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N-nitrosodimethylamine (NDMA) formation potential of amine-based water treatment polymers: Effects of in situ chloramination, breakpoint chlorination, and pre-oxidation

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HIGHLIGHTS

- NDMA formation potential (NDMA-FP) of two amine polymers (polyamine and polyDADMAC) was evaluated under various conditions.
- NDMA-FP of the polymers was higher using ammonia + chlorine addition sequence.
- Maximum NDMA-FP of the polymers occurred at the breakpoints.
- Pre-oxidation generally reduced NDMA-FP of the polymers.
- Pre-ozonation, in contrast, significantly increased polyDADMAC's NDMA-FP.

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ABSTRACT

Recent studies show that cationic amine-based water treatment polymers may be important precursors that contribute to formation of the probable human carcinogen *N*-nitrosodimethylamine (NDMA) during water treatment and disinfection. To better understand how water treatment parameters affect NDMA formation from the polymers, the effects of in situ chloramination, breakpoint chlorination, and pre-oxidation on the NDMA formation from the polymers were investigated. NDMA formation potential (NDMA-FP) as well as dimethylamine (DMA) residual concentration were measured from poly(epichlorohydrin dimethylamine) (polyamine) and poly(diallyldimethylammonium chloride) (polyDADMAC) solutions upon reactions with oxidants including free chlorine, chlorine dioxide, ozone, and monochloramine under different treatment conditions. The results supported that dichloramine ($NHCl_2$) formation was the critical factor affecting NDMA formation from the polymers during in situ chloramination. The highest NDMA formation from the polymers occurred near the breakpoint of chlorination. Polymer chain breakdown and transformation of the released DMA and other intermediates were important factors affecting NDMA formation from the polymers in pre-oxidation followed by post-chloramination. Pre-oxidation generally reduced NDMA-FP of the polymers; however, the treatments involving pre-ozonation increased polyDADMAC's NDMA-FP and DMA release. The strategies for reducing NDMA formation from the polymers may include the avoidance of the conditions favorable to $NHCl_2$ formation and the avoidance of polymer exposure to strong oxidants such as ozone.

1. Introduction

N-nitrosamines are among emerging disinfection by-products (DBPs) that have generated significant concern among water treatment community since the discovery that *N*-nitrosodimethylamine (NDMA) can be formed in chlorinated and chloraminated drinking

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waters and wastewaters [1–4]. Nitrosamines are probable human carcinogens, with one in a million lifetime cancer risks at the levels from several to less than 1 ng/L [5]. Because nitrosamines are much more toxic than the currently regulated DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) (current allowable maximum contaminant levels (MCL) in drinking water are 80 and 60 μg/L for total THMs and total HAAs, respectively), the presence of nitrosamine DBPs in drinking water is of concern. California Department of Health Care Services has established notification levels for NDMA, *N*-nitrosodiethylamine (NDEA) and *N*-nitrosodipropylamine (NDPA) at 10 ng/L [6]. The U.S. nationwide nitrosamines occurrence survey as a part of the second Unregulated Contaminant Monitoring Rule (UCMR2) found that NDMA was the most prevalent one among the six surveyed nitrosamines (i.e., NDMA, NDEA, NDPA, *N*-nitrosodimethylethylamine (NMEA), *N*-nitroso-n-dibutylamine (NDBA) and *N*-nitrosopyrrolidine (NPYR)), and was detected in 10% of drinking water samples at a median concentration of 4.1 ng/L [7]. Among the nitrosamines, NDMA, NDEA, NDPA, NPYR and *N*-nitrosodiphenylamine (NDPhA) are also included in the 3rd version of Contaminant Candidate List (CCL 3) for drinking water in the U.S. [8]. Regulation of nitrosamine DBPs is currently being evaluated by the USEPA.

Due to the significant health risk and occurrence frequency of nitrosamines in drinking water, much research has been conducted in recent years to identify nitrosamine precursors and formation mechanisms during disinfection processes. Favorable NDMA formation occurs in water treatment from reactions of amine-containing precursors with chloramine species, mainly dichloramine [9–12]. The precursors for nitrosamines' amine moiety have been shown to originate from wastewater-impacted surface waters, tertiary amine-based pharmaceuticals, fungicides containing secondary amines as a moiety, quaternary ammonium-based chemicals, anion exchange resins, amine-based organic coagulants, and low to medium molecular weight natural organic matter (NOM) [12–20]. Among the potential NDMA precursors, amine-based water treatment polymers that are commonly used as coagulant or flocculant aids have received considerable attention because of their intentional usage in water and wastewater treatment systems. Several coagulant/flocculant polymers have been reported to form NDMA in water that contained free chlorine, chloramines, or ozone [14,15,21–28]. The dimethylamine (DMA)-based moieties in the water treatment polymers were responsible for their NDMA formation potential (NDMA-FP). Park et al. [25] and Padhye et al. [27] showed how the structures of water treatment polymers and reaction conditions affect the NDMA-FP during chloramination and ozonation, respectively, and provided insight for the mechanisms of polymer degradation and NDMA formation under conditions relevant in water disinfection.

Water treatment parameters such as the sequence of chlorine and ammonia addition for in situ chloramines formation have been discussed as important factors affecting NDMA formation. Schreiber and Mitch [10,11] investigated chloramination of DMA (a model precursor of NDMA) to form NDMA in deionized water and disclosed the important role of dichloramine. The authors proposed that DMA primarily reacted with dichloramine to form a chlorinated unsymmetrical dimethylhydrazine (Cl-UDMH) intermediate, which was further oxidized by dissolved oxygen to yield NDMA. Formation of dichloramine is determined by free chlorine to ammonia (Cl_2:NH_3) ratio and water pH at the point of chlorine and ammonia mixing during in situ chloramination. A high Cl_2:NH_3 ratio fosters dichloramine formation when chlorine is added to water containing ammonia, which results in enhanced NDMA formation [10]. Farre et al. [29] also showed that in situ chloramination of secondary wastewater effluents by adding ammonia first followed by NaOCl produced higher NDMA than preformed monochloramine. Thus, adding chlorine first followed by ammonia should be utilized to reduce NDMA formation. Furthermore, increase of the contact time with free chlorine prior to ammonia addition could decrease NDMA formation from DMA, NOM, and source waters [10,23,24,30–32] by chlorinating the amine precursors, although this practice might increase the formation of halogenated DBPs. Chlorination beyond the breakpoint also could decrease NDMA formation by destroying chloramine species [10,24,33]. Among the above studies, the investigations by Wilczak et al. [23] and Charrois and Hrudey [24] tested source waters that were impacted by the water treatment polymer poly(diallyldimethylammonium chloride) (polyDADMAC).

Apart from chlorine and ammonia addition strategy and breakpoint chlorination, pre-oxidation of source waters prior to chloramination may also be used to reduce NDMA formation. Pretreatment oxidants such as chlorine, chlorine dioxide (ClO_2), and ozone (O_3) have been frequently used in water treatment plants to remove taste and odor, oxidize iron and manganese, and even help coagulation in some waters [34,35]. Chen and Valentine [30] showed that pre-oxidation by permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), ultraviolet light (UV), and O_3 reduced NDMA-FP of NOM during chloramination. Lee et al. [36] showed that pre-oxidation by ClO_2 and O_3 reduced NDMA-FP of DMA and several model alkylamines that contained the DMA moiety. Shah et al. [37] showed that in general preoxidation by O_3, chlorine at high *ct* (i.e., oxidant dosage × contact time), and UV at high fluences could reduce NDMA formation during post-chloramination of water samples that were impacted by treated wastewater, amine treatment polymers (polyDADMAC), and anion exchange resins. However, pre-oxidation might increase NDMA formation in some cases and might promote the formation of other DBPs such as trihalomethanes, haloacetic acids, trichloroacetaldehyle, and chloropicrin, depending on the type of pre-oxidation and water characteristics involved [37].

To date, only several studies have assessed how some of the aforementioned treatment parameters may affect the NDMA formation in real waters that have been subjected to cationic amine-based water treatment polymers [21–24,37], studies focusing on the water treatment polymers for their NDMA formation are still limited and the impact of water treatment parameters are not well understood. In this study, a broad evaluation of the effect of chloramine generation, breakpoint chlorination, and pre-oxidation by a variety of oxidants on NDMA formation from amine-based water treatment polymers was conducted. Formation potential experimental conditions were adopted for the purpose of screening the wide range of reactions. Two widely used water treatment polymers, poly(epichlorohydrin dimethylamine) (polyamine) and polyDADMAC were focused on in the study. Free chlorine, ClO_2, and O_3 were chosen as pre-oxidants. As will be discussed later, interesting results were obtained from the pre-ozonation of polyDADMAC prior to chloramination, resulting in the increase of NDMA-FP, contrary to the general tendency of NDMA-FP reduction upon pre-oxidation of NDMA precursors.

2. Materials and methods

2.1. Chemical reagents

Details of chemical reagents and preparations for this study are provided in the Supplementary materials (Text S1).

2.2. Experimental procedures

Unless specified otherwise, all reactions were conducted in amber borosilicate bottles at pH 7.5 (maintained by 10 mM sodium phosphate buffer) and 23 °C. For in situ chloramination

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