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ABSTRACT

This study elucidates the recent trends in the formation, prevention, and removal of N-nitrosamines such as N-nitrosodimethylamine (NDMA) from wastewater or drinking water. Reports are rife on the occurrence of NDMA in areas such as amine degradation during postcombustion CO_2 capture (PCC), chlorinated/chloraminated and ozonated drinking water, smoked or cooked foods personal care, tobacco and pharmaceutical products. The major routes responsible for the formation of NDMA in portable waters include chlorination/chloramination and ozonation. The major NDMA precursors are secondary, tertiary, and quaternary amines such as dimethylamine, diethanolamine, and triethanolamine. Due to the environmental and public health concerns posed by this contaminant, a proactive approach is necessary towards suppressing their occurrence, as well as their removal. Consequently, this study critically reviewed the formation, prevention, and removal of N-nitrosamines. The study discussed NDMA prevention techniques, such as physical adsorption, pre-oxidation, and biological activated carbon. The removal techniques discussed here include physicochemical (such as combined adsorption and microwave irradiation and UV photolysis), bioremediation, catalytic reduction, and dope technology. Irrespective of the effectiveness and seemingly economic viability of some of these technologies, preventing the occurrence of NDMA right from the outset is more potent because the treatments consume more energy.

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1. Introduction

NDMA and other nitrosamine such as N-nitrosomethylethylamine (NMEA), N-nitrosomorpholine (NMOR), N-nitrosopyrrolidine (NPYR), N-nitroso-di-phenylamine (NDPhA), N-nitrosopiperidine (NPIP), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-butylamine (NDBA), and N-nitrosodipropylamine (NDPA) could be found in secondary treated effluent and raw wastewater as well as drinking water (Krauss et al., 2010; Reyes-Contreras et al., 2012; Yoon et al., 2012). Some of these nitrosamines including NDMA are categorized as probable human carcinogens (USEPA, 1993). According to USEPA's Integrated Risk Information System database, six nitrosamines water concentration at a low level (ng/L) could lead to 10^{-6} lifetime excess cancer risk. Therefore, several organizations and institutions have set different public health thresholds. For instance, the Office of Environmental Health Hazard Assessment (OEHHA) in California recommends 3 ng/L N-NDMA (Shen and Andrews, 2011). The Australian Guidelines for Water Recycling recommends 10 ng/L (Pisarenko et al., 2015), while California's Department of Public Health (CDPH) recommends 10 ng/L limit for 3 nitrosamines (Krasner et al., 2013). However, the cancer potency of NDMA is much higher than those of the trihalomethanes (Mitch et al., 2003). A number of the latest pilot- and full-scale studies revealed that rejection efficiency of NDMA by RO membranes varies widely, thereby making it a trace organic substance of concern (Farré et al., 2011; Fujioka et al., 2014; Khan and McDonald, 2010). NDMA, which is the most significant N-nitrosamine based on occurrence and abundance is formed during the chloramination of biologically treated effluent as a non-halogenated disinfectant by-product (Qian et al., 2015; Russell et al., 2012). NDMA is also a disinfectant by-product of ozonation processes (He and Cheng, 2016). Further, oxidation of unsymmetrical dimethylhydrazine, a commonly utilized constituent of liquid rocket fuel also produces NDMA (Mitch et al., 2003). This is predicated on the recorded occurrence of NDMA (up to 400 μg/L) in the groundwater on a testing facility of a rocket engine, and about 20 μg/L was observed in the down gradient well waters of Sacramento County, California (Mitch et al., 2003). The formation of N-nitrosamines during the process of postcombustion capture of CO_2 and after releasing amine wastes into the atmosphere is also possible (Strazisar et al., 2003; Svendsen and Asif, 2013).

Prominent N-nitrosamine precursors are secondary, tertiary, and quaternary amines, which include dimethylamine, DMA and trimethylamine (TMA) (Callura, 2014). NDMA precursors include DMA, dimethylformamide (DMFA), trimethylamine (TMA), and dimethylaminobenzene (DMAB).

DMA and tertiary amines with DMA functional group mostly found in municipal wastewater (Wang et al., 2014) are the protuberant precursors. NDMA is the first N-nitrosamine discovered in drinking water in Ontario, Canada (Taguchi et al., 1994), while other types were detected in a number of places such as the

United Kingdom, Asia, Australia, and North America (Asami et al., 2009; Krasner et al., 2013; Russell et al., 2012; Wang et al., 2010).

Removal of NDMA from portable water is an uphill task due to the complex nature of NDMA. This includes strong hydrophilicity, low molecular weight, structural stability, which makes their removal exceptionally difficult by conventional and advanced treatment processes. Several authors have identified prevention of NDMA formation *via* destruction of NDMA precursors as a viable alternative (Li et al., 2017; Liao et al., 2015). Some proceed towards finding a more efficient NDMA removal technique (Han et al., 2017; Su et al., 2017), while others applied both strategies (He and Cheng, 2016; Wang et al., 2014). Consequently, to proffer solution to these challenges, this study critically reviewed the formation, prevention, and removal of N-nitrosamines. NDMA prevention techniques include physical adsorption, resin fractionation, polarity rapid assessment method, PRAM, pre-oxidation, and biological activated carbon. The removal techniques discussed here include physicochemical, combined physicochemical and microwave irradiation, UV photolysis, bioremediation, catalytic reduction, and dope technology.

2. Formation of nitrosamine

2.1. Chloramination

In compliance with disinfection byproduct (DBP) regulation for minimizing halo-acetic acids formation (Weidhaas et al., 2012) and trihalomethanes (halogenated DBPs) (USEPA, 2014; Zhai et al., 2014), mono-chloramine replaced free chlorine (FC) (Hollender et al., 2009) in drinking water treatment plants (DWTPs). However, disinfection with MCA engenders formation of nitrogenous DBPs such as N-nitrosamines in a solution containing hydrophilic dissolved organic matter (DOM) with low molecular weight (Krasner et al., 2012; Wang et al., 2013). These nitrogenous DBPs obtained *via* chloramination have associated risks greater than that of the halogenated DBP by two to three orders of magnitude (Charrois and Hrudey, 2007). Prominent of all the N-nitrosamines is NDMA, which has been reported as a low-level carcinogenic contaminant with cancer risk at 0.7 ng/L (Wang et al., 2013). Moreover, the health hazard of N-nitrosamines exposure tends to increase due to the wide acceptance of MCA in DWTPs (West et al., 2016). This warrants a systematic investigation of N-nitrosamine formation under different conditions. Consequently, USEPA placed NDMA and 5 other N-nitrosamines in the unregulated contaminant monitoring rules and in their contaminant candidate list (CCL) and in the draft of CCL 4 (Krasner et al., 2009).

NDMA may be formed as a byproduct of disinfection of wastewater and drinking water treated with polymers such as poly(diallyldimethylammonium chloride) (polyDADMAC) and poly(epichlorohydrin dimethylamine) (polyamine), and pharmaceuticals and personal care products (PPCPs) substituted amine groups when exposed to chloramines. For polymer-based, the formation pathway significantly depends on properties of the polymer. These include purity, structure and

molecular weight, residual DMA, and other intermediate compounds used during polymer synthesis. Reaction variables like contact time, pH, and oxidant dosage also influence the formation mechanism (Park et al., 2009). Park et al. (2009) studied the formation mechanisms of NDMA by direct chloramination of intermediate monomers and polymers in reagent water. The result showed polyamines have greater potential to form NDMA when compared with polyDADMAC. The formation of NDMA from both polymers was significantly associated with degradation of polymer and release of DMA as chloramination proceeds. When polyamine is used, NDMA formation proceeds by degradation of tertiary amine chain ends, while the formation of NDMA proceeds by degradation of the quaternary ammonium ring group. (Park et al., 2009) also stated that presence of polymer impurities such as catalysts, intermediate compounds, oligomers, and monomers also increases the formation tendency of NDMA. Furthermore, low molecular weight polymers have a higher NDMA formation potential when compared with high molecular weight polymers. The increase in oxidant dosage above the optimum amount raises the formation potential of NDMA after a long contact time. The effect of pH is also vital in water treatment (Naje et al., 2016), even towards the formation of DMA and NDMA. For instance, the optimum degradation pH for both polyDADMAC and polyamine is 8 (Park et al., 2009). West et al. (2016) recently reported the speedy formation of NDMA in the presence of seven N-nitrosamine precursors in the presence of mono-chlorine disinfectant. The precursors include dimethylamine, 3-(dimethylaminomethyl) indole, trimethylamine, 4-dimethylaminoantipyrine, ethylmethylamine, dipropylamine and diethylamine. Other observed N-nitroamines include NDEA, NDPA, N-nitrosomethylamine, NMOR, NPYR, NPIP, and NDBA. However, changes in pH do not influence the formation of NDMA, while the formation of other N-nitrosamines slightly decreases with increase in pH from 7 to 9.

Amine-based PPCPs (i.e., PPCPs containing diethylamine [DEA] or DMA in their structures) fall within tertiary and quaternary amine groups that could contribute to the nitrosamines formation during chloramine disinfection of wastewater effluent organic matter (EfOM) (Krasner, 2009; Shen and Andrews, 2011). PPCPs could be discharged to the environment and infiltrate into drinking water treatment plant either via wastewater treatment plant effluent or via natural water (Shen and Andrews, 2013b; Zhang et al., 2014).

(Shen and Andrews, 2011) reported twenty amine-based PPCPs with potentials for NDMA formation during disinfection via chloramination (Table 1). Eight of the reported pharmaceuticals exhibit relatively high potential for NDMA formation (more than 1% molar yield) out of which ranitidine shows the highest potential. The presence of dichloramine is responsible for the formation of NDMA from the precursors because the molar transformation of the precursor increases with the molar ratio of Cl_2:N. However, it is not likely those PPCPs will constitute the bulk of nitrosamine precursors in water since most of them are in trace level in the source waters but significant NDMA formation could be ascribed to additive

Table 1. Nitrosamine formation potentials of selected PPCPs under the modified formation potential conditions (Initial concentration of PPCPs = 25 nM) (Shen and Andrews, 2011).

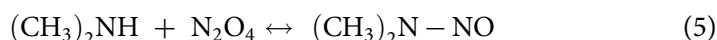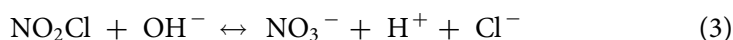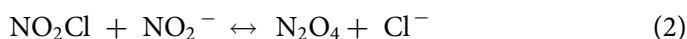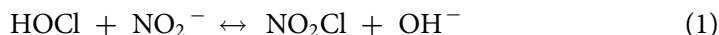|	Molar yield (%)	
PPCP	Milli Q	Tap water
NDMA precursors		
Ranitidine	89.9	94.2
Doxylamine	8.0	9.7
Sumatriptan	6.1	6.1
Chlorphenamine	5.2	5.5
Nizatidine	4.5	4.8
Diltiazem	2.1	2.6
Carbinoxamine	1.0	1.4
Tetracycline	0.8	1.2
Diphenhydramine	0.63	0.65
Azithromycin	0.51	0.78
Clarithromycin	0.34	0.86
Erythromycin	0.62	0.79
Roxithromycin	0.39	0.54
Amitriptyline	0.66	0.61
Escitalpram	0.74	0.55
Metformin	0.37	0.41
Tramadol	0.46	0.44
Venlafaxine	0.41	0.63
NDEA Precursors		
DEET	0.65	0.71
Lidocaine	0.52	0.52

formation from multiple, low-yielding compounds (Hanigan et al., 2017). Furthermore, transformation products and metabolites of some PPCPs could also constitute nitrosamines formation potential. Therefore, the overall potential of PPCPs to form nitrosamine formation depends on the possible transformation products, the parent compounds, as well as their metabolites.

Moreover, the dissolved oxygen and solution pH significantly affect nitrosamne formation. The yield of NDMA decreases with a decrease in the concentration of dissolved oxygen during chloramination of ranitidine (Le Roux et al., 2011). This shows that rather than dichloroamine, dissolved oxygen is the major oxidant during chloramination of ranitidine. According to the report of Shen and Andrews (2013a) on influence of pH on the formation of NDMA from sumatriptan and ranitidine, the most favorable pH for NDMA formation is from 7 to 8. A lower pH results in protonation of all the amines, thereby limiting NDMA formation. Although a higher pH increases the amount of non-protonated amines, formation of NDMA is limited due to shortage of dichloroamine.

Apart from the 20 listed reported by Shen and Andrews (2011), methadone is another newly identified pharmaceutical with relatively high potential for NDMA formation (Hanigan et al., 2017). Methadone is a pharmaceutical containing organic nitrogen (tertiary amine) and is basically used for treatment of heroin addiction. Recently, methadone becomes a commonly prescribed pill for chronic non-cancer pain and mitigation of withdrawal symptoms ascribed to prescription opiates such as morphine (Control and Prevention, 2012). According to the report of (Hanigan et al., 2015), the molar yield of NDMA ranges from 23% to 70%
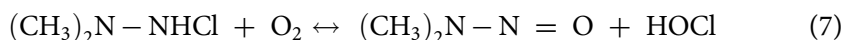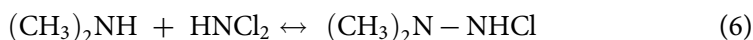
depending on the dosage of chloramine (1–150 mgCl$_2$/L). This is responsible for NDMA formation potential between 1% and 10% in most raw surface waters, and up to 62% of NDMA formation potential in wastewater. Both methadone and ranitidine are high-yielding NDMA precursors found in domestic sewage as microconstituents (Zeng and Mitch, 2015).

NDMA could be formed when free chlorine is used as a disinfectant in the presence of nitrite (Choi and Valentine, 2003). The proposed pathway is as follows:

$$HOCl \ + \ NO_2{}^- \ \leftrightarrow \ NO_2Cl \ + \ OH^- \tag{1}$$

$$NO_2Cl \ + \ NO_2{}^- \ \leftrightarrow \ N_2O_4 + \ Cl^- \tag{2}$$

$$NO_2Cl \ + \ OH^- \ \leftrightarrow \ NO_3{}^- \ + \ H^+ + \ Cl^- \tag{3}$$

$$H^+ + \ NH_2Cl \ + \ NO_2{}^- \ \leftrightarrow \ NO_2Cl \ + \ NH_3 \tag{4}$$

$$(CH_3)_2NH \ + \ N_2O_4 \leftrightarrow \ (CH_3)_2N-NO \tag{5}$$

Although DMA is the popular source of NDMA, the nitrosation reaction between DMA and nitrites is extremely slow (Najm and Trussell, 2001). The interaction of chloramine with DMA to form unsymmetrical dimethylhydrazine (UDMH), could be simply oxidized to different compounds, among which is NDMA at a low yield (Scheme 1) (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Nawrocki and Andrzejewski, 2011), with the highest NDMA formation at a pH range of 6 to 8 (Mitch and Sedlak, 2002). Therefore, UDMH oxidation is not a rate-determining step but the NDMA formation increases as the concentration of chloramine increase, indicating that chloramine is the nitrogen source towards the formation of NDMA. In the view of this, Gerecke and Sedlak (2003) suggested that natural organic matter could be an N-nitrosamine precursor in wastewater treatment plants.

Schreiber and Mitch (2006) revisited the NDMA formation pathway and suggested that formation of NDMA is largely influenced by the presence of dichloramine rather than mono-chloramine. The proposed mechanism for this process is given by:

$$(CH_3)_2NH \ + \ HNCl_2 \leftrightarrow \ (CH_3)_2N-NHCl \tag{6}$$

$$(CH_3)_2N-NHCl \ + \ O_2 \leftrightarrow \ (CH_3)_2N-N \ = \ O \ + \ HOCl \tag{7}$$

DMA reacted with dichloramine to produce chlorinated UDMH derivative that was oxidized by dissolved oxygen. The formation of NDMA was revealed to be absolutely associated with the concentration of the dissolved oxygen. Furthermore, this pathway leads to the generation of a stronger oxidant (HOCl) after reaction with oxygen (a weaker oxidant) (Schreiber and Mitch, 2006). NDMA formation via this pathway may be about 2–10 times greater compared with the one generated via monochloramine pathway at a neutral
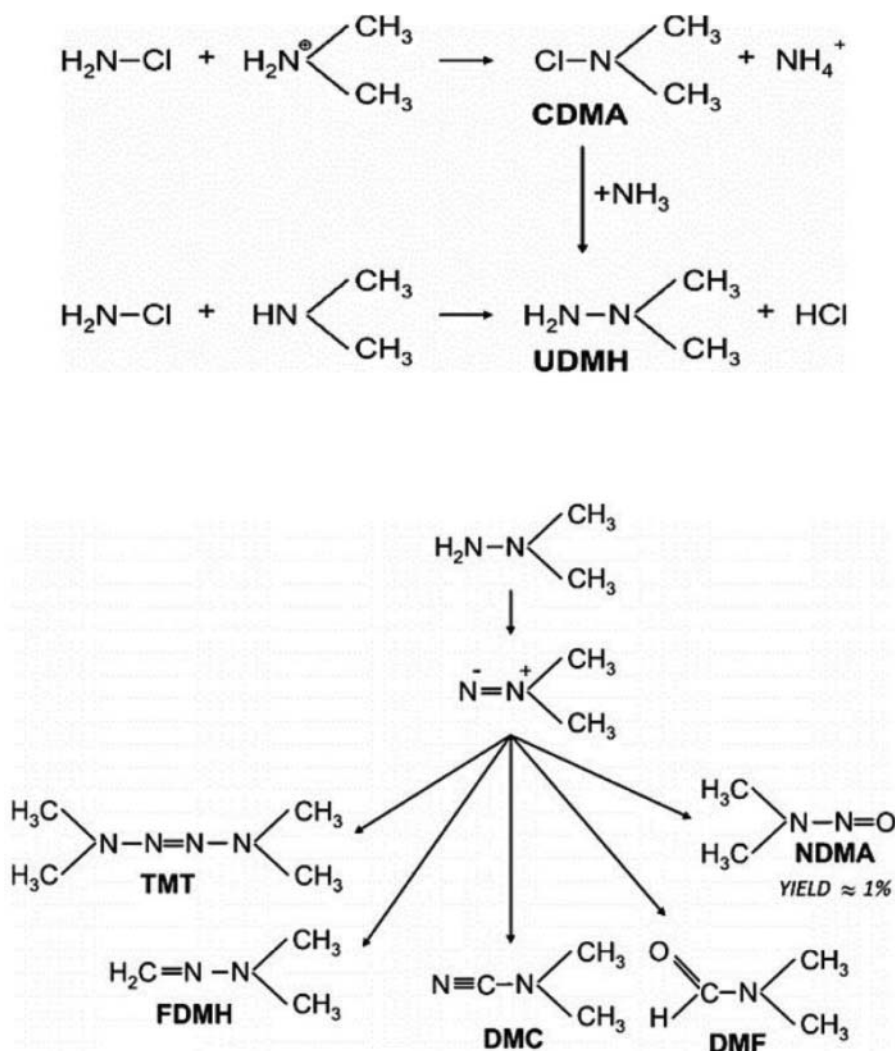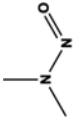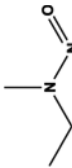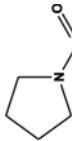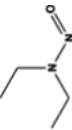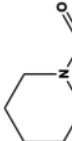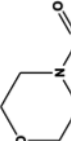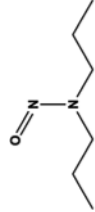
Scheme 1. Pathway for chloramination induced the formation of DBPs (Nawrocki and Andrzejewski, 2011).

pH (Schreiber and Mitch, 2005). Therefore, it is essential to seek to minimize dichloramine formation in water treatment plant.
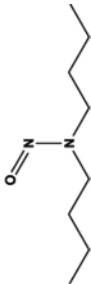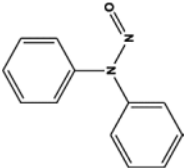
On the other hand, the study of Roux et al. (2012) on chloramination of ranitidine revealed that NDMA could also be formed by direct substitution on the DMA group of ranitidine (Table 2). This explains the reason for high yield of NDMA from ranitidine. The density functional theory (DFT) conducted recently by Liu et al. (2014) revealed that the formation mechanism of NDMA from trimethylamine (TMA) and ranitidine involves 4 steps (Scheme 2). Step 1 involves nucleophilic substitution by chloramine to produces a Complex I. Step 2 is oxidation reaction, which involves elimination of HCl from Complex I (X = H or Cl) first occurs and simultaneously generates an active intermediate [XN-R-Model], which

Table 2. Properties and cancer risk of some N-nitrosamine in drinking water (Huang et al., 2013).

Nitrosamine species	Symbol	MW (g/mol)	Structure	Reported concentration (ng/L)	10^{-6} Cancer risk concentration (ng/L)
N-Nitrosodimethylamine	NDMA	74.1		3.0 – 36	0.7
N-Nitroso-n-methylethylamine	NMEA	88.1		2.9 – 4.5	2
N-Nitrosopyrrolidine	NPYR	100.1		2.4 – 13	20
N-Nitrosodiethylamine	NDEA	102.1		6.4 – 19.5	0.2
N-Nitrosopiperidine	NPIP	114.2		4.1 – 23	3.5
N-Nitrosomorpholine	NMOR	116.1		2.5 – 12	5
N-Nitrosodi-n-propylamine	NDPA	130.1		1.7 – 79	5
N-Nitroso-n-methylaniline	NNMA	136.2		N/A	0.8

Table 2. (*Continued*)

Nitrosamine species	Symbol	MW (g/mol)	Structure	Reported concentration (ng/L)	10^{-6} Cancer risk concentration (ng/L)
N-Nitrosodi-*n*-butylamine	NDBA	158.2		4.0 – 6.2	6
N-Nitrosodiphenylamine	NDPhA	198.2		ND – 6.0	7,000
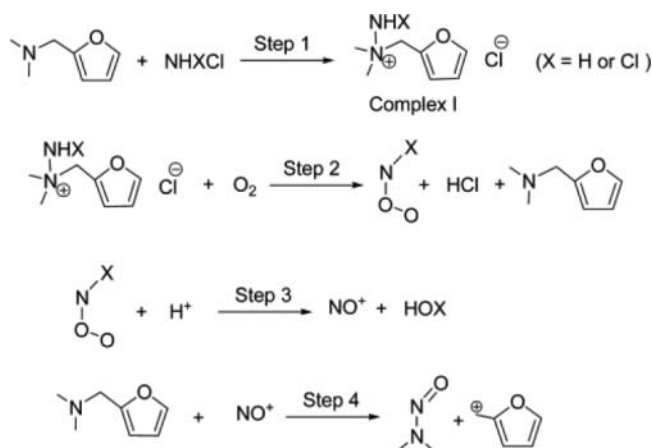
Scheme 2. Proposed NDMA Formation Pathways from Ranitidine Model during Chloramination (Liu et al., 2014).

was simply trapped by O_2. According to the DFT model, the chloramination process in step 1 is not as difficult as the oxidation in step 2Step 3 involves endothermic dehydration of OONX (X = H or Cl) after trapping of proton to form a NO^+ cation. NO^+ cation is a confirmed nitrosating agent; therefore, it can react with the anime immediately after its generation (step 4). The rate-limiting step is nitrosation reaction, which also determines the yield of NDMA for tertiary amines. The products of the nitrosation are NDMA and a stable furan-2-ylmethanlium cation, which could interact with nucleophiles to produce alcohols. These results corroborate with the pathway reported by Roux et al. (2012) using HPLC−MS.

2.2. Ozonation

Formation of NDMA is of great concern in treatment systems for portable water reuse that involves ozonation. This is mainly because molecular ozone
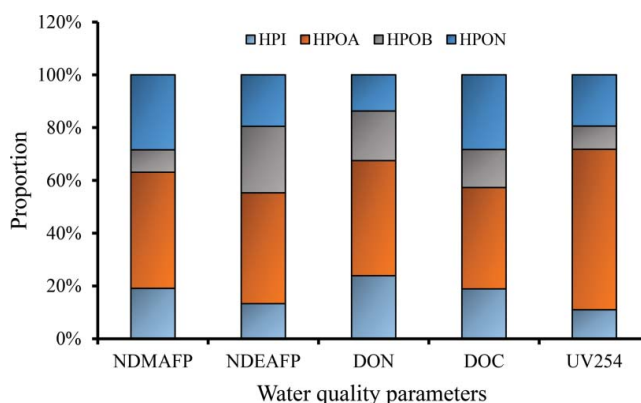
Figure 1. Distribution of resin fractions to bulk organic matter and NA precursors adopted from (Liao et al., 2015).
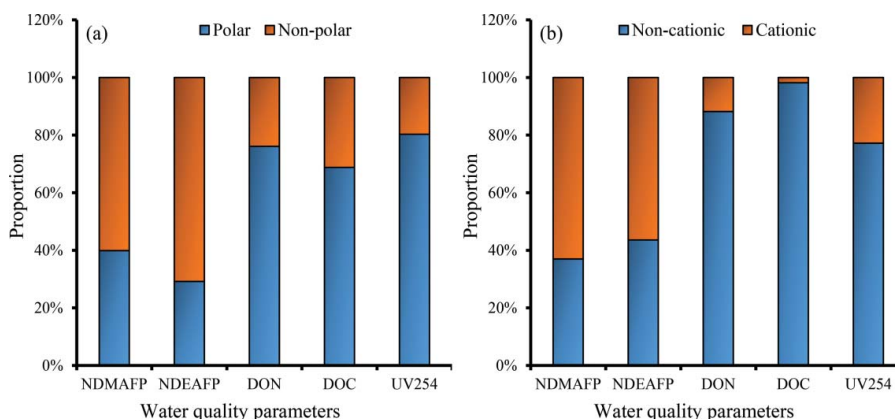
Figure 2. Distribution of PRAM fractions of bulk organic matter and N-nitrosamine precursors (Note: C_{18} and SCX were conducted simultaneously. RSDs of NDMAFP, NDEAFP, DON, DOC, and UV_{254} determination were <20%, <20%, <20%, <5%, and <2%, respectively) adopted from (Liao et al., 2015).

is a primary oxidant capable of NDMA formation. Ozonation helps to remove trace organic contaminant (TOrC) in water (Pisarenko et al., 2015). Efforts made to mitigate NDMA formation by adjustment of pH and/or addition of H_2O_2 were to no avail since they both exhibit similar overall exposure to *OH in wastewater under a sufficient reaction time (Pisarenko et al., 2015; Pisarenko et al., 2012). Therefore, the addition of H_2O_2 to ozone is not always necessary in an advanced oxidation process. Furthermore, significant formation of NDMA is limited to wastewater matrices from industrial discharges. The rate
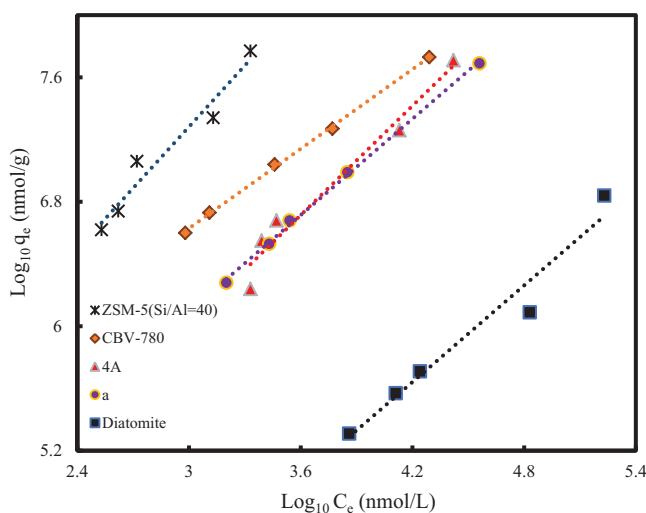
Figure 3. Sorption of DMA on 4A, CBV-780, diatomite, MCM-41, and dealuminated Na-ZSM-5 analogues (Si/Al = 12.5, 25, 40, and 130) adopted from (He and Cheng, 2016).

of formation of NDMA approaches its peak at O3: TOC (total organic carbon) above 0.5 (Pisarenko et al., 2015).

Recently, several works have been done on NDMA formation during ozonation (Gunten et al., 2010; Hollender et al., 2009; Schmidt and Brauch, 2008; Zimmermann et al., 2011). Unfortunately, the pathway to the formation of this carcinogenic contaminant seems complex. Consequently, it is essential for researchers to make concerted efforts towards identifying the precursor in order to strategize on how to curtail its occurrence. (Gunten et al., 2010; Schmidt and Brauch, 2008) suggested that something similar to N, N-dimethylsulfamide (DMS), which was previously said to be an unknown metabolite of the tolylfluanid and fungicide, could be a NDMA precursor when reacted with ozone in the presence of bromide. (Nawrocki and Andrzejewski, 2011) also suggested a number of other compounds such as 1,1,1',1'-tetramethyl-4,4'-(methylenedi-p-phenylene)disemicarbazide (TDMS) and 4,4'-hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS).

3. Nature of nitrosamine precursor

3.1. Resin fractionation technique

One of the technique used for characterizing N-nitrosamine precursor is the resin approach. This is achieved by extracting non-humic and humic (natural organic matter, NOM) matters in various resins at acid pH and basic pH. Several authors have worked extensively on this technique for characterization NOM (Singer et al., 2007; Wang et al., 2013). Resin fractionation technique separates bulk organic substance into the hydrophilic (HPI) and hydrophobic (HPO) fractions (Chen et al., 2008) by using resin like acrylic ester XAD-8, which adsorb HPO NOM, while the filtrate is HPI NOM. Furthermore, the HPO fraction could be fractionated into hydrophobic neutral (HPON), hydrophobic base (HPOB), and hydrophobic acid (HPOA) NOM by methanol elution, 0.1 M sodium hydroxide or 0.1 M hydrochloric acid, respectively (Liao et al., 2015). The characteristics of NDMA precursor depend on the source of water. The study of (Chen et al., 2008) on a water treatment plant, Northern China revealed that the HPO fraction is mainly haloacetic acids (Weidhaas et al., 2012) and trihalomethanes, THM precursors. While (Chen and Valentine, 2007) studied chloraminated in Iowa River water; (Dotson et al., 2009; Wang et al., 2013) studied Luan River, Northern China, all reported that N-nitrosamine precursors are more of HPI NOM. Meanwhile, the recent study of (Liao et al., 2015) on aquaculture-impacted lake water in the Yangtze River Delta, China revealed that the HPOA fraction forms the largest part to NDMAFP (45%), UV254 (61%), NDEAFP (42%), DON (44%), and DOC (39%), followed by HPON, HPI, and HPOB (Figure 2). The HPI fraction is about 19% of the NDMAFP, which is lesser when compared with the HPOA fraction. The main drawback of the resin technique is a lack of selectivity for NDMA precursors. This is due to the similarity in the normalized NDMAFP between the four resin fractions.

3.2. Polarity rapid assessment method

PRAM is also used for characterization of the N-nitrosamine precursor in water. However, unlike resin technique, it enables the use of a small sample size (minimum of 100 ml) (Chen et al., 2014; Rosario-Ortiz et al., 2007). This technique isolates and fractionates N-nitrosamine precursors at ambient pH in a parallel arrangement of solid-phase extraction (SPE) cartridges. The cartridges consist of non-polar C18 SPE cartridges, which fractionates organic matter based on polarity, and strong cation exchange (SCX), which fractionates based on the charge of the organic matter. The non-polar C18 SPE cartridges (with a matrix such as octadecyl-silyl) is responsible for adsorption of the non-polar fraction of NDMA, while the non-polar fraction is the filtrate (Figure 3(a)) (Liao et al., 2015). The SCX SPE type (with matrix-like benzenesulfonic acid-silyl) isolates the amine-type functional group, which is referred to as the cationic fraction and the filtrate is referred to as the non-cationic (Figure 3(b)) (Liao et al., 2015). It is easy to carry out quality assurance as the PRAM operation proceeds. The quality test could be performed by using ultraviolet absorbance at 254 nm (UV_{254}) and surrogate indicators of dissolved organic carbon (DOC). This has been reported to give relative standard deviation (RSD) below 15% for replicate SPE cartridges and for water sample reload (Chen et al., 2014). The study of (Liao et al., 2015) on sample obtained from one aquaculture-impacted lake water in the Yangtze River Delta, China, revealed that the non-polar fraction contributes the largest to NDMAFP and NDEA (60 and 70% respectively), while it only contributes 24% of the DON, 19% of the UV_{254}, and 31% of the DOC in this water (Figure 3(a)). They also allude that the cationic fraction contributes the largest to NDMAFP and NDEA (63 and 56% respectively), while it only contributes 11% of the DON, 22% of the UV_{254}, and 1% of the DOC in this water (Figure 3(b)). Unlike the resin fractionation technique, PRAM is a viable tool with high for fractionation selectivity of N-nitrosamine precursor (Philibert et al., 2012).

Water softening processes cation exchange technology is also a viable means of quantifying NDMA precursors prior to chloramination or other disinfection process. This is predicated on the fact that NDMA precursors comprises of the non-polar moiety and protonated dialkylamine functional group (Chen et al., 2014; Liao et al., 2015). The pH of NDMA precursors is commonly higher than 7, signifying that these precursors will protonate and the charge will turn out to be positive when the pH is neutral (Chen et al., 2014). Recently, (Li et al., 2017) also asserted that N-nitrosamine precursors comprise of cationic DMA group and organic matter with a non-polar moiety. They therefore, developed a strong acidic cation exchange resin (Amberlite IR-120, purified and transformed into Na$^+$ form) for removal of NDMA precursors (ranitidine (RNTD) and DMA). The matrix of the resin consists of Styrene, divinyl benzene. The removal efficiency of these precursors depends greatly on pH. At pH < pka-1 and the molar ratio of exchange capacity to the precursor of 4, the removal efficiency of RNTD are above 94% and that of DMA is

above 78%. This cation exchange technology is also potent for removal of other 7 model NDMA precursors. These include N,N-dimethylbutylamine, doxylamine, N, N-dimethylisopropylamine, N,N-dimethylphenethylamine, N,N-dimethylbenzyl-amine, N,N-dimethylaniline and N,N-dimethyloctylamine.

4. Prevention

Quite a lot has been done towards identifying N-nitrosamine precursors and preventing the formation of N-nitrosamine rather than their removal because of their continuous occurrence in portable water distribution system (West et al., 2016). Some researchers have established that presence of bromide, ammonia, and nitrite can intensify formation of NDMA in a system that involves formation of reactive bromamine species and nitrosation (Mitch et al., 2003; Shah and Mitch, 2011) Prominent N-nitrosamine precursors are secondary, tertiary, and quaternary amines, which include DMA and trimethylamine (TMA).

Their origin includes cationic shampoos, polymers, ion-exchange resins, and pharmaceuticals (Shah and Mitch, 2011). To reduce the formation potential (FP) of NDMA, the number of tertiary amine chain ends must be minimized to produce polyamines with less branching and high MW (Park et al., 2009). Another viable strategy reported by Park et al. (2009) is ensuring a suitable capping of the tertiary amine chain ends, which prevent chlorine oxidants from degrading them to evolve DMA. The occurrence of NDMA and DMA can be minimized by decreasing the amount of residual oligomers, by reducing the overall NDMA-FP of the polymers (Park et al., 2009). Rational design of new water treatment polymers for, food and/or domestic applications should incorporate NDMA-FP testing and assessment of the tendency of amine-based polymers to release free amine, thereby producing safer products.

4.1. Physical adsorption of nitrosamine precursors

Formation of NDMA could be prevented by targeting physical adsorption of precursors such as DMA. N-nitrosamine precursors can be absorbed on porous mineral adsorbents such as zeolites (Alaba et al., 2015b, 2017), kaolin (Alaba et al., 2015a) and activated carbon (AC) (Adebisi et al., 2017). Zeolites are known for their remarkable shape selectivity and adjustable pore structure (Alaba et al.,
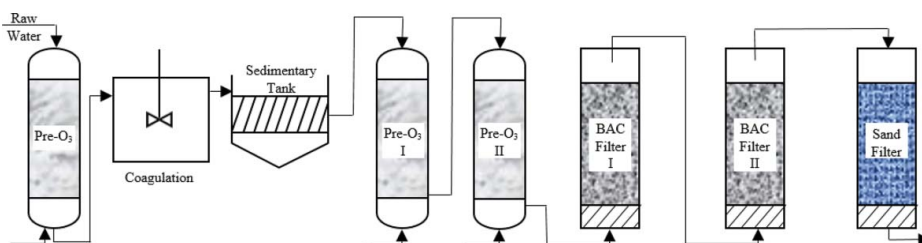

Figure 4. Diagram of O3-BAC technology adopted from (Liao et al., 2013).

2016a) and have been investigated on adsorption of NDMA from various solutions and gas streams (Kamaloo et al., 2013; Li et al., 2013; Pinisakul et al., 2008; Sun et al., 2014). Conventional zeolites are generally microporous but they can be transformed to mesopore (Alaba et al., 2016b) since porosity is key in adsorption. Recently, (He and Cheng, 2016) extensively studied the use of porous mineral sorbents with different pore sizes for removal of N-nitrosamine precursor, DMA (Figure 1). The sorbents and their pore size range include diatomite (400 nm), CBV-780 (0.58–0.70 nm), MCM-41 (2–5 nm), 4A (0.4 nm), and Na-ZSM-5 zeolites (Si/Al = 12.5, 25, 40, and 130) (0.51–0.56 nm). The sorption performance of DMA for 4A and MCM-41 are similar, and a little lower than that of CBV-780 but considerably higher when compared with that of diatomite. The best sorption performance was obtained when they modified the Na-ZSM-5 (Si/Al = 40) by dealumination and the sorption capacity increases with increase in the degree of dealumination. The suitability of Na-ZSM-5 (Si/Al = 40) is ascribed to the hydrophobic nature of its pore wall surface and porosity due to dealumination. The adsorbed DMA on the zeolite was degraded by microwave irradiation, whose activity hardly affects the transparent framework of the zeolite matrix.

4.2. Pre-oxidation

Recently, pre-oxidation with ozone, chlorine (Jeon et al., 2016; Qian et al., 2015), chlorine dioxide (Lee et al., 2007), hydrogen peroxide, permanganate, sunlight (Chen and Valentine, 2008) and ferrate (Lee et al., 2008) have been reported as remarkable techniques for removal of NDMA precursor towards elimination or substantial reduction of N-nitrosamine formation in drinking water. However, the attention of researchers on the reduction of NDMA formation by peroxidation is yet not encouraging. (Wilczak et al., 2003) are the first to attempt the reduction of NDMA formation via peroxidation using chlorine. Subsequently, (Charrois and Hrudey, 2007) reported that 2 hr of free-chlorination prior to chloramination significantly reduces the formation of NDMA by about 93% in a bench-scale experiment. Meanwhile, there is no convincing explanation or mechanism to explain this reduction. (Lee et al., 2008) explored the reaction kinetics for oxidation of NDMA and its precursors in a peroxidation process using ferrate (VI) as the oxidant. They reported that the rate constant follows the second-order model for reactions of Fe(VI) with NDMA and DMA including 7 tertiary amines with DMA functional group such as TMA, DMAI, DMEA, DMAP, DMAB, DMFA, and DMDC at pH ranging from 6–12. Pre-oxidation with Fe(VI) completely removed the NDMA-FPs of most of the NDMA precursors without formation of any other NDMA precursors. However, the pre-oxidation has no significant effect on DMA. By using a high dose Fe(VI) on various natural waters, they achieved about 46–84% removals of the NDMA formation potentials.

However, exposure of the pre-oxidant must be minimized to avoid the formation of both regulated and unregulated DBPs. Of all the pre-oxidant, chlorine and
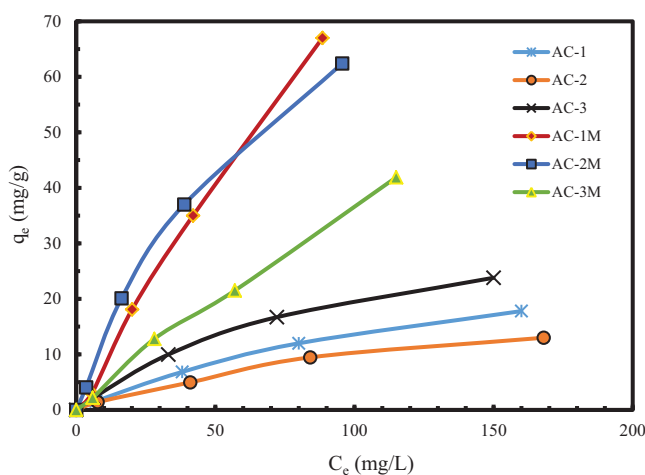
Figure 5. NDMA adsorption isotherms adopted from adopted from (Xiaodong et al., 2012).

ozone have been recommended as more effective for deactivation of NDMA precursor (Chen and Valentine, 2008; Lee et al., 2008). For instance, pre-ozonation could effectively reduce NDMA-FP at low exposures relevant to disinfection, thereby reducing the risk of formation of both regulated and unregulated DBPs (Krasner et al., 2013). Despite the effectiveness of ozonation towards a reduction in NDMA-FP and the NDMA removal benefits for wastewater treatment, there is a need for further mitigation strategies to prevent the direct formation of NDMA in wastewater treatment (Pisarenko et al., 2012).

4.3. Biological activated carbon technique

Biological activated carbon (BAC) process combines both physical adsorption and bio-treatment (biodegradation) (Carvalho et al., 2007). Therefore, the organic substance could be removed, biodegraded and some could be adsorbed on the activated carbon (AC) surface and subsequently biodegraded by the microorganism in the BAC filter (Liao et al., 2015). The microorganism degraded the N-nitrosamine precursors that occupy the adsorption sites, thereby extending the life of the AC. Several researchers have successfully removed NDMA precursors from wastewater (Farré et al., 2011; Liao et al., 2015; Liao et al., 2014). The influent in BAC process is usually an effluent of pre-ozonation/mid-ozonation process as a vital part of reverse osmosis-free advanced treatment for reuse of portable water. The report of (Liao et al., 2014) on aquaculture-affected drinking water source in China revealed that BAC techniques removed up to 90% of several N-nitrosamine (NDEA, NDMA, NPIP, NPYR, and NMOR) precursors. In order to clarify the relative significance biodegradation and physical adsorption, (Liao et al., 2015) performed both lab-scale and pilot-scale experiment using mid-ozonation effluent as BAC influent. They ascribed 42% removal efficiency to physical adsorption and 70% efficiency to biodegradation of NDMAFP for the lab-scale experiment. The overall
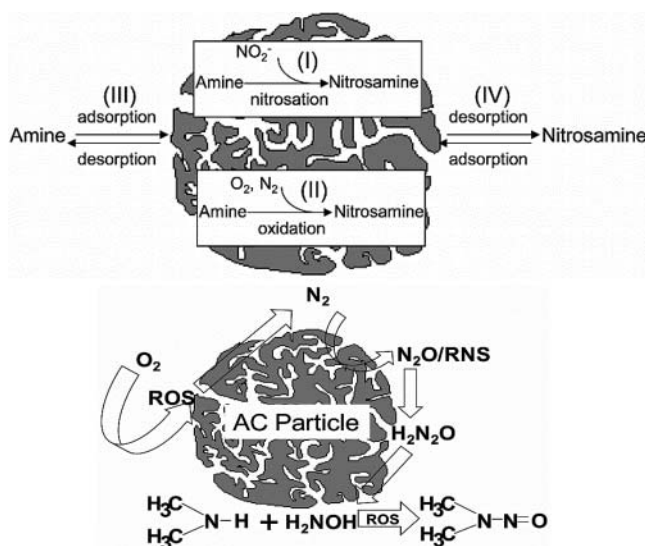
Figure 6. (a) Possible reactions involved in the AC-catalyzed transformation of amine to N-nitrosamine; (b) Proposed mechanism for the formation of N-nitrosamine from secondary amine on the surface of AC particles adopted from (Huang et al., 2013; Padhye et al., 2011).

removal efficiency of 9 N-nitrosamine FP in the pilot-scale experiment is 59%, which is higher those of coagulation and sedimentation, pre-ozonation, intermediate ozonation (18, 14 and 30, respectively).

Furthermore, the pilot plant setup suggested by Liao et al. (2013) for the treatment of organic matter and antibiotic contaminants could be adopted (Figure 4). This process includes pre-ozonation, coagulation, and sedimentation, mid-ozonation, BAC and post sand filter.

It is tenable to allude that the collaborative effect of ozonation and BAC filtration is effective towards upgrading wastewater treatment plants to prevent the occurrence of N-nitrosamine in drinking water, thereby protecting human life and the environment. However, the mechanism for removal of N-nitrosamine precursors via BAC filtration needs further clarification.

5. Removal techniques

In spite of the potential health risk of NDMA being a carcinogenic N-DBP, the treatment routes towards removing it from drinking water are few. This is because of the complexity of the removal process. NDMA is highly soluble in water (290 gL^{-1} at 20°C) with 2.63×10^4 atm m^{3}mol^{-1} Henry's Law constant at 20°C, which is low (Mitch et al., 2003b), therefore it cannot be removed or degraded effectively from drinking water via air stripping or volatilization. Furthermore, the low hydrophobicity (1ogKow$\frac{1}{4}$ 0.57) of NDMA has rendered sorption technique inefficient for its removal from water (Dai et al., 2009). The following sections are the promising removal techniques.

5.1. Physicochemical

Removal of NDMA in portable water treatment poses a significant technical challenge due to its high solubility in water (290 gL^{-1} at 20 °C) with 2.63×10^4 atm m^3mol^{-1} Henry's Law constant at 20 °C, which is low (Mitch et al., 2003), therefore it cannot be removed or degraded effectively from drinking water via air stripping or volatilization. Furthermore, the low hydrophobicity (1ogKow¼ 0.57) of NDMA has rendered sorption technique inefficient for its removal from water (Dai et al., 2009). NDMA also has small molecular size, and poor biodegradability (He and Cheng, 2016).

5.1.1. Adsorption

Despite the complication in the removal of NDMA, AC adsorption was recognized as a suitable treatment method as far back as 1996 at a prominent site of NDMA contamination on Rocky Mountain Arsenal, near Denver, CO (Fleming et al., 1996) due to a lack of better alternative technologies. This is because the adsorption capacity of AC is limited for NDMA (Gunnison et al., 2000), the cost associated with replacement or regeneration of adsorbent dictates the budget for this technology. Other technology such as advanced oxidation process or reduction by zero-valent metals, which involves the use of ultraviolet light and/or hydrogen peroxide are limited by formation of radical scavengers in water (Lee et al., 2007; Lv et al., 2013) and are more expensive and require a significantly more experience when compared with implementation and operation of AC (Kommineni et al., 2003). To proffer solution to the reusability challenge of AC, (Kommineni et al., 2003) studied the feasibility of regenerating NDMA absorbed commercial granular AC (GAC) using Fenton's reagent. They were able to achieve NDMA reduction below the detection limit (4 μg/L) from 1 mg/L within 30 min in homogeneous Fenton process with total Fe > 1.2 g/L and H2O2 > 2.7 g/L at pH of 1.90. For NDMA adsorbed on GAC, they achieved a NDMA destruction efficiency of 99% in some hours at a low pH (close to 2). They applied addition of complexing ligand to boost solubility of iron at neutral pH, thereby improving the destruction efficiency. However, the efficiency is still below what was recorded at low pH. They also reported that the destructive regeneration of GAC does not affect its adsorption capacity for NDMA although the adsorption sites were slightly affected as shown by iodine number, and the regeneration cost is not outrageous. The products of Fenton reaction are nitrate or nitrogen gas, monomethylamine, and formaldehyde, subject to reaction conditions.

To further reduce the treatment cost, some researchers have studied the synthesis of AC from biomass (Wang et al., 2013), and commercial AC modification (Xiaodong et al., 2012). (Wang et al., 2013), comparatively investigated N-nitrosamine removal with AC nanoparticles (NPs) prepared from coconut shell, charcoal, and bamboo at two distinct pH (6.6 and 8.6). They reported that the ACNPs synthesized from coconut shell gives the best removal efficiency at 4 hr contact time.

The effect of pH within the investigated range is not significant. (Xiaodong et al., 2012) studied the use of several commercial and modified commercial AC for removal of NDMA. Three commercial AC with textural properties: AC-1, AC-2 and AC-3 with micropore volume 0.46, 0.24 and 0.40 cm³/g, and pore size 2.13, 3.89 and 2.15 nm respectively. The adsorption capacity is in the order of AC-3 > AC-1 > AC-2 (Figure 5), indicating that the capacity to adsorb NDMA depends on the pore size and microporosity of AC. The molecular size on NDMA is 0.45 nm, and AC-3 has the biggest micropore volume at 0.46 nm, which offers the best adsorption potential close to pore walls. This justifies the best adsorption performance exhibited by AC-3. They modified the ACs by thermal treatment at 850°C for 2 hr (to produce AC-1M, AC-2M, and AC-3M), which eliminate the carbon atoms and oxygen groups on pore walls, and slightly lessen the pore size and homogenize the morphology of the pore. Furthermore, the hydrophobicity of the pore walls increases, thereby increasing the adsorption capacity (Figure 5) due to a reduction in the competition between NDMA and water in the pore, which facilitates dispersive interaction between the aromatic rings of the AC surface and the non-polar –CH_3 of NDMA.

On the other hand, researchers need to be careful in the use of AC due to its ability to catalyze the formation of N-nitrosamines from secondary amines (DMA, DPA, DEA, and DBA) to trace levels at ambient aerobic conditions (Padhye et al., 2010). This occurs mostly at high pH (>6), in the presence of O_2 and N_2 (especially drying in air for a long period). Two types of reactions are possible via AC catalysis to form N-nitrosamine: nitrosation of the amine with nitrite at AC surface, and amine oxidation in the presence of O_2 and H_2 (Figure 6a) (Huang et al., 2013). Fig. 6b presents the mechanism of the later. The surface active sites of AC interact with O_2 molecules to yield reactive O_2 species (ROS). The ROS formation enables fixation of N_2 on the surface of carbon to form reactive nitrogen species (RNS) such as hydroxylamine and nitrous oxide, which could react with adsorbed amines to generate nitrosamines (Padhye et al., 2011). Furthermore, the formation of N-nitrosamine can be promoted by ACs with higher carbonyl group content, reduced surface properties, more surface defects, higher O_2 uptake capacity, and higher surface area. Therefore, it is essential to carefully select the reaction condition and the AC to be used for N-nitrosamine adsorption. Table 3 presents the variation of formation of NDMA from DMA among the AC materials. Siemens Aquacarb particles (AqC) exhibited the utmost yield, while AC fibers and Ambersorb 572 showed the lowest NDMA yields (Padhye et al., 2010).

5.1.2. Combined adsorption and microwave irradiation

Removal of NDMA and its precursors from portable water with the aid of porous mineral sorbents prior to degradation by microwave irradiation is an emerging technology. In a recent study (He and Cheng, 2016), examined a wide variety of mineral sorbents (Figure 7a). The sorbents and their pore size

Table 3. NDMA formation from DMA in the presence of AC materials (Padhye et al., 2010).

Carbon materials	Specific surface area S_{BET} (m^2/g)	pH$_{zpc}$	Test condition	NDMA (nano moles)	NDMA (ng/L)	NDMA (ng/L) by NDMA-d6 isotope dilution
Ambersorb 572	1020	7.0	[a]	0.45 ± 0.33[c]	333 ± 244	972 ± 702
AqC	1202	9.6	[a]	2.14 ± 0.18	1584 ± 133	11337 ± 954
PSC	1114	9.7	[a]	0.57 ± 0.07	422 ± 52	4971 ± 618
UCT	NA	NA	[a]	1.68 ± 0.09	1243 ± 67	4463 ± 249
GAC	819	7.4	[a]	0.28 ± 0.03	207 ± 22	2316 ± 258
F400	1044	9.2	[b]	0.61 ± 0.08	451 ± 59	3773 ± 509
OLC	983	9.3	[b]	0.86 ± 0.02	636 ± 15	5794 ± 141
HD4000	706	6.6	[b]	0.60 ± 0.01	444 ± 7	4459 ± 74
ACF 10	972	7.3	[b]	0.17 ± 0.01	126 ± 7	1275 ± 73
ACF 15	1520	8.9	[b]	0.21 ± 0.01	155 ± 7	1558 ± 71
ACF 20H	1740	9.5	[b]	0.16 ± 0.02	118 ± 15	627 ± 80

[a]222 μM DMA, 200 mg carbon, 2 hr suspension shaking time, 3 hr carbon drying time. [b]200 μM DMA, 150 mg carbon, 1.5 hr suspension shaking time, 6 hr carbon drying time. [c]Experiments were conducted with regenerated Ambersorb 572 particles which were washed with methanol and then dichloromethane, followed by drying in a 100 °C oven. All reaction suspensions were buffered at pH 7.5 by 10 mM phosphate buffer. Instrument detection limit for NDMA = 2 pico moles; Mean ± standard deviation (n = 3); NA = not available; pH$_{zpc}$: zero point of charge.
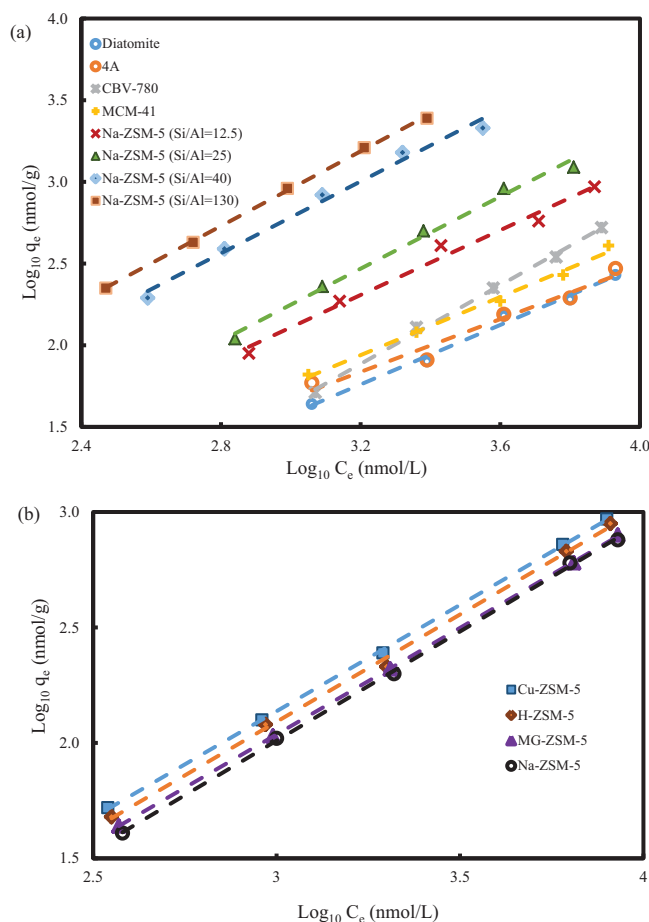

Figure 7. Sorption of NDMA on porous mineral sorbents at 25°C: (a) NDMA sorption on 4A, CBV-780, diatomite, MCM-41, and dealuminated Na-ZSM-5 analogues (Si/Al = 12.5, 25, 40, and 130); (b) NDMA sorption on dealuminated Na-ZSM-5 (Si/Al = 25) with different types of surface cations adopted from (He and Cheng, 2016).

range include diatomite (400 nm), CBV-780 (0.58–0.70 nm), MCM-41 (2–5 nm), 4A (0.4 nm), and Na-ZSM-5 zeolites (Si/Al = 12.5, 25, 40, and 130) (0.51–0.56 nm). The sorption performance of DMA for CBV-780 and MCM-41 are similar, which is slightly higher than those of diatomite and 4A. This indicates the dependence of NDMA sorption on the porosity of mineral sorbent. Bulky molecules could only access the external surface of microporous sorbent rather than the pore opening due to mass transfer limitation (Alaba et al., 2016c). The adsorption of NDMA on 4A proceeds by deposition on the external surface and insertion of the N-nitroso functional groups (N-N = O) into the micropore channels (Cao et al., 2007). This shows the reason for the poor capacity of 4A to adsorb NDMA. On the other hand, the poor adsorption performance of diatomite is due to its macroporosity, because the external surface of NDMA molecules is almost similar to the pore wall surfaces (He and Cheng, 2016). The best sorption performance was obtained from modified Na-ZSM-5 (Si/Al = 40). The sorption capacity increases with increase in the degree of dealumination. The suitability of Na-ZSM-5 (Si/Al = 40) is ascribed to the hydrophobic nature of its pore wall surface and porosity due to dealumination. The critical molecular size of NDMA is 0.42 nm (Li et al., 2013). This enhances adsorption potential energy (better geometric confinement) through the micropores (0.51–0.56 nm) of Na-ZSM-5 zeolites compared with those of other microporous minerals with higher pore size.

The surface ions attached to the zeolite micropores influence the adsorption capacity of the mineral sorbent as shown in Figure 7b. For instance, the incorporation of Cu^{2+} in the ZSM-5 micropores significantly improved the sorption of NDMA compared to using Na-ZSM-5, because of the complexing between the lone pairs of electrons in the vacant d-orbitals in Cu^{2+} ions and the N atoms of the molecules of NDMA. Similarly, HZSM-5 exhibited promising NDMA sorption than Na-ZSM-5 because the weak base N atoms of NDMA molecules are capable of forming hydrogen bonds with the protons existing in the micropores of HZSM-5 (Li et al., 2013). On the other hand, the sorption performance of Mg-ZSM-5 is marginally lower compared to that of Na-ZSM-5 since the divalent Mg^{2+} cations (with 0.065 nm radius) exhibit a significantly stronger interaction with water molecules than Na^{2+} cation (with 0.099 nm radius), although at half of the density of the Na-ZSM-5.

Microwave irradiation degraded the adsorbed NDMA and DMA on the zeolite. Hence, their activity hardly affects the transparent framework of the zeolite matrix. Mostly, the micropores adsorb the irradiation energy absorbed by the hydroxyls, surface cations, and polar molecules (water, DMA, NDMA, and the products of their destruction). Micro-scale formation of "hot spots" at low bulk temperatures (<160°C) of the mineral sorbents within 600 sec of microwave irradiation treatment degrades the adsorbed DMA and NDMA. Degradation time, surface cation and the Si/Al ratio of Na-ZSM-5, which determines the surface cation density as illustrated in Figure 8 are the major factors influencing degradation. The mineral
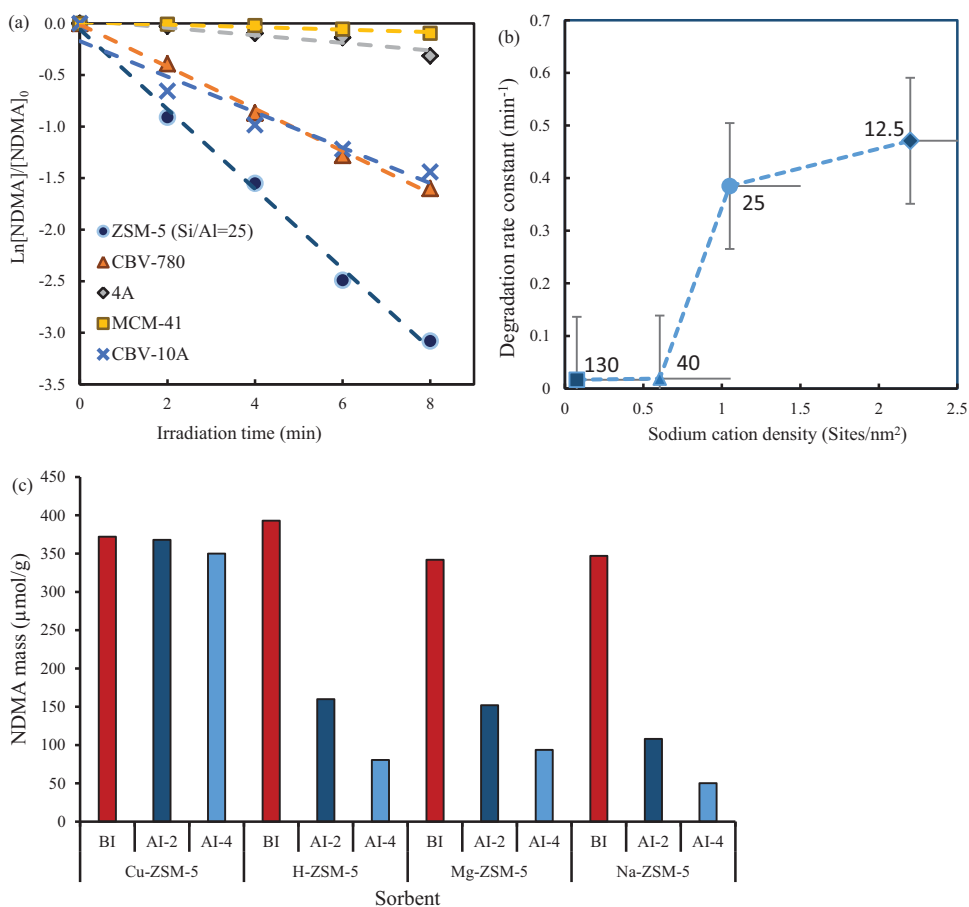
Figure 8. Microwave induced degradation of NDMA adsorbed on porous minerals at 120 W: (a) Degradation of NDMA adsorbed on Na-ZSM-5 (Si/Al = 25), CBV-780, MCM-41, 4A, and CBV-10A; (b) Effect of cation density on degradation of NDMA adsorbed on dealuminated Na-ZSM-5 analogues (Si/Al = 12.5, 25, 40, and 130); and (c) Effect of surface cation type on microwave-induced degradation of NDMA adsorbed on dealuminated ZSM-5 (Si/Al = 25) with different of surface cations (BI: before irradiation; AI-2: After 2 min irradiation; AI-4: after 4 min irradiation) adopted from (He and Cheng, 2016).

sorbents are readily reusable after a complete removal of DMA and NDMA because microwave irradiation scarcely influences the microwave-transparent structure of the sorbents. This is an emerging and promising treatment technique for removal of NDMA and other N-nitrosamines from wastewater and drinking water.

5.1.3. UV photolysis

Among other prominent NDMA destruction technology is direct UV photolysis (Lee et al., 2005; Stefan and Bolton, 2002) designed for treating effluent-dominated river consisting N-nitrosamines (Swaim et al., 2006). UV-based treatment is an advanced oxidation process (AOP), which generates reactive

free radicals such as hydroxyl (HO·), and is mainly employed for the removal of 1,4-dioxane N-nitrosamines (Fujioka et al., 2017). Direct UV photolysis easily decomposes NDMA at wavelengths below 260 nm. The maximum absorbance wavelength of NDMA is 227 nm, originating from a $\pi \rightarrow \pi^*$ transition, and absorbs UV irradiation intensely at 254 nm ($\varepsilon = 1974$ M^{-1} cm^{-1}) (Lee et al., 2005; Sharpless and Linden, 2003) and weakly at 332 nm ($\varepsilon = 109$ M^{-1} cm^{-1}) (Stefan and Bolton, 2002). A commercial UV lamp like low-pressure mercury-vapor UV lamp is capable of such emission. Conversely, medium-pressure UV lamp light is more efficient than low-pressure because medium-pressure UV exhibits higher quantum yield and absorption coefficient (Sakai et al., 2012). The study of (Sakai et al., 2012) revealed that medium pressure UV exhibits the highest degradation at a wavelength range of 230–270 nm (7.2 cm^2/J), which is close to three times larger than that recorded for low-pressure UV (2.6 cm^2/J). The estimated quantum yield for medium-pressure UV is 0.42, which is larger than that recorded for low-pressure UV (0.28). The report of (McCurry et al., 2015) also affirmed the superior performance of medium-pressure UV.

The wavelength of the UV light and the initial solution pH affect the behavior of N-nitrosamine during UV irradiation. Generally speaking, the N-nitrosamine degradation rate declines with an increase in pH (Xu et al., 2010; 심재구 et al., 2016). The study of (Lee et al., 2005) on the mechanism of NDMA UV degradation at pH below 8.5 revealed homolytic cleavage of N–NO bonds, heterolytic cleavage of N–NO bonds, and photo-oxidation. The mechanism is initialized by NDMA protonation to form NDMA*–H* (excited NDMA) prior to UV irradiation. Homolytic cleavage of N–NO bonds entails decay of NDMA* into two species—nitric oxide [($^•$N O) and aminium radical (CH$_3$)$_2$NH$^+$)] (Eq. 8), and further decayed to protonated Nmethylidenemethylamine (CH$_2 = N^+HCH_3$) and hyponitrous acid (Zakaria *et al.*); (Chow et al., 1972). The CH$_2 = N^+HCH_3$ go through hydrolysis to form formaldehyde (HCOH) and methylamine (CH$_3$NH^{3+}, MA) (Eq. 9). At a pH above 5.5, the reaction between $^•$N O and (CH$_3$)$_2$NH$^+$ produces amidoxime (CH$_3$NHC $=$ NOH) (Eqn. 10), while N-methylformamide (CH$_3$NCOH) and N$_2$O are produced from the interaction between nitrite ion (NO$_2^-$) and CH$_3$NHC $=$ NOH.

$$NDMA^* \rightarrow (CH_3)_2NH^+ + {}^*NO \qquad (8)$$

$$(CH_3)_2NH^+ + {}^*NO \underset{-HNO}{\rightarrow} CH_2 = N\,CH_3 \xrightarrow{\text{Hydrolysis}} CH_3NH_3{}^+ + HCOH \qquad (9)$$

$$(CH_3)_2NH^+ + {}^*NO \rightarrow CH_3NHC = NOH \xrightarrow{+NO_2{}^-} CH_3NCOH + N_2O \qquad (10)$$
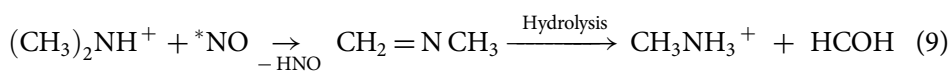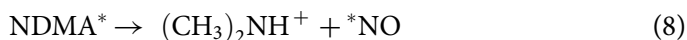
Heterolytic cleavage of N–NO bonds entails reaction of $NDMA^*$ with NO_2^- or water molecule to form DMA and nitrite (Eq. 11) (Lee et al., 2005).

$$NDMA^* \xrightarrow[H^+/H_2O \text{ or } NO_2^-]{} (CH_3)_2NH_2^+ + HNO_2 \qquad (11)$$
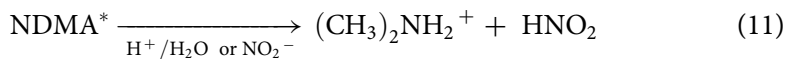
Photooxidation involves a one-electron transfer from $NDMA^*$, which reacts with O_2 to form superoxide radical ($O_2^{\bullet-}$), $^\bullet NO$ and $CH_2 = N^+HCH_3$ (Eq. 12). The $CH_2 = N^+HCH_3$ further undergoes hydrolysis and decay to form CH_3NH_3 (MA) and HCOH (Eq. 12) (Lee et al., 2005). Lastly, $O_2^{\bullet-}$ and $^\bullet N O$ interact to form peroxynitrite ($ONOO^-$), which further converts into nitrate ion (NO_3^-) (Eq. 13).

$$NDMA^* \underset{O_2^-}{\to} CH_2 = N^+HCH_3 + {}^*NO + O_2^{*-} \qquad (12)$$

$${}^*NO + O_2^{*-} \rightarrow ONOO^- \rightarrow NO_3^- \qquad (13)$$
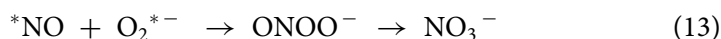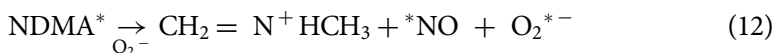
The presence of some degradation products, MA and DMA in water can lead to regeneration of NDMA. Heterolytic cleavage of N–NO bonds is a dominant pathway, at pH range of 3 to 4, with NO_2^- and DMA as the main degradation products. Formation of DMA declines with increase in pH, favoring formation of MA, which is better since DMA is the most important precursor of NDMA. The three pathways occur simultaneously at pH range of 3 to 4 resulting in the formation of both MA and DMA at the same level. UV degradation of NDMA at a pH above 8 exhibits very low quantum yield (Lee et al., 2005; Lee et al., 2005) because of the light scavenging effects of dissolved organic matter (DOM) carbonate ions (CO_3^{2-}), and bicarbonate ions (HCO_3^-) (Xu et al., 2009; Zhou et al., 2012).

Meanwhile, NDMA regeneration can be checked effectively by inhibiting DMA and NO_2 formation UV treatment technique is combined with ozonation, being one of the most proficient approaches for the destruction of NDMA (Xu et al., 2009; Xu et al., 2009). This approach takes advantage of a synergistic effect of UV and ozone (UV/O_3) to effectively degraded N-nitrosamine in chloraminated drinking water. The rate of HO· generation of was accelerated by the photolysis of O_3 (Chen et al., 2016a) and the DMA yield decreases with increase in O_3 dosage (Xu et al., 2009). (Xu et al., 2009) investigated the ability of UV/O_3 to prevent NDMA regeneration after degradation by comparing the products of degradation and the NDMA regeneration possibility between UV irradiation alone and UV/O_3. They reported that NO_2^- and DMA yields during the UV/O_3 process were less than for only UV photolysis. The NO_2^- and DMA yields were 3.22 mg L^{-1} and 2.25 mg L^{-1} from UV photolysis, while they were 0.45 mg L^{-1} and 0.92 mg L^{-1} from the UV/O_3 process. Moreover, NDMA regeneration was also lower for the UV/O3 (7.37 μg L^{-1}) process than for UV photolysis (51.8 μg L^{-1}) under similar operating condition. They suggested that during the UV/O_3 process, DMA and NO_2^- were oxidized by both O_3 and HO· and the interaction between HO· and NDMA favors formation of MA rather than DMA, thereby minimizing NDMA

regeneration potential. Despite the effectiveness of this technique, preventing NDMA formation right from the outset is preferable because the treatment processes consume exorbitant energy and are expensive.

Other factors affecting UV photolysis include dissolved oxygen and Natural organic matter (Gonzalez et al.). (Xu et al., 2009) established that the presence of dissolved O_2 and humic substance (a component of NOM) favor photodegradation of NDMA. The NDMA* induced by $\pi \rightarrow \pi^*$ transition engenders its interaction with dissolved O_2 (Lee et al., 2005), leading to breakage of N–N bond rather than $N = O$ bond under O_2 saturated condition (Lee et al., 2005). The humic substance is photoactive in nature, making it induce degradation of NOMs with UV light (Gerecke et al., 2001; Lam et al., 2003).

Incorporating H_2O_2 reduces the energy consumption of UV photolysis to some extent. UV/ H_2O_2 achieved this by removing the UV absorbing constituents such as nitrates and NOM, thereby minimizing the competition for UV light (Martijn et al., 2010). (Martijn et al., 2010) revealed that nitrate absorbs UV radiation at a similar wavelength to H_2O_2 but a higher molar adsorption, which introduces competition for photons particularly when broad spectrum UV light is used. NOM, which is measured as DOC strongly absorbs UV radiation is the most significant HO· scavenger. H_2O_2 also act as HO· scavenger other than NDMA degrading agent. However, UV photolysis dominates the degradation mechanism of NDMA because H_2O_2 concentration has a little impact on the degradation of NDMA (Martijn et al., 2010).

Recent development in AOP is the utilization of heterogeneous photocatalysts (anodizing TiO_2) based UV irradiation (UV/TiO_2), which is without continuous addition of chemical and yet proved to be a superior technique to UV photolysis alone (Amy Kampa, 2015). The UV/TiO_2 process produces singlet oxygen molecules and HO· for the destruction of NDMA into MA and DMA (Lee et al., 2005). (Kim et al., 2012) reported that UV/TiO_2 technique is so potent that it can remove the entire NDMA from water at a pH range of 4 to 6. An increase in NDMA concentration decreases the yield of MA and increases the yield of DMA. Raising the initial pH of the solution from 4 to 9 leads to a decrease in the NDMA removal efficiency. Scheme 3 presents the
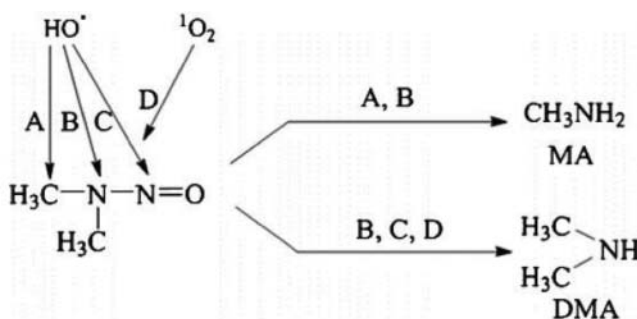
Scheme 3. Pathways of NDMA destruction by UV/TiO_2 AOP (C. Lee, W. Choi, and J. Yoon, 2005).

pathway for degradation of NDMA. Modification of TiO_2 to enhance the surface morphology can enhance destruction of NDMA and also change the degradation by-products composition (Fujioka et al., 2017). TiO_2 modification by silica-loading and Nafion-coating favored the yield of DMA rather than MA, while modification by surface-fluorination favored the yield of MA rather than DMA (Lee et al., 2005).

5.2. Bioremediation technology

A number of studies have revealed that organic contaminants can be biodegraded under anaerobic and aerobic environments in various locations such as lake water, groundwater, and surface and vadose soils (Bradley et al., 2005; Chung et al., 2008; Yang et al., 2005). However, the natural enzymes responsible for NDMA metabolism are mostly unknown. Previous work on biodegradation shows that the technique needs a lot of improvement. The study of Tate and Alexander (1975) and Mallik and Tesfai (1981) reported slow NDMA degradation rate and long lag times in aerobic systems. Meanwhile, the more recent study of Gunnison et al. (2000) on anaerobic and aerobic degradation revealed the capability of native microorganisms cultured from soils for biodegradation of NDMA.

Moreover, Sharp et al. (2005) studied the capability of bacteria strains that express monooxygenase enzymes to degrade NDMA. Some of the enzymes investigated include the propane monooxygenase (PMO) enzyme of Mycobacterium vaccae JOB-5, Methylosinus trichosporium OB3b expressing the soluble methane monooxygenase (sMMO), and the toluene 4-monooxygenases obtained from Pseudomonas mendocina KR1 and Ralstonia pickettii PKO1, which are able to degrade NDMA. However, exposure to acetylene gas (suicide substrate) inhibits NDMA degradation for a specific monooxygenases. Conversely, the particulate form of MMO expressed by M. trichosporium OB3b, the toluene 2-monooxygenase expressed by Burkholderia cepacia G4, and the toluene side-chain monooxygenase expressed by Pseudomonas putida mt-2 have no capacity to degrade NDMA. Sharp et al. (2005) further stated that the aromatic dioxygenases expressed by bacteria have no capacity to degrade NDMA, while *Rhodococcus* sp. RR1 is capable of degrading NDMA by an unknown enzyme that is constitutively expressed, unlike the monooxygenases earlier mentioned, was not subdued by contact with a suicide substrate. Table 4 presents the bacterial strains verified for NDMA degradation ability and Table 5 shows the effects of exposure of NDMA to suicide substrate.

The study of Fournier et al. (2006) on biodegradation pathway of NDMA in a pure culture under the natural environment (using toluene-4-monooxygenase (T4MO) expressed by *Pseudomonas mendocina* KR1). Their study reported initial oxidation of NDMA to a novel metabolite [N-nitrodimethylamine (NTDMA)] by the strain KR1 as catalyzed by T4MO. The O_2 expended during this biotransformation was obtained from the atmosphere in the form of $^{18}O_2$ and $H_2^{18}O$. The

Table 4. Bacterial strains tested for degradation of NDMA (Sharp et al., 2005).

Bacterial strain	Induced enzyme[a]	Growth substrate[b]	Detectable degradation[c]	Rate[d] [ng/mg/min]
Methylosinus trichosporium OB3b	Soluble methane monooxygenase	Methane	Yes	3
Methylosinus trichosporium OB3b	Particulate methane monooxygenase	Methane	No	—
Mycobacterium vaccae JOB-5	Propane monooxygenase	Propane	Yes	100
Pseudomonas mendocina KR1	Tol 4-monooxygenase	Toluene	Yes	5
Ralstonia pickettii PKO1	Tol 4-monooxygenase	Toluene	Partial	1
Burkholderia cepacia G4	Tol 4-monooxygenase	Toluene	No	—
Pseudomonas putida mt-2	Tol side chain monooxygenase	Toluene	No	—
Pseudomonas sp. W31	Tol 2,3 dioxygenase	Toluene	No	—
Pseudomonas putida F1	Tol 2,3 dioxygenase	Toluene	No	—
Pseudomonas flourescens CFS215	Tol 2,3 dioxygenase	Toluene	No	—
Pseudomonas sp. JS150	Tol 2,3 dioxygenase	Toluene	No	—
Rhodococcus sp. RR1	Unknown	Soy broth	Yes	13
Escherichia coli pCR 2.1-TOPO	No oxygenase	Soy broth	No	—

[a]The list depicts the primary enzyme expected to be induced under the growth conditions. OB3b grown in the absence of copper induces sMMO while copper addition promotes pMMO. Secondary enzymes as identified by gene presence have been observed in the case of JS150 (tol 2 and 4-monooxygenase).
[b]Strain RR1 degraded NDMA whether grown on soy broth or toluene. Strains PKO1 and JS150 were amended with casamino acids in addition to toluene to facilitate robust growth.
[c]Partial degradation denotes f40% NDMA disappearance over the course of 1 day. Undetectable degradation was identified as having no significant difference when comparing the degradation curve to incubated controls.
[d]Rates are reported as the average of at least 3 data points from the maximum slope of NDMA degradation curves and are expressed as a function of protein density. Controls demonstrated that headspace partitioning and sorption were not significant factors to consider when calculating rates of disappearance over the duration of these experiments.

produced NTDMA was further metabolized to form N-nitromethylamine (88% to 94% recovery) and a trace of formaldehyde (HCHO), as well as a small amount of CH_3OH through a second, minor pathway facilitated by an initial α-hydroxylation of NDMA. The bio-transformation process is suggested to be cometabolic oxidation since the strain neither mineralizes substantial amount of the compound to CO_2 nor grow on NDMA. Fournier et al. (2006) reported over 75% NDMA biodegradation efficiency by using propanotroph Rhodococcus ruber ENV425. The biotransformation occurred after growth on propane, and the concentrations metabolites generated pose no important risk.

Table 5. Effects of acetylene gas exposure on NDMA degradation (Sharp et al., 2005).

Bacterial strain (enzyme)[a]	Inhibition of NDMA degradation
Methylosinus trichosporium OB3b (sMMO)	Yes
Methylosinus trichosporium OB3b (pMMO)	—
Mycobacterium vaccae JOB-5	Yes
Pseudomonas mendocina KR1	Yes
Ralstonia pickettii PKO1	Yes
Burkholderia cepacia G4	—
Pseudomonas putida mt-2	—
Pseudomonas sp. W31	—
Pseudomonas putida F1	—
Pseudomonas flourescens CFS215	—
Pseudomonas sp. JS150	—
Rhodococcus sp. RR1	No

[a]The enzyme form expressed by OB3b (sMMO or pMMO) was controlled by growth conditions (F copper).

Recently, Hatzinger et al. (2011) constructed a lab-scale membrane bioreactor (R. Lee and Ambrose) (Figure 9) for evaluation of *ex situ* NDMA biotransformation capability using propanotroph Rhodococcus rubber ENV425 on a long-term basis. The primary growth substrate is propane, while the electron acceptor is O_2. They achieved more than 99.95% removal efficiency after 70 days. Similar to Fournier et al. (2006) the oxidation process is cometabolic. However, the aerobic treatment of NDMA in MBR is not viable in the presence of high concentration of trichloroethene (TCE).

Weidhaas et al. (2012) comparatively studied the effect of different growth substrates on the kinetics of biotransformation of NDMA and N-nitrodimethylamine (DMNA), a structural analog to NDMA in a contaminated groundwater. The investigated substrates include methane, butane, benzene, propane, and toluene. They reported that the cometabolic oxidation rates of NDMA is in the order toluene > methane > butane > benzene > propane, while of DMNA is methane > propane > butane > benzene > toluene. Webster et al. (2013) examined the applicability and viability of lab-scale fluidized bed reactor (FBR) for cometabolization of NDMA using Rhodococcus ruber ENV425. They reported that the technology is effective for treatment of 10–20 μg/L of NDMA to effluent concentrations below 100 ng/L at 20 min hydraulic resident time (HRT), while at 30 min HRT and optimized propane, the effluent concentration dropped to below 10 NH/L. They also stated that the presence of TCE at 6 mg/L as a co-contaminant has no significant effect on NDMA treatment. A more feasible NDMA biotransformation pathway is bio-reduction by hydrogenation, which comprises three steps that result in the
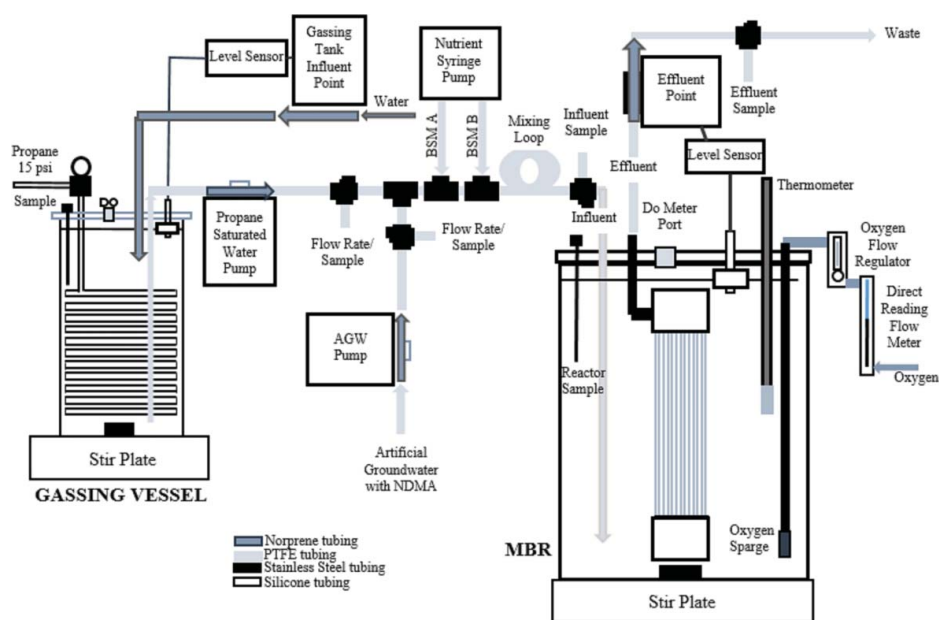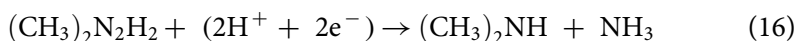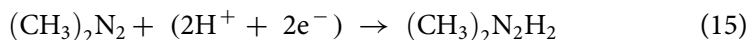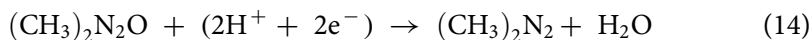

Figure 9. Components of the propane-fed membrane bioreactor (MBR) adopted from (Hatzinger et al., 2011).

formation of ammonia and DMA. Each step involves a two-electron $(2H^+ + 2e^-)$ reduction:

$$(CH_3)_2N_2O + (2H^+ + 2e^-) \rightarrow (CH_3)_2N_2 + H_2O \tag{14}$$

$$(CH_3)_2N_2 + (2H^+ + 2e^-) \rightarrow (CH_3)_2N_2H_2 \tag{15}$$

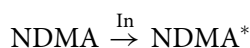$$(CH_3)_2N_2H_2 + (2H^+ + 2e^-) \rightarrow (CH_3)_2NH + NH_3 \tag{16}$$

The latest technology for this NDMA bio-reduction is H_2-based membrane biofilm reactor (MBfR) (Nerenberg and Rittmann, 2004; Rittmann et al., 2004). (Chung et al., 2008) investigated NDMA bio-reduction in an H_2-based MBfR, which is active in the reduction of nitrate and sulfate. The studied the effect of H_2 pressure and the relative concentrations of sulfate, nitrate, and NDMA, which possibly are rival electron acceptors. They reported not less than 96% NDMA reduction efficiency with the availability of H_2 (i.e., H_2 pressure being the primary and nitrate reduction, the secondary) being the most vital factor influencing the kinetics of NDMA-reduction.

N-nitrosamines can also be bio-reduced by exploring bacterial community structure in BAC filters. Recently, several authors reported bacterial community structure involved in the reduction of organic compounds in portable water or in groundwater using bio-filtration processes (Das et al., 2012; Livermore et al., 2013; Wolff et al., 2015) constructed two biofilters by using BAC and N-nitrosamine-containing drinking water from treatment plants. They observed that the relative abundance at both the class and phylum levels were altered by N-nitrosamines as they detected the genus Rhodococcus, containing many nitrosamine-reducing strains after cultivating BAC2 filter. The detected bacterial culture Rhodococcus cercidiphylli A41 AS-1 was isolated and was reported to exhibit bio-reduction ability for NDMA, NDEA, NDPA, NPYR, and NDBA with removal efficiency ranging from 38.1% to 85.4%. A better biodegradation ability N-nitrosamine as the carbon source rather than as the nitrogen source (Scheme 3).

5.3. Catalytic reduction

Catalytic reduction with H_2 gas has remarkable potential for speedy degradation of NDMA in water in a similar manner the technique is used for reduction of halogenated hydrocarbons. However, halogenated hydrocarbon reduction is considerably faster and more viable economically than the existing NDMA reduction techniques. This technology has been extensively studied using catalysts such as Fe and Ni-enhanced Fe (Gui et al., 2000; Odziemkowski et al., 2000) and Zn (Han et al., 2011), palladium-Indium (Pd-In) (Davie et al., 2008), Cu enhanced Pd (Davie et al., 2006) to yield a combination of NH_4^+, NH_3, NO, and DMA depending on the catalyst used at pseudo-first-order reaction rates. The previous challenges with this technique are catalyst

deactivation and long half-lives, which necessitates large reactor bed in above-ground applications to ensure adequate contact time for reduction of NDMA (Davie et al., 2006). However, the study of Davie et al. (2006) proffers solution to this by using nickel, palladium, and copper enhanced palladium catalysts. They reported that 10 mg/L each of these catalysts exhibits short half-lives (about hours). Palladium can effectively treat wastewater contaminated with TCE (Mcnab et al., 2000). To further enhance the efficacy of this reductive destruction technology (Davie et al., 2008), promoted Pd-based catalyst (5% Pd by weight on γ-Al$_2$O$_3$) with In. This catalyst synergistically combines the capacity of Pd to activate H2 with the NDMA activation capability of In. Their report shows that there is a remarkable increase in the NDMA destruction pseudo-first-order rate constant with increase in In loading from 0.057 hr^{-1} for 0% In to a maximum of 0.25 hr^{-1} for 1% In. Further increase in In loading decreases the destruction rate due to pore blockage by In, thereby restricting access to Pd sites. The proposed mechanism for NDMA destruction is as follows:

$$H_2 \rightarrow 2H^* \tag{17}$$

$$NDMA \xrightarrow{Pd} NDMA^* \tag{18}$$

$$NDMA \xrightarrow{In} NDMA^*$$

$$NDMA + 4H^* \xrightarrow{Pd} DMA + NH_4^+ + OH^- \tag{19}$$

$$NDMA + 4H^* \xrightarrow{In} DMA + NH_4^+ + OH^- \tag{20}$$

The Pd-In catalysts could be regenerated by aggressive oxidation with hypochlorite. This bimetallic catalyst offers a significant enhancement over earlier investigated Pd-Cu Catalysts by Chaplin et al. (2006) and Davie et al. (2006), which was severely destroyed at the first incidence of sulfide poisoning. The study of Frierdich et al. (2009) also proffers solution to the challenges by using air-tolerant and non-pyrophoric nickel–boron (Kawamura et al., 1997) rather than Raney Ni, which is pyrophoric and non-air-tolerant, making it prone to deactivation (Frierdich et al., 2007). Their kinetic study reveals that NiB has the capacity to reduce NDMA to DMA, and ammonia rapidly *via* hydrogenation. The reductive destruction of NDMA is neither affected by prolonged pre-exposure of the dry catalyst to air nor the pH solution. However, further study is required towards enhancing the performance of NiB catalysts for treatment of NDMA in complex matrices (such as disinfected wastewater, effluent contaminated groundwater) in more realistic flow-through pilot reactors like packed column systems).

A 100% NDMA reduction was reported by Chen et al. (2016b) when they promoted Pd supported γ-Al$_2$O$_3$ using Ni for 1 hr. The mechanism for reduction of NDMA over 3% (Pd0.8Ni0.2) catalyst follows activation of H$_2$ by Pd, and H atom spillover from Pd to Ni/NiO, thereby reducing NDMA via N-N cleavage. No

significant effect was recorded for pH variation above neutral, and no internal and external diffusion limitation was experienced. The catalyst exhibits excellent stability for no significant variation in performance was recorded after recycling for three times. This shows that 3%(PdxNi1−x) is a promising catalyst for the reductive destruction of NDMA.

A more economical NDMA reduction technique was studied by Han et al. (2017). The technology operates at neutral pH and does not require a supply of H_2 gas as it generates H_2 from the water to be treated. They did this by rational design of bimetallic catalyst by using Cu(II) to enhance the performance of zero-valent Fe and Zn. The concentration of Cu(II) was varied from 0.1 to 2.0 mM with Fe and Zn separately. NDMA Removal efficiency increases with increase in Cu(II) concentration. At the same Cu(II) concentration, the Zn/Cu(II) system performed remarkably better than the Fe/Cu(II) system. For instance, at 2.0 mM Cu(II), almost all the NDMA was reduced at about 1 hr using Zn/Cu(II), while a similar amount of NDMA was reduced for about 18 hr using Fe/Cu(II).

5.4. Dope technology

Dope technology is an electrochemical mediated treatment technique using boron-doped diamond (BDD) film electrodes, which is capable of overcoming some limitations associated with other treatment techniques. Several authors revealed that BDD electrodes are capable of oxidizing compounds by HO· formed from water oxidation (Marselli et al., 2003) and by combining direct electron transfer (Carter and Farrell, 2008; Zhi et al., 2003); the later mitigates problems regarding scavenging of HO·. BDD electrodes exhibit a high over the potential for oxidation of water, and the potential at the surface of the electrode can oxidize better than that of other AOPs generated HO·. This feature enables BDD electrodes for oxidation of nitrogenous DBPs like NDMA via direct electron transfer reactions (Chaplin et al., 2009). Furthermore, BDD electrodes resist fouling by components in water and exhibit a longer service-life when compared with other electrode materials (Chen et al., 2003). However, information regarding the use of this technology for oxidation of N-nitrosamine is limited. The first report on NDMA oxidation was provided by Chaplin et al. (2009). They studied the capability of BDD-film electrodes supported on p-silicon to oxidize NDMA in batch experiments. The oxidation rates of NDMA were measured based on current density, electrode potential, and flow-through reactors and temperature using rotating disk. This technology shows a remarkable performance, however since it involves chloride, the technology is limited by perchlorate formation (Donaghue and Chaplin, 2013). In another study of Chaplin et al. (2010), they reported that the presence of DOC, $Cl^−$, or HCO^{3-} at RO concentrates concentrations does not affect the rate of oxidation of NDMA. The technique only experiences a change in NDMA oxidation mechanism to direct electron transfer oxidation from hydroxyl radical facilitated in the presence of hydroxyl radical scavenger at 100 mM concentrations of Cl and $HCO^{3−}$.

Electrochemical mediation has also been reported for reduction of various organic contaminants including N-nitrosamines. However, they operate at high potentials [up to 4 V vs the standard hydrogen electrode (SHE)] (Chaplin et al., 2010). Meanwhile, the recent work of Su et al. (2017) proffers solution to this challenge by rational design of hemin-functionalized carbon nanotubes based redox electrodes, which exhibit high electrocatalytic performance for reduction of N-nitrosamine at low potentials (−0.5 V vs Ag/AgCl or −0.27 vs SHE) and with above 700 turnover numbers. The N-nitrosamine degradation mechanism involves a proton-facilitated transformation of the nitroso group to secondary amines and hydrazines.

6. Conclusion

The goal of eliminating and preventing the formation of N-nitrosamine is to ensure carcinogenic contaminants-free water. However, it is evident that formation and destruction mechanisms of N-nitrosamine are complex. Consequently, this study elucidated and developed an understanding of the reactions leading to the N-nitrosamine formation and efficient treatment routes for ensuring portable water. Prevention of NDMA formation by degrading or destroying the precursors is more important and cheaper than N-nitrosamine removal. The physical adsorption of N-nitrosamine precursors is carried out using porous adsorbents with hydrophobic pore walls. This is despite the effectiveness of pre-ozonation towards NDMA-FP reduction and the benefits of NDMA removal. Biological activated carbon process combines both physical adsorption and bio-treatment. Coupling pre-ozonation with BAC filtration could be effective towards upgrading wastewater treatment plants to prevent the occurrence of N-nitrosamine. However, the mechanism for removal of N-nitrosamine precursors *via* BAC filtration needs further clarification.

Combined adsorption and microwave irradiation is employed to improve NDMA removal by degrading the adsorbed NDMA using microwave irradiation. However, the energy requirement makes the process uneconomical. Similarly, conventional UV photolysis poses an economic challenge. This is aside from the formation of radical scavengers associated with the addition of oxidants such as H_2O_2, O_3, and O_3/H_2O_2 in water making the process ineffective. However, photocatalytic reduction technique, which involves incorporation of TiO_2 with the traditional UV photolysis is a better choice but further research is needed on surface morphology modification and TiO_2 doping techniques to improve the TiO_2 lifetime, photocatalytic reactor design, of, and cleaning techniques towards scaling up of photo-reduction applications. Bioremediation of NDMA is one of the alternative technique to the above-mentioned techniques due to its cost effectiveness. Despite advances over the years, this technique needs further evaluation as a potential substitute for traditional UV photolysis for NDMA removal.

Interestingly, reductive destruction *via* heterogeneous catalysis appears a more efficient alternative technology towards mitigating the health risks posed by the

occurrence of NDMA. Meanwhile, additional investigations into catalyst poisoning and regeneration strategies are necessary to determine the practicability of this technology to treat NDMA infected portable water streams. Conclusively, regardless of the effectiveness and seeming economic viability of some of this technology, preventing the occurrence of NDMA right from the outset is more potent because the treatments consume more energy.

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