [9]; Choi and Valentine, [3]). The second suggested mechanism is related to *N*-nitrosation, a reaction involving a precursor amine and a nitrosyl cation or similar nitrogen-containing species such as dinitrogen trioxide (N_2O_3) generated during acidification of nitrite (Choi and Valentine, [4]). The *N*-nitrosation mechanism has been considered less relevant under water treatment conditions because this reaction occurs most rapidly at acidic conditions (pH 3.4) (Mirvish, [8]).

Although *N*-nitrosation has a slow reaction rate at circumneutral pH, there could potentially be reagents present in the water matrix that enhance nitrosation reaction at neutral pH conditions. An early study by Keefer and Roller [7] demonstrated that formaldehyde could catalyze reaction of diethylamine and nitrite to yield *N,N*-diethylnitrosamine (NDEA) under neutral pH conditions. Formaldehyde is one of the leading industrial products in the US and is widely distributed in the environment. Chlorination of water may also form aldehydes (Alouni and Seux, [1]). On the basis of the above information, experiments were conducted to investigate whether the presence of formaldehyde could potentially enhance NDMA formation from the reaction of nitrite and NDMA precursors.

Along with studies on the mechanisms of NDMA formation, there has been much research on identifying precursors of NDMA in water sources (e.g., Mitch and Sedlak, [10]; Mitch et al., [11]). Polymeric coagulants and flocculants that are used in potable water and wastewater treatment plants to facilitate suspended solids removal and sludge dewatering have been suspected NDMA precursors due to the presence of amine functional groups in their structures. The presence of DMA residues in polymer products is also possible because DMA is frequently used as a starting reagent in amine-based monomer and polymer production. A few recent studies have shown that some treatment polymers such as (polyDADMAC)s, cationic polyacrylamides, and polyamines may contribute to NDMA formation in chlorine-based disinfection processes (Najm and Trussell, 2002; Wilczak et al., [19]; Mitch and Sedlak, [12] Najm et al., [16]).

Experiments were conducted in this study to investigate four types of water treatment polymers (wastewater: Mannichs and cationic polyacrylamides; potable water: polyDADMACs and polyamines) for their potential to form NDMA upon exposure to oxidant of nitrite, monochloramine, free chlorine and chlorine dioxide. Thus far, screening tests under relatively high concentrations of polymer and oxidant have been conducted. Additional experiments that investigate the potential NDMA formation under conditions representative of water treatment plants are currently underway.

2 Materials and methods

2.1 Materials

All experiments were conducted using deionized water and all glassware was rinsed with methanol and baked at 300 °C for 3 h prior to use. Standard-grade NDMA, DMA hydrochloride, sodium nitrite, formaldehyde (37% w/w), sodium hypochlorite (4-6% w/w), ammonium chloride, sodium phosphate monobasic and dibasic, and sodium borate were obtained at > 98% purity from Acros or Fisher Scientific. All the above reagents were used without further purification. The isotope NDMA-d_6 was obtained from Cambridge Isotope Laboratories. All of the polymers used in this study were provided by the SNF Holding Company (Riceboro, GA). The Mannich stock was 4% active, the cationic polyacrylamide stock was 95% active, the poly(DADMAC) stock was 40% active, and the polyamine stock was 50% active.

Monochloramine solutions were prepared by adding sodium hypochlorite solution slowly into ammonium chloride solution adjusted to pH 9.5 with Cl/N molar ratio of 0.7 and were used within one day. The pH was maintained at 9.5 or slightly higher during the above reaction to minimize disproportionation of monochloramine to dichloramine. This preformed monochloramine solution was aged in the dark at least one hour before use. The concentration of monochloramine was determined by the DPD-FAS titration method specified in the Standard Methods (APHA, 1998).

Chlorine dioxide was generated by slowly adding 100 ml of 8.0 N sulfuric acid (H_2SO_4) to 250 ml of 160 g/L solution of sodium chlorite (Pitochelli, 1995). The reaction between the two chemicals produced chlorine dioxide gas, which was captured in solution by passing through chilled de-ionized water. After all the chemicals were mixed, the second set of sulfuric acid and sodium chlorite solution was added together and passed through the same chilled water, yielding a solution concentration of 5.798 g/L as active chlorine. The concentration of chlorine dioxide was determined by titrating with sodium thiosulfate in the presence of potassium iodide, acid and starch indicator as specified in the Standard Methods (APHA, 1998).

2.2 Experimental procedures

Experiments to evaluate the effect of formaldehyde on the reaction of DMA and nitrite were conducted in 30 mL amber glass batch reactors at room temperature (23 °C) under continuously stirring for 24 h. The solution pH was maintained by 10-50 mM of buffers (acetate for pH 5, bicarbonate for pH 6, phosphate for pH 7 and 8, and borate for pH 9). Concentrations of DMA and nitrite varied from 0.1 to 5 mM.

Experiments with polymers were conducted using 1 L amber glass batch reactors continuously agitated by a platform shaker at 23 °C. The solution pH was maintained at 7 using 10 mM bicarbonate buffer. Typically, each polymer (0.8-19 mg/L active) was allowed to react with nitrite (20 mg/L), free chlorine (10 mg/L as Cl_2), chlorine dioxide (8 mg/L as Cl_2) or preformed monochloramine (10 mg/L as Cl_2), respectively. After 24-48 h, reactions were stopped by ascorbic acid (20 mg/L) and analyzed for NDMA. For all the experiments, matrix and reagent controls as well as duplicate experiments were conducted for each condition.

2.3 NDMA analysis

NDMA was extracted using solid-phase extraction method adapted from Taguchi et al. (1994). 100 ng/L of NDMA-d_6 was spiked into water sample as an internal standard, and 200 mg of Ambersorb 572 resins (from Supelco) prebaked at 300°C for 3 h was added to extract NDMA. . After shaking for 2 h, Ambersorb resins were collected on a filter, air-dried at room temperature for 30-60 min and transferred to a 2 mL amber vial. Dichloromethane (400 μL) was added to the vial, which was tapped before GC/MS analysis. NDMA was analyzed using an Agilent GC/MS (6890/5973) system with a HP-5MS column (30m × 250μm × 0.25μm). NDMA and NDMA-d_6 were quantified using m/z 74.1 parent and 42 daughter ions for NDMA and m/z 80.1 parent and 48 daughter ions for NDMA-d_6. The extraction recoveries were 20-75% depending on sample matrices.

3 Results and discussion

3.1 Effect of Formaldehyde on NDMA formation in the reaction of DMA and Nitrite

Formation of NDMA from the reaction of DMA and nitrite was studied in the presence and absence of formaldehyde. The initial experiment was conducted with 5 mM of DMA and nitrite at pH 7 and 23 °C for 24 h. The presence of 5 or 10 mM of formaldehyde increased the NDMA formation by a factor of 2.8 and 4.4, respectively. The study by Keefer and Roller [7] indicated that formaldehyde mediated *N*-nitrosation with an overall catalytic role. Whether formaldehyde acts as a catalyst in this study will be evaluated by additional experiments.

Further experiments with DMA, nitrite and formaldehyde were conducted at pH 7 for 24 h at three different concentrations but maintaining the same molar ratio among the three reagents. The results showed that the degree of enhancing NDMA formation by formaldehyde increased as the concentration of reagents increased (Table 1). NDMA formation increase was only 8% by formaldehyde when 0.1 mM of reagents were used, while 135% when 5 mM of reagents were used.

The effect of pH on NDMA formation was evaluated in the range of 5 to 9 and yielded surprising results (Figure 1). If NDMA were formed via N-nitrosation mechanism, NDMA formation would decrease as pH increases based on the earlier study results because protonation of nitrite (nitrous acid) was reported to be most critical in facilitating N-nitrosation (Mirvish, [8]. However, experiments showed that formation of NDMA was lowest at pH 6-7 and higher when the pH was decreased to 5 or increased to 8-9. It was also observed that the increase of NDMA formation by formaldehyde was not affected by pH significantly overall.

Table 1: The reaction conditions employed for reagent concentration effect.

Without formaldehyde				**With formaldehyde**				
Batch No	DMA conc. [mM]	Nitrite conc. [mM]	**NDMA conc. [µg/L]**	Batch No	DMA conc. [mM]	Nitrite conc. [mM]	HCHO conc. [mM]	**NDMA conc. [µg/L]**
1	0.1	0.1	**5.0 ± 0.3**	4	0.1	0.1	0.1	**5.4 ± 0.3**
2	1	1	**117 ± 3.5**	5	1	1	1	**145 ± 7.0**
3	5	5	**566 ± 1.7**	6	5	5	5	**1334 ± 10.1**

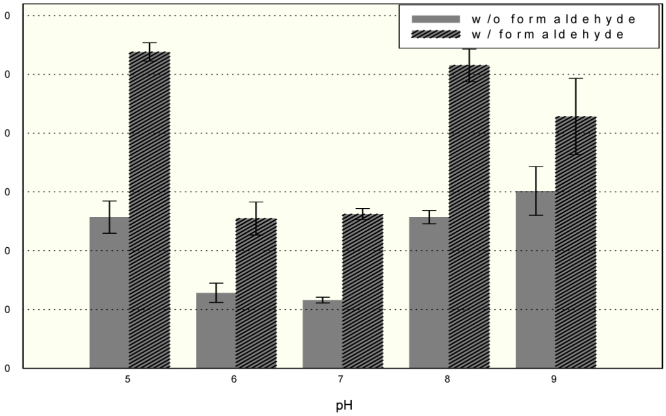
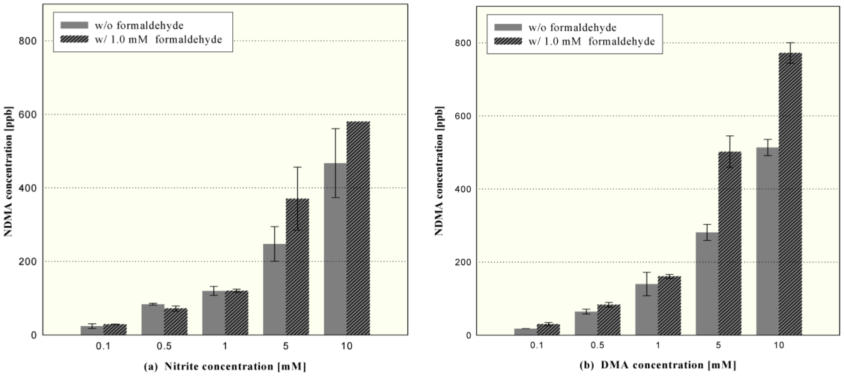


Figure 1: The effect of pH on NDMA formation from reaction of DMA and nitrite in the presence and absence of formaldehyde. Reaction conditions: 5 mM of DMA, nitrite and formaldehyde each initially at 23 °C for 24 h.

The formation of NDMA in the presence and absence of formaldehyde was studied as a function of DMA and nitrite concentration (Figure 2). In general, increase of DMA concentration was more influential on NDMA formation than increase of nitrite concentration.



(a) Nitrite concentration [mM]

(b) DMA concentration [mM]

Figure 2: NDMA formation from reaction of DMA and nitrite in the presence and absence of formaldehyde (pH 7, 23 °C and 24 h): (a) DMA concentration was fixed at 1.0 mM with varying nitrite concentration from 0.1 to 10 mM; (b) Nitrite concentration was fixed at 1.0 mM with varying DMA concentration from 0.1 to 10 mM.

3.2 NDMA formation from water treatment polymers

As shown in Figure 3, the polymer solutions (0.8-19 mg/L active) alone contained 20 ± 1 ng/L or less NDMA. Thus, these polymers alone do not appear to be significant sources of NDMA based on the typical polymer dosage (0.3-1.5 mg/L active) at potable water and wastewater treatment plants. In the screening tests in which the above high concentrations of polymers were exposed to high concentrations of oxidants (nitrite, free chlorine, preformed monochloramine and chlorine dioxide, respectively, at 8-20 mg/L), formation of NDMA was observed. It should be pointed out that in practice, such high dosages of polymers are impossible because it leads to poor coagulation and the problem of redispersion of polymer particles. The employed oxidant concentration and the contact time were also much greater than in real treatment conditions in order to observe and compare the degree to which each polymer could generate NDMA.

Overall, reactions with monochloramine yielded considerably higher levels of NDMA than reactions with nitrite, free chlorine, or chlorine dioxide (Figure 3). Reactions with nitrite yielded significant levels of NDMA for the Mannich and polyDADMAC polymers; however, the employed polymer dosages and nitrite concentration was much higher than what would be seen at typical treatment plants. Reactions with free chlorine generated relatively low levels of NDMA with the highest NDMA concentration observed with polyamine (Figure 3). Reactions with chlorine dioxide yielded the lowest levels of NDMA. However, NDMA formation was 2-10 times higher when adding both chlorine dioxide and nitrite to the polymers than the sum of NDMA formed from adding either chlorine dioxide or nitrite, respectively (data not shown). Further studies are needed to understand this reaction.

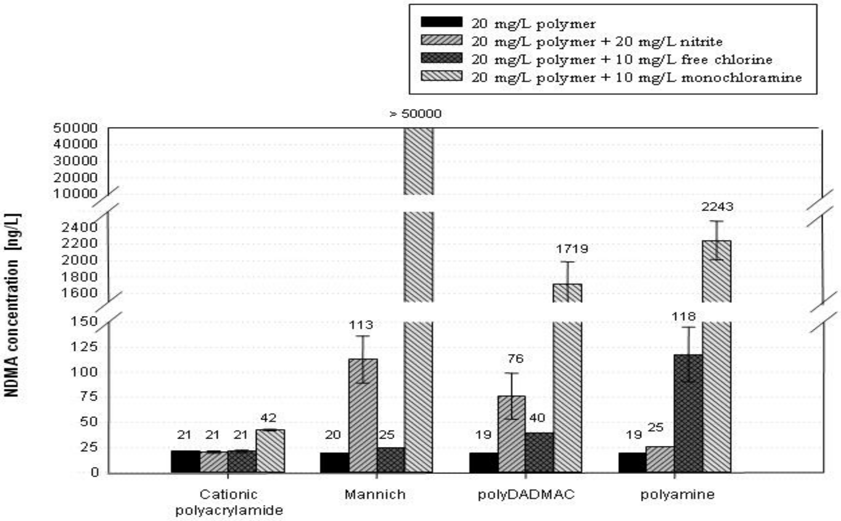


Figure 3: NDMA formation upon exposure of water treatment polymers to nitrite, free chlorine and preformed monochloramine (24 h reaction at room 23 °C). The pH was maintained at 7.0 with 10 mM bicarbonate buffer. Active ingredients of original polymer stock: 4% Mannich, 95% cationic polyacrylamide, 40% poly(DADMAC), and 50% Polyamine.

Among the four polymers, cationic polyacrylamide yielded the least amount of NDMA when reacted with the oxidants (Figure 3). The Mannich polymer yielded the highest concentration of NDMA, particularly in reaction with monochloramine. The polyDADMAC and polyamine polymers also yielded NDMA most significantly in reactions with monochloramine. Preliminary analyses showed the Mannich polymer contained a much higher amount of DMA than the other polymers. However, it should be noted that in water treatment plants not using primary disinfection prior to coagulation, polymers are not likely to come in direct contact with chlorine because most are removed by sedimentation and filtration processes before final disinfection.

4 Conclusions

The study results show that formaldehyde can enhance NDMA formation from the reaction of DMA and nitrite; however, the degree of enhancement becomes significant only when the reagent concentration is high enough (≥ 5 mM) and varies with reagent concentration. The effect of pH on the above reaction does not follow the typical trend that would be expected for *N*-nitrosation reaction, suggesting that other mechanisms may play a role.

The potentials of four water treatment polymers to form NDMA upon exposure to nitrite, free chlorine, monochloramine or chlorine dioxide is shown in batch studies that employed high concentrations of polymers (0.8-19 mg/L active) and oxidants (8-20 mg/L). The NDMA formation potential follows the general trend of Mannich >> polyDADMAC ~ polyamine > cationic polyacrylamide. Note that preparation of Mannich polymers involves the use of DMA and formaldehyde – both reagents could potentially contribute to NDMA formation. Further studies to understand the involved reactions and control reactant dosages are necessary to minimize NDMA formation potential. This study shows that monochloramine will likely result in the highest amount of NDMA while chlorine dioxide the least amount. Further studies to investigate potential NDMA formation under conditions representative of water treatment plants (e.g., lower concentrations of polymers, shorter contact time with oxidant, etc.) are necessary to discern the potential role of polymers as NDMA precursors in actual treatment systems.

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