

Formation Characteristics of N-Nitrosodimethylamine during Chloramines of PolyDADMAC

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Abstract

Interactions of chloramine with organic nitrogen compounds during purification of water for drinking may generate carcinogenic N-nitrosodimethylamine (NDMA) as byproduct, and it has been found that cationic amine-based water treatment polymers may be one of the important precursors of NDMA. We have analyzed experimentally the influence rule of NDMA formation during chlorination and disinfection, in order to provide technical support for reducing or even avoiding the formation of NDMA. The formation characteristics of nitrosamines during the chlorination of poly-diallyldimethylammonium chloride (polyDADMAC) have been studied during our experiments. The results show that the type of chlorinating agent is crucial for the generation of NDMA; if pH = 7, NDMA has the great potential formation; the NDMA potential formation increases with temperature. The yield of NDMA will be higher as the concentration of monochloramine is 1.5 to 2.5 times of the precursor; the variation of polymer with reaction time can explain the concentration of NDMA in terminal water of pipe network is higher than that in drinking water.

Keywords

N-Nitrosodimethylamine, Poly-Diallyldimethylammonium Chloride, Monochloramine, Coconut Charcoal SPE Tube

1. Introduction

In order to reduce the yield of disinfection by-products (DBPs), the process of chlorination during the production of drinking water has been replaced with disinfectants such as chlorine dioxide, chloramines and ozone, but the consequent problem is that nitrogen-containing disinfection by-products (N-DBPs)

are often discovered. There are nine N-Nitrosamines frequently detected in drinking water, *i.e.*, N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodinpropylamine (NDPA), N-Nitrosodibutylamine (NDBA), N-nitrosomethoxine (NMor), N-nitrosopyrrolidine (NPyr), N-nitrosopiperidine (NPip) and N-nitrosodiphenylamine (NDPhA). NDMA is the most typical representative of N-Nitrosamines. It has been found that the concentration of N-Nitrosamines in drinking water pipe network in mega cities of China is about 5 - 50 ng/L [1]. Although the concentration of N-Nitrosamines in drinking water is only a few, it has higher genotoxicity, cytotoxicity, and potential carcinogenicity than traditional carbonaceous DBPs [2].

Due to the frequent detection and obvious health risk of N-Nitrosamines in drinking water, a lot of experimental researches and theoretical analyses on how to control the yield of N-Nitrosamines in drinking water have been made in recent years, and some valuable results have been obtained, such as the reaction of amine-containing compounds (N-Nitrosamines precursors) with chloramines (mainly dichloramines) in water treatment favors NDMA formation [3] [4], the precursors of N-Nitrosamines derive from effluent scouring of surface water, tertiary amines, fungicides containing secondary amine moieties, quaternary ammonium chemicals, anion exchange resins, amine-based organic coagulants, and lower & middle molecular weight Natural organic matter (NOM) [5]. In the precursor of NDMA, amine-based polymers water treatment polymers have been got considerable attention, which are commonly used as coagulants or flocculants in water and wastewater treatment systems. Mechanisms of NDMA formation from free chlorine, chloramination or ozone of several coagulants/flocculant polymers (amine-based polymers) most commonly used in potable water treatment, have been also reported [6] [7] [8]. However, there are no reports in the literature about the specific influencing factors and the formation rules of flocculant polymer in the process of chlorination.

In order to find out the formation characteristics of N-nitrosodimethylamine during Chloramines of PolyDADMAC for reducing the risk of NDMA, we took polyDADMAC as Nitrosamine precursors, in which polyDADMAC is frequently applied as coagulant during the process of water purification, and made a serial of chlorinating experiments to reveal the effect of chlorinating agent type, pH value, reaction temperature, precursor initial concentration and reaction time on the formation of NDMA during the chlorination of amine-based water treatment polymers polyDADMAC.

2. Materials and Methods

Materials and Instruments

The main instruments used in the experiment were as follows: GC/MS-QP2010 Ultra Gas Chromatography-Mass Spectrometer (Shimadzu Corporation); PTA-5 type chromatography column (Supelco USA): 30 m × 0.25 mm × 0.5 μm; Cross-contamination solid phase extraction device (Supelco, USA); R-300 rotary

evaporator (BUCHI, Switzerland); SPE cartridge (2 g coconut charcoal cartridge, 6 mL, Supelco, USA); MILLI-Q A10 ultrapure water Machine (Millipore, USA).

The main materials and reagents used in the experiment were: PolyDADMAC (molecular weight 200,000 - 350,000, aqueous solution of 20 wt.%, 250 - 500 cP (25°C), Macklingent Company); mixed standard solution of 9 N-nitrosamines NAs, 2000 µg/L, dissolved in dichloromethane, (Supelco, USA); deuterated N-nitrosodimethylamine (NDMA-d₆, 1000 µg/mL, dissolved in methanol, O2Si, USA) and deuterated N-Nitrosodipropylamine (NDPA-d₁₄, 1000 µg/L in methanol, O2Si USA); methylene chloride City Keke a Division Miou Chemical Reagent Co, Ltd.); anhydrous sodium sulfate; ascorbic acid; sodium hypochlorite (analytical grade, Tianjin Damao Chemical Reagent Factory); ammonium chloride (Tianjin Fu Chen Chemical Reagent Factory); deionized water.

3. Experiment Methods

3.1. NDMA Chlorination Method

All glassware was washed with deionized water and baked at 450°C for 4 h before use. All reactions were conducted in a 1 L amber borosilicate bottle at 24.0°C ± 1.0°C. The samples were held for 24 h in a dark place. With deionized water to prepare the polymer active ingredient 500 mg/L of stock solutions, the experiment was diluted to 2 - 10 mg/L of the reaction solution, adding an appropriate amount of 0.2 M phosphate buffer, and adjusted to pH = 7 ± 0.2. In order to simplify the interpretation of the results and avoid the substrate with sodium hypochlorite reaction, In experiment, we used preformed monochloramine (The molar ratio of Cl/N is 0.7) to add to polyDADMAC-containing solution, instead of adding ammonia first then adding sodium hypochlorite in solution to form monochloramine. Determination of residual chlorine after the chlorination reaction was completed, adding an appropriate amount of ascorbic acid to quench excess chlorine. All experiments were done in triplicate.

3.2. Monochloramine Preparation and Analysis Methods

Approximately 1800 mg Cl₂/L of monochloramine stock solution (Cl/N molar ratio of 0.7) was freshly prepared for each experiment, adding about 3500 mg/L sodium hypochlorite slowly into 1000 mg/L ammonium chloride solution of pH = 9. The pH of monochloramine was maintained above 9.0 using 10 mM bicarbonate or phosphate buffer during the reaction to minimize disproportionation to dichloramine. This preformed monochloramine solution was aged in the dark for one hour and used for experiments within one day. The exact concentrations monochloramine were determined for every sample by the N,N-diethyl-p-phenylenediamine-ferrous ammonium sulfate (DPD-FAS) titration method specified in the Standard Methods.

3.3. Nitrosamine Analysis Methods

Nine nitrosamines in water were extracted by solid phase extraction (SPE) and

quantitative analysis by gas chromatography-mass spectrometry (GC-MS) [9]. During our experiments, GC-MS conditions are as follows: the ion source is EI source, the electron energy is -70 eV, the carrier gas is high purity helium, and the sample is injected $1\ \mu\text{L}$ without splitting, the temperature of the sample inlet is 250°C , the temperature of the transmission line is 280°C , the temperature of the ion source is 210°C , and the carrier gas flow rate is $2.0\ \text{mL/min}$.

4. Results and Analyses

4.1. Effect of Types of Chlorinating Agents on NDMA Formation

At $24.0^\circ\text{C} \pm 1.0^\circ\text{C}$, $\text{pH} = 7$, diluting the stock solution with deionized water to prepare a $1\ \text{L}$ water sample with a polymer active ingredient of $10\ \text{mg/L}$. Separately chlorinated $24\ \text{h}$ with $10\ \text{mg/L}$ monochloramine and $10\ \text{mg/L}$ sodium hypochlorite in the dark. The result is shown in **Figure 1**.

From **Figure 1**, it can be seen that under the same conditions, polyDADMAC and sodium hypochlorite chlorinated for $24\ \text{h}$ to generate NDMA only $50\ \text{ng/L}$, however monochloramine for chlorination generated $1000\ \text{ng/L}$ of NDMA, which is much higher than that generated by sodium hypochlorite chlorinated. Meanwhile the concentration of NDMA generated by sodium hypochlorite is 5% of monochloramine generated. Therefore, it is crucial to choose of chlorinating agent for the formation of NDMA. In addition, although the concentration of NDMA formed by sodium hypochlorite is low, it also has health risks in drinking water. Therefore, the precursor substances should be removed as much as possible before chlorination.

4.2. Effect of pH on NDMA Formation

At a temperature of $24.0^\circ\text{C} \pm 1.0^\circ\text{C}$, $1\ \text{L}$ of polymer active ingredient of $5\ \text{mg/L}$ and react with $10\ \text{mg/L}$ of monochloramine in the dark for $24\ \text{hours}$ to determine residual chlorine in the water. The result is shown in **Figure 2**. The effect of pH on NDMA formation in chlorination was shown in **Figure 3**.

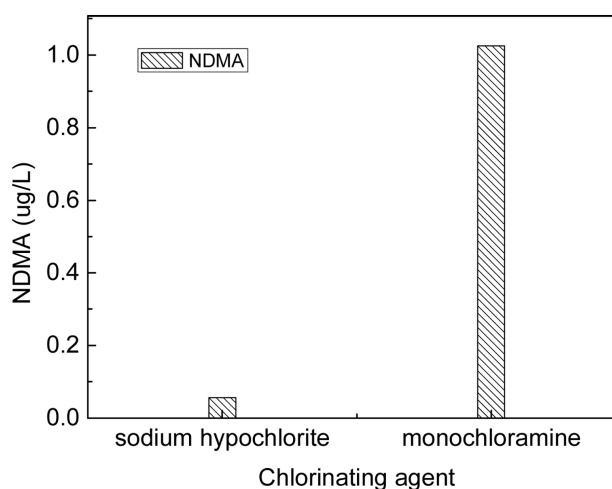


Figure 1. Effect of chlorinating agents on NDMA formation.

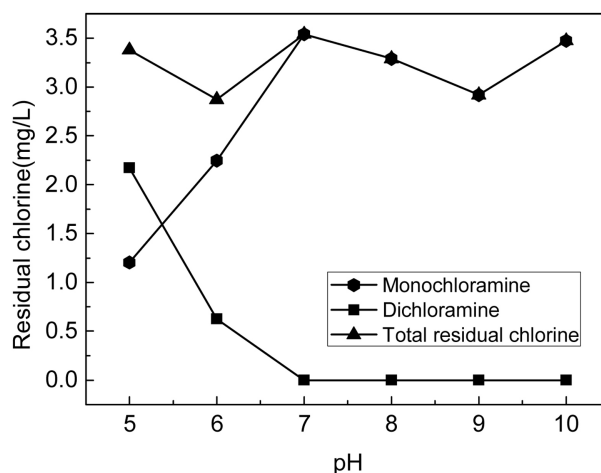


Figure 2. Residual chlorine in different pH.

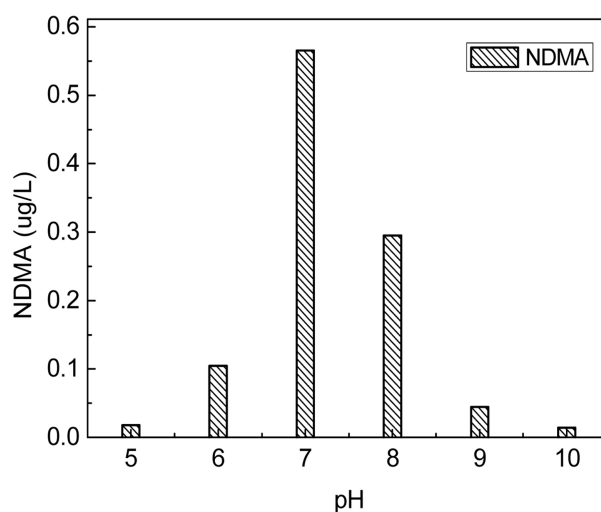


Figure 3. Effect of pH on NDMA formation.

It can be seen from **Figure 4** that when the reaction solution is at pH = 7, the concentration of NDMA is the highest, which can reach about 550 ng/L, and the concentration is significantly different from that at other pH; secondly, at pH = 8, the concentration of NDMA is 300 ng/L; and the rest are below 100 ng/L. It can be seen from **Figure 2** that monochloramine has been produced dichloramine by disproportionation at pH 5 and pH 6. Some scholars have proposed that the reaction of dichloramine and DMA generated NDMA as the main reaction, because the reaction rate is higher than the monochloramine reaction by two orders of magnitude. It can also be found from **Figure 3** that the yields at pH 5 and 6 are higher than those at pH 9 and 10. The experimental law is also consistent with the previous literature [10]. The proposed reaction of monochloramine cannot completely explain the amount of NDMA formed in the water. The nucleophilic substitution of secondary amines and dichloramines forms the chlorinated asymmetric dialkyl fluorene intermediate, which is then oxidized by dissolved oxygen or chloramine in water to form NDMA and other unidentified

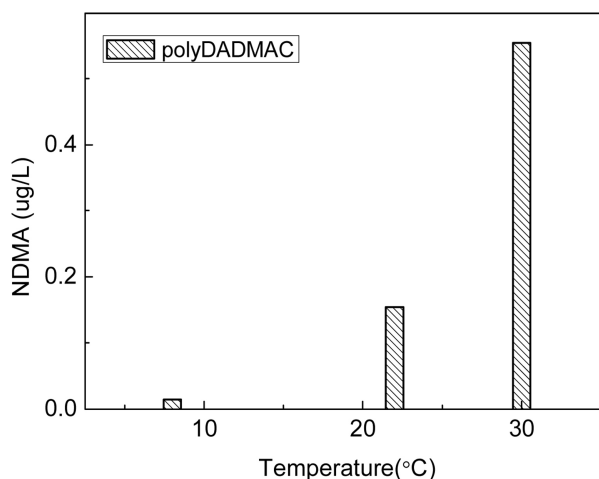


Figure 4. Effect of reaction temperature on NDMA formation.

products. The percentage of unprotonated amine groups in the experiment increased with increasing pH, however, the rapid decay of dichloramine at alkaline pH led to limited conversion of NDMA; more dichloramine was available at acidic pH, the concentration of non-protonated amine groups is low, NDMA conversion rate is also not high. Eventually, both reach equilibrium at pH = 7, and NDMA has the maximum conversion rate. The following experiments are performed at pH = 7, so total residual chlorine replaced by monochloramine.

4.3. Effect of Temperature on NDMA Formation

It was confirmed that the pH was 7, 10 mg/L polyDADMAC active ingredient 1 L and 3.5 mg/L monochloramine were mixed and chlorinated at the water temperature of 8°C, 22°C and 30°C for 24 hours in the dark. The effect of temperature on the amount of NDMA generated is shown in **Figure 4**.

It can be seen from **Figure 4** that the yield of NDMA increases with the increase of temperature. On the one hand, the increase in temperature accelerates the reaction rate, on the other hand, concentration of DMA in water increases with increasing polyDADMAC hydrolysis, so that the NDMA formed by chlorination also increases. In contrast, the low temperature reduces the NDMA reaction rate and the hydrolysis of polyDADMAC in water, the resulting NDMA, of course, is also relatively reduced. At the same time, it can be found that the reaction rate of NDMA at a temperature of to 30°C is much higher than that of 8°C to 22°C.

4.4. Effect of Precursor PolyDADMAC Concentration on NDMA Formation

At $24.0^{\circ}\text{C} \pm 1.0^{\circ}\text{C}$, pH = 7.0, prepare 1L of water samples with 2.16, 4.32, 6.48, 8.64, 10.80 mg/L active polymer concentration in deionized water, and then reacted with 10 mg/L monochloramine in the dark for 24 hours. The effect of precursor concentration on NDMA yield in chlorination is shown in **Figure 5**.

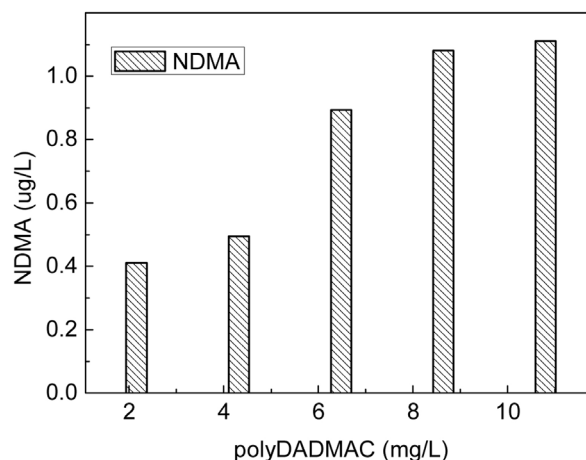


Figure 5. Effect of precursor concentration on NDMA formation.

As can be seen from **Figure 5**, the concentration of NDMA increased with the increase of precursor concentration. Among them, 2 mg/L polyDADMAC with 10 mg/L monochloramine also formed about 400 ng/L NDMA, while the 10 mg/L polyDADMAC with 10 mg/L monochloramine formed NDMA up to 1000 ng/L. Therefore, to reduce the risk of large amounts of NDMA formed by chlorination in drinking water system, the concentration of polyDADMAC needs to be controlled during the treatment of flocculation and sedimentation. From **Figure 5**, it also found that the fastest growth rate of the reaction solution from 4 mg/L to 6 mg/L, it shows that the ratio of the concentration of chloramine to the precursor has a great relationship, when the monochloramine concentration is 1.5 - 2.5 times the precursor concentration, the yield of NDMA is higher.

4.5. Effect of Reaction Time on NDMA Formation and Kinetics

In the polyDADMAC chlorination experiment, after the effects of the type of chlorinating agent, pH, temperature, and initial concentration of the precursor on NDMA formation have been tested, we continue to study the trend of NDMA concentration with chlorination time. At $24^{\circ}\text{C} \pm 1^{\circ}\text{C}$, $\text{pH} = 7$, 10 mg/L polyDADMAC water sample 1 L with 12 mg/L monochloramine was reacted in the dark, and samples were taken at 1.5 h, 13 h, 22 h, 49 h, 96 h, and 156 h respectively. The amount of NDMA was formed at different reaction times. The results are shown in **Figure 6**, the curve of concentration fitting is shown in **Figure 7**.

As can be seen from **Figure 6**, it is known that 25% of NDMA was formed in 24 hours, reaching 1000 ng/L, and then the reaction proceeded, NDMA exceeded 4000 ng/L at 156 hours. The reaction of precursors with monochloramine formed NDMA is a slow reaction, which explains that the concentration of NDMA in the peripheral water of the pipe network is generally higher than the concentration in the factory water. If the precursors were not removed from the tap water, it will be continuing to form new NDMA with residual chlorine in the

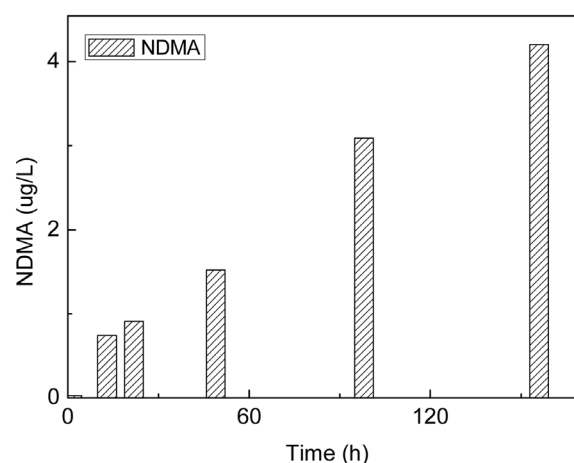


Figure 6. Effect of time on NDMA formation.

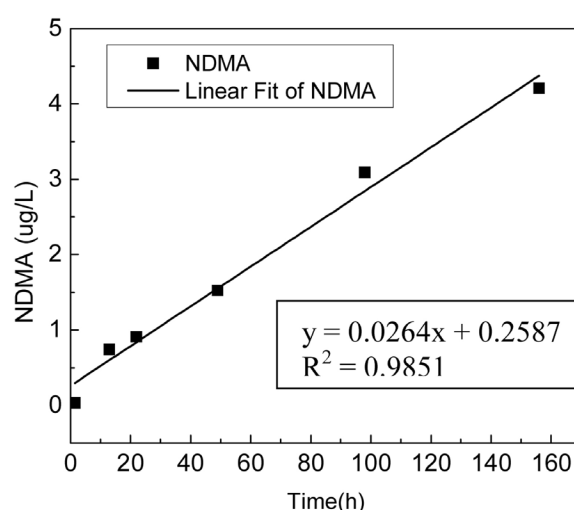


Figure 7. The kinetics of NDMA formation.

pipe network. The kinetic equation for the formation of NDMA by pseudochlorination of polyDADMAC with an excess of monochloramine is shown in **Figure 7** as a zero-order reaction.

5. Conclusions

Our experimental results show that polyDADMAC has great potential for releasing DMA, and the dimethylamine (-DMA) moiety in polyDADMAC is responsible for the formation of NDMA.

Different chlorinating agent induces different amounts of the formation of NDMA, for example, the yield of NDMA formed by monochloramine is much higher than those formed by sodium hypochlorite.

Under the reacting temperature of $24.0^{\circ}\text{C} \pm 1.0^{\circ}\text{C}$ and solution pH of 7.0, the NDMA formation will arrive at the highest efficiency if the monochloroamine concentration was 1.5 - 2.5 times of the substrate concentration.

It is recommended that avoiding direct contact of chloramine with poly-

DADMAC is efficient to reduce the risk of NDMA formation during water purification. Moreover, it is conducive to reduce the DMA release of poly-DADMAC or reduce the risk of NDMA formation by lowering the reaction temperature and inhibiting alkaline pH of the solution.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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