

Degradation of *N*-nitrosodimethylamine (NDMA) and its precursor dimethylamine (DMA) in mineral micropores induced by microwave irradiation



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ABSTRACT

Removal of *N*-nitrosodimethylamine (NDMA) in drinking water treatment poses a significant technical challenge due to its small molecular size, high polarity and water solubility, and poor biodegradability. Degradation of NDMA and its precursor, dimethylamine (DMA), was investigated by adsorbing them from aqueous solution using porous mineral sorbents, followed by destruction under microwave irradiation. Among the mineral sorbents evaluated, dealuminated ZSM-5 exhibited the highest sorption capacities for NDMA and DMA, which decreased with the density of surface cations present in the micropores. In contrast, the degradation rate of the sorbed NDMA increased with the density of surface cations under microwave irradiation. Evolutions of the degradation products and C/N ratio indicate that the sorbed NDMA and DMA could be eventually mineralized under continuous microwave irradiation. The degradation rate was strongly correlated with the bulk temperature of ZSM-5 and microwave power, which is consistent with the mechanism of pyrolysis caused by formation of micro-scale “hot spots” within the mineral micropores under microwave irradiation. Compared to existing treatment options for NDMA removal, microporous mineral sorption coupled with microwave-induced degradation has the unique advantages of being able to simultaneously remove NDMA and DMA and cause their full mineralization, and thus could serve as a promising alternative method.

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1. Introduction

N-nitrosodimethylamine (NDMA), which is typically formed during chlorination/chloramination and ozonation processes in drinking water and wastewater treatments, is a disinfection byproduct of significant concern (Mitch and Sedlak, 2002; Andrzejewski et al., 2008; Zhang et al., 2014; Lv et al., 2015). NDMA typically occurs at less than 10 ng/L in drinking water, while its concentrations in chlorinated secondary wastewater effluent could exceed 100 ng/L (Najm and Trussell, 2001). NDMA is commonly formed by nitrosation between dimethylamine (DMA) and nitrite or various nitrogen oxides (Andrzejewski et al., 2008). It can also be formed through the oxidation of unsymmetrical dimethylhydrazine, which is a widely used component of liquid

rocket fuel (Mitch et al., 2003a). NDMA was detected at concentrations as high as 400 µg/L in the groundwater on the site of a rocket engine testing facility, and 20 µg/L in the downgradient drinking water wells in Sacramento County, California (Mitch et al., 2003b; USEPA, 2014).

The occurrence of NDMA in drinking water poses a significant public health risk because it is known to have extremely potent carcinogenic, mutagenic, and teratogenic activities, and its hepatotoxicity and genotoxicity on various animal species are well documented (Stefan and Bolton, 2002). The U.S. Environmental Protection Agency (USEPA) has classified NDMA as a probable human carcinogen, and determined a screening level of 0.42 ng/L in tap water, based on a lifetime excess cancer risk of 10^{-6} in 2013 (USEPA, 2014). The UK Drinking Water Inspectorate (DWI) lists NDMA as a genotoxic carcinogen (DWI, 2008). To protect the public health, many countries and regions have set drinking water standards or guideline values for NDMA. The maximum contaminant level of NDMA in drinking water set by the state of California in the

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U.S. is 3 ng/L (CDPH, 2013), while the guidance value, which riggers measures to reduce NDMA concentration in water supply as soon as is practicable in the UK, is 10 ng/L (DWI, 2008). The World Health Organization (WHO) set a drinking water guideline value of 100 ng/L for NDMA (WHO, 2011), which is also the target value for future study in drinking water regulations in Japan (MHLW, 2015). The standards for NDMA in drinking water are 10 and 40 ng/L in Germany and Canada, respectively (Schmidt and Brauch, 2008; CDW, 2014).

Despite of the significant potential public health risk of NDMA, there are very few treatment options for its removal from drinking water. NDMA cannot be effectively removed from water by volatilization or air stripping, due to its high water solubility (290 g/L at 20 °C) and low Henry's Law constant (2.63×10^{-4} atm m³/mol at 20 °C) (Mitch et al., 2003b). Sorption is a potential method for removing NDMA from aqueous solution, but the efficiency is rather low due to its relatively low hydrophobicity ($\log K_{ow} = -0.57$) (Dai et al., 2009). Reverse osmosis (RO) can only achieve up to 70% of NDMA removal because of its small, polar, and uncharged molecule (Steinle-Darling et al., 2007; Fujioka et al., 2012). Meanwhile, the significant capital and operating costs of RO restrict its universal application. Limited by the presence of radical scavengers in water, advanced oxidation processes (e.g., O₃, H₂O₂, and O₃/H₂O₂) are relatively ineffective at NDMA destruction (Lee et al., 2007; Lv et al., 2013). Metal-catalyzed reduction, which has high efficiency and fast reaction kinetics, has been developed as a promising treatment method for NDMA removal (Davie et al., 2006). However, the high costs of noble metals (e.g., Pd and In) and catalyst poisoning are obstacles for the implementation of catalytic reduction. Electrochemical oxidation using boron-doped diamond film electrodes has also been shown to oxidize NDMA, although the formation of perchlorate in the presence of chloride can be a major problem in its application (Chaplin et al., 2009; Donaghue and Chaplin, 2013). Direct UV photolysis has been the most commonly used technology for destruction of NDMA in drinking water treatment (Stefan and Bolton, 2002; Lee et al., 2005), but NDMA can be regenerated from the degradation products in water (Sharpless and Linden, 2003). The problem of NDMA regeneration can be effectively inhibited through controlling the yields of DMA and NO₂ when UV treatment is coupled with ozonation, and their combination is deemed as the most efficient method for NDMA removal (Xu et al., 2009a,b). Nonetheless, UV treatment is not cost-effective for large-scale implementation because the intensity of UV light required is 10 times higher than that needed for virus disinfection (Mitch et al., 2003b). Overall, the existing technologies on NDMA removal from water are either inefficient or costly. Furthermore, DMA, which is a precursor of NDMA, is formed from decomposition of NDMA in some of these treatments, and re-generation of NDMA can occur in the presence of chloramine or nitrite (Mitch and Sedlak, 2002).

With the unique shape selectivity, zeolites have been studied for adsorbing nitrosamines from gas stream and solution (Zhou and Zhu, 2005; Pinisakul et al., 2008; Kamaloo et al., 2013; Li et al., 2013; Sun et al., 2014). Strong binding of NDMA molecules occurs in the zeolitic channels because of the interaction between the oxygen or nitrogen atoms of NDMA molecules and the silicon atoms of all-silica MFI framework, sodium atoms of Na-ZSM-5, and hydrogen of H-ZSM-5 (Kamaloo et al., 2013). It is expected that NDMA and its precursor, DMA, can be removed from aqueous solution by adsorption on zeolites with suitable pore sizes and surface chemistry. On the other hand, it can be difficult to desorb the NDMA molecules encapsulated in the micropores and regenerate the sorption capacities of the zeolites.

A limited number of studies on mitigating the risk of nitrosamines in tobacco and tobacco smoke have shown that these compounds could be decomposed by microwave treatment (Xu et al.,

2008; Gao et al., 2009). Up to one-third of the *N*-nitrosodiphenylamine sorbed (from dichloromethane solution) on mesoporous siliceous SBA-15 containing 10% CuO degraded after being irradiated by 1000 W microwave for 45 s (Xu et al., 2008). Irradiation of cigarettes sealed in its packaging by microwave (1000 W) for 90 s reduced the contents of nitrosamines in the tobacco and mainstream smoke by 25–30 and 50–60%, respectively (Gao et al., 2009). Nonetheless, no previous study has investigated the destruction of NDMA or other nitrosamines sorbed in the micropores of microwave-transparent mineral sorbents.

This work was conducted to investigate the sorptive removal of NDMA and DMA from aqueous solution by porous minerals and their degradation when sorbed in mineral micropores under microwave irradiation, with the ultimate goal of developing an alternative method for removing and destructing NDMA and its precursor, DMA, in drinking water treatment. While other organic compounds containing methylamine functional group can also be the precursors of NDMA, DMA is the most prevalent precursor of NDMA, and it is also the most frequently studied model precursor of NDMA (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Mitch et al., 2003a,b). The sorption of NDMA and DMA on a series of porous minerals with different pore sizes, and surface cation types and densities, were studied, followed by degradation of the sorbed NDMA by microwave irradiation. Mineralization of sorbed NDMA and DMA during the course of microwave irradiation was verified with C/N ratios, and the degradation pathway of NDMA was elucidated based on the degradation products identified. The results help build the foundation for the development of a novel treatment method for removal and destruction of NDMA and its precursor DMA from water.

2. Materials and methods

2.1. Materials

Table 1 summarizes the major physicochemical properties of the porous mineral sorbents evaluated in this study. Samples of H-ZSM-5, Cu-ZSM-5, Mg-ZSM-5 were prepared from Na-ZSM-5 (Si/Al = 25) by exchanging with the respective cations for three times, following the method used previously in our group (Hu and Cheng, 2013a). Their dielectric properties were characterized using the coaxial transmission line technique (Table S1). Diatomite was dehydrated at 200 °C for 5 h, while the other minerals were calcined at 380 °C for 12 h prior to use. Details on the chemicals used are summarized in the Supplementary data. Laboratory triple-distilled water was used in the preparation of all aqueous solutions. All stock solutions were prepared fresh biweekly and stored at 4 °C in the dark.

2.2. Experimental procedures

Sorption isotherms of NDMA and DMA on the porous minerals were obtained with batch sorption experiments. Accurately weighted sorbents (~100 mg) were added into 40 mL glass vials containing 30 mL of NDMA or DMA solutions at varying concentrations, and equilibrated in a constant temperature shaker (25 °C) for 24 h. Although 30 min was sufficient for NDMA sorption on Na-ZSM-5 (Si/Al = 25) to reach equilibrium (Fig. S1), a much longer equilibration time was used to ensure full sorption equilibrium on all the porous minerals evaluated and minimize the equilibration time differences among the samples processed within the same batch. After centrifugation, the supernatants were withdrawn from the vials and filtered with 0.22 μm PTFE membrane filters for analysis. The porous minerals were used to remove NDMA from water by adding 2.0 g of solid into 100 mL NDMA solution (initial

Table 1
Summary of the major physical and chemical properties of porous minerals used in this study.

Porous mineral	ZSM-5 (Si/Al = 12.5, 25, 40, and 130)	4A	CBV-780 (Si/Al = 40)	CBV-10A (Si/Al = 6.5)	MCM-41	Diatomite	α -Quartz sand
Particle size (μm)	<2.5 ^a	2–4	1–2	1–2	0.4–1	35 (median)	4–5
Specific surface area (m^2/g)	$\geq 320^a$	856 ^b	780 ^a	425 ^a	847 ^c	1.60 ^c	1.59 ^a
Structure	KFI	LTA	FAU	MOR	Templated mesoporous silica	Amorphous silica	Tectosilicate
Pore size (nm)	0.51–0.56	0.40 (nominal)	0.74–1.2	0.58–0.70	2–5 ^a	400 (median)	–
Surface cation	Na ⁺	Na ⁺	H ⁺	Na ⁺	–	–	–
Hydrophobicity	Hydrophobic	Hydrophilic	Hydrophobic	Hydrophilic	Moderately hydrophobic	Hydrophilic	Hydrophilic
Supplier	Nankai University Catalyst (Tianjin, China)	Jinzhou Chemicals (Shanghai, China)	Zeolyst (Valley Forge, PA)	Zeolyst (Valley Forge, PA)	JCNANO Technology (Nanjing, China)	Kermel Chemicals (Tianjin, China)	Guangzhou Institute of Geochemistry, CAS (Guangzhou, China)

Notes:

^a Value provided by supplier.

^b Calculated from static water adsorption data reported by the supplier.

^c BET surface area measured on an ASAP 2020 apparatus (Micromeritics, U.S.).

concentration of ~ 5 mg/L). After equilibration (24 h), the NDMA-laden minerals were obtained after separating the solution phase by vacuum filtration, followed by freeze-drying (-45 °C for 10 h). The efficiency of NDMA sorptive removal was evaluated by measuring its residual concentration in the solution after filtration (Table S2). Na-ZSM-5 (Si/Al = 25) was equilibrated with NDMA solution at ~ 2 mg/L when investigating the formation of degradation products during microwave irradiation of the NDMA-laden ZSM-5.

Degradation of NDMA or DMA sorbed on the mineral sorbents was conducted using a Discovery SP microwave system (CEM, U.S.), which is equipped with a highly energy-efficient focused single-mode cavity. Accurately weighted NDMA- or DMA-laden sorbents (~ 0.2 g) were added into 10 mL Pyrex glass vessels and sealed by snap-on caps with Teflon liners, followed by microwave (2.450 GHz) irradiation. The vessel could also be cooled by a stream of pressurized air during irradiation, which allows the magnetron to be operated at high power levels while maintaining a constant bulk sample temperature (monitored by an infrared sensor located under the irradiated vessel). After the microwave treatment, the sorbents were quantitatively transferred to the Greenchem extraction vessels and extracted by microwave-assisted extraction (MAE) in a MARS system (CEM, U.S.). NDMA was extracted by 20 mL of methanol/water mixture (1:1, v/v) at 80 °C for 15 min, which had been developed for recovering atrazine from Y zeolites and could achieve satisfactory recovery of NDMA (89.2%) from ZSM-5 zeolites (Hu and Cheng, 2013b). Due to its low boiling point (6.9 °C), DMA was recovered from the mineral sorbents with ultrasound-assisted extraction (UAE), instead of MAE. As DMA is a weak base ($\text{pK}_a = 10.64$) (Hall, 1957), HCl solution ($\text{pH} = 4$) was used as the extraction medium in UAE (200 W, 30 min). The same procedure was also applied for extracting the degradation products (NO_3^- , NH_4^+ , HCOOH , and CH_3COOH) of NDMA. Results of control experiment showed no indication of NDMA degradation during MAE under the conditions used or degradation of DMA during UAE (Table S3). All solution samples obtained were stored at 4 °C in the dark and analyzed within a week.

2.3. Chemical analyses

NDMA was analyzed with ultra-high performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS), while its potential degradation products (HCOOH , CH_3COOH , NO_3^- , NH_4^+ , methylamine, and DMA) were analyzed with ion chromatography (Supplementary data). The limits of quantification for all analytes are listed in Table S4. The C/N ratio of Na-ZSM-5 (Si/Al = 25) laden

with NDMA or DMA after microwave irradiation was also measured on a Vario EL Cube elemental analyzer (Elementar, Germany) to evaluate their mineralization.

3. Results and discussion

3.1. Sorption of NDMA and DMA

Fig. 1a shows the sorption isotherms of NDMA on Na-ZSM-5 zeolites (Si/Al = 12.5, 25, 40, and 130), CBV-780, 4A, MCM-41, and diatomite. The sorption of NDMA on these mineral sorbents with different pore size ranges could all be fitted with the Freundlich isotherm model reasonably well. The highest NDMA sorption capacities were observed on the Na-ZSM-5 analogues, whose sorption capacities increased with the level of dealumination. MCM-41 and CBV-780 exhibited comparable NDMA sorption capacities, which were slightly higher than those of 4A and diatomite. These results clearly indicate that the pore sizes of the porous minerals play a very important role in NDMA sorption. When the diameter of the sorbate molecules is larger than the pore opening, it could only access the external surfaces of the porous minerals due to steric hindrance. Besides the external surface, NDMA molecules can only sorb on 4A by inserting the *N*-nitroso functional groups ($\text{N}-\text{N}=\text{O}$) inside the narrow pore channels (0.4 nm) (Cao et al., 2007), which explains its low sorption on 4A. On the other hand, sorbents with very large pore sizes also have low sorption capacities as their pore wall surfaces are essentially identical to the external surface to the sorbate molecules (Hu et al., 2012). That's why NDMA sorption was also very poor on diatomite, which is a silica-based macroporous bio-mineral with a mean pore size of 400 nm. When the pore dimension is comparable or slightly larger (up to 3–5 times) than the sizes of the sorbate molecules, the dispersion force fields acted by various parts of the surface overlap within the pores, resulting in significant enhancement of the sorption potential energy (Kidder et al., 2011; Hu et al., 2012). As a result, microporous minerals can have high sorption capacities towards organic contaminants, such as trichloroethylene (molecular diameter: 0.53 nm) and atrazine (molecular diameter: 0.54 nm) (Cheng and Reinhard, 2006; Hu et al., 2012). Greater sorption of NDMA (critical molecular dimension of 0.42 nm (Li et al., 2013)) was observed on Na-ZSM-5 than on CBV-780, which could be explained primarily by the stronger effect of geometric confinement (i.e., the enhancement of adsorption potential energy) within the narrower micropores of Na-ZSM-5 (0.51–0.56 nm) compared to those of CBV-780 (0.74–1.2 nm). In contrast, the weak sorption of NDMA on the mesoporous MCM-41 resulted from lack of significant enhancement of the adsorption

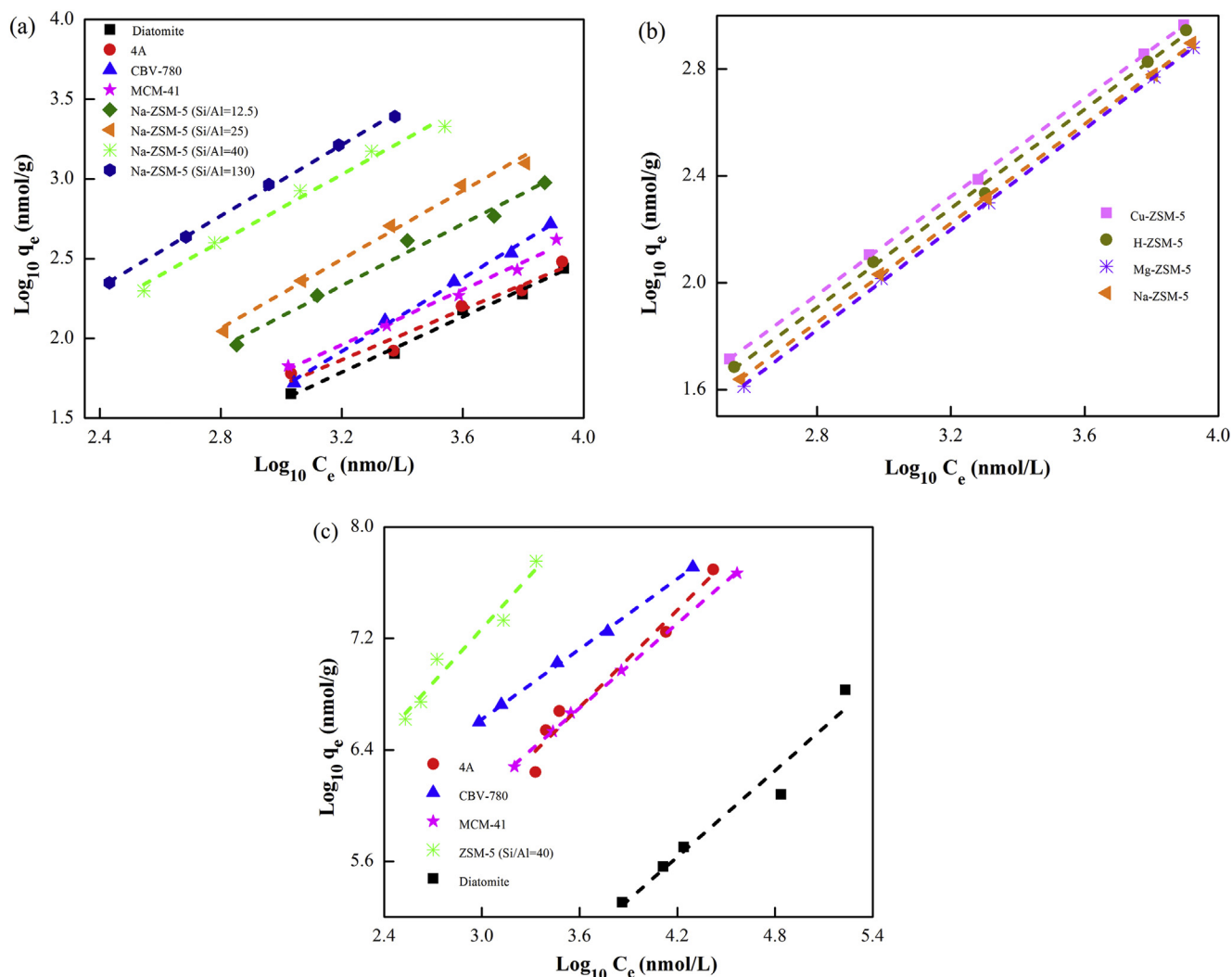


Fig. 1. Sorption of NDMA and DMA on porous mineral sorbents at 25 °C: (a) NDMA sorption on 4A, CBV-780, diatomite, MCM-41, and dealuminated Na-ZSM-5 analogues (Si/Al = 12.5, 25, 40, and 130); (b) NDMA sorption on dealuminated Na-ZSM-5 (Si/Al = 25) with different types of surface cations (Cu^{2+} , H^+ , Na^+ , and Mg^{2+}); and (c) DMA sorption on 4A, CBV-780, MCM-41, Na-ZSM-5 (Si/Al = 40), and diatomite. The data points represent the mean values determined from triplicated experiments while the dashed lines represent Freundlich isotherm fits (see Tables S5–S7 for the fitting parameters).

potential energy in its relatively large mesopores (2–5 nm).

In addition to pore size, surface hydrophobicity is also an important factor that influences NDMA sorption on porous minerals (Li et al., 2013). The Al content is a key factor in determining the hydrophilicity or hydrophobicity of dealuminated zeolites (Zhou and Zhu, 2005; Cheng and Reinhard, 2006). As the Si/Al ratio of zeolite increases (i.e., the Al content decreases), the density of surface cations balancing the negative charge associated with the aluminum-oxygen tetrahedra in the framework decreases, weakening the electrostatic field in the zeolitic cages and channels. Thus, the micropores of ZSM-5 with higher Si/Al ratios are more hydrophobic and have lower affinity for water molecules. Consequently, nitrosamine molecules can be captured more favorably by the more hydrophobic Na-ZSM-5 zeolites (i.e., with higher Si/Al ratios), due to the weaker competition from water molecules (Zhu et al., 2001). These results are also consistent with previous observations on sorption of trichloroethylene and atrazine on dealuminated Y zeolites (Cheng and Reinhard, 2006; Hu and Cheng, 2013a).

Fig. 1b shows the sorption isotherms of NDMA on Na-ZSM-5 with a Si/Al ratio of 25 but different types of surface cations. The results indicate that the surface cations present in the micropores

could play a small, but not insignificant role in NDMA sorption. As a weak base, the N atoms of NDMA molecules can form hydrogen bond with the protons present in the micropores of acidic zeolites (Li et al., 2013). This is why sorption of NDMA from water on H-ZSM-5 was slightly higher than on the basic Na-ZSM-5. NDMA sorption on Mg-ZSM-5 was slightly lower than on Na-ZSM-5 because the divalent Mg^{2+} cations (radius of 0.065 nm) could interact with water molecules much more strongly compared to the monovalent Na^+ cation (radius of 0.099 nm), even though at half of the density of the latter. In contrast, the presence of Cu^{2+} in the micropores of ZSM-5 enhanced the sorption of NDMA appreciably, due to the complexing between the lone pairs of electrons in the N atoms of NDMA molecules and the vacant *d*-orbitals in Cu^{2+} ions.

Similar sorption experiments were also conducted for DMA. Fig. 1c shows that sorption of DMA on 4A, CBV-780, MCM-41, Na-ZSM-5 (Si/Al = 40), and diatomite also exhibited the Freundlich-type isotherms. The overall trends of DMA sorption on these porous mineral sorbents were similar to those of NDMA. DMA sorption on ZSM-5 (Si/Al = 40) was the highest due to its suitable pore sizes and hydrophobic pore wall surface. The DMA sorption capacities of MCM-41 and 4A were comparable, and were much

higher than that of diatomite, but slightly lower than that of CBV-780. For all the mineral sorbents evaluated, the sorption capacities for DMA were higher than those for NDMA, which could be explained by its greater hydrophobicity ($K_{ow} = 10^{-0.38}$ vs. $10^{-0.57}$ of NDMA (Hansch et al., 1995)) and smaller molecular size. Together, these results indicate that organic sorption on porous minerals is determined jointly by the degree of matching between the sizes of the sorbate and the porous mineral, the hydrophobicity of pore wall surface, and the presence of specific interactions between the sorbate and species within the mineral micropores. Among the porous minerals evaluated, dealuminated ZSM-5 zeolites with high Si/Al ratios appear to be more suitable for sorptive removal of both NDMA and DMA from water.

3.2. Degradation of NDMA sorbed on porous minerals induced by microwave irradiation

Fig. 2a shows the degradation of NDMA sorbed on various porous minerals under microwave irradiation at 120 W. Pseudo-first-order kinetics was observed for NDMA degradation in all cases (Fig. S2), although the apparent degradation rates varied largely. Degradation of NDMA proceeded at the slowest rate when

sorbed on MCM-41 compared to the other minerals. Hydrated cations on the mineral surface are effective microwave absorbers, and have been shown to play an important role in microwave-induced degradation of atrazine by forming “hot spots” after absorbing microwave energy (Hu and Cheng, 2013a). MCM-41 is a mesoporous silica and has essentially no cations on its pore wall surface. As a result, the sorbed NDMA degraded only slowly due to the lack of cationic “hot spots” under microwave irradiation. Furthermore, the NDMA molecules sorbed in the relatively large mesopores can escape from the surface easily (i.e., thermal desorption), and are thus not subjected to interfacial superheating during the course of microwave irradiation. The degradation rate of NDMA sorbed on 4A was only slightly faster than on MCM-41, which could be attributed to the fact that NDMA molecules sorbed on its external surface could also desorb easily during microwave irradiation. Overall, the degradation rates of NDMA were much faster when confined in the micropores of CBV-780, CBV-10A, and Na-ZSM-5 compared to sorbed in the mesopores of MCM-41 or on the external surface of 4A. NDMA molecules sorbed in mineral micropores, along with the co-existing metal cations and water molecules, were selectively superheated during the course of microwave irradiation, and the resulting micro-scale “hot spots”

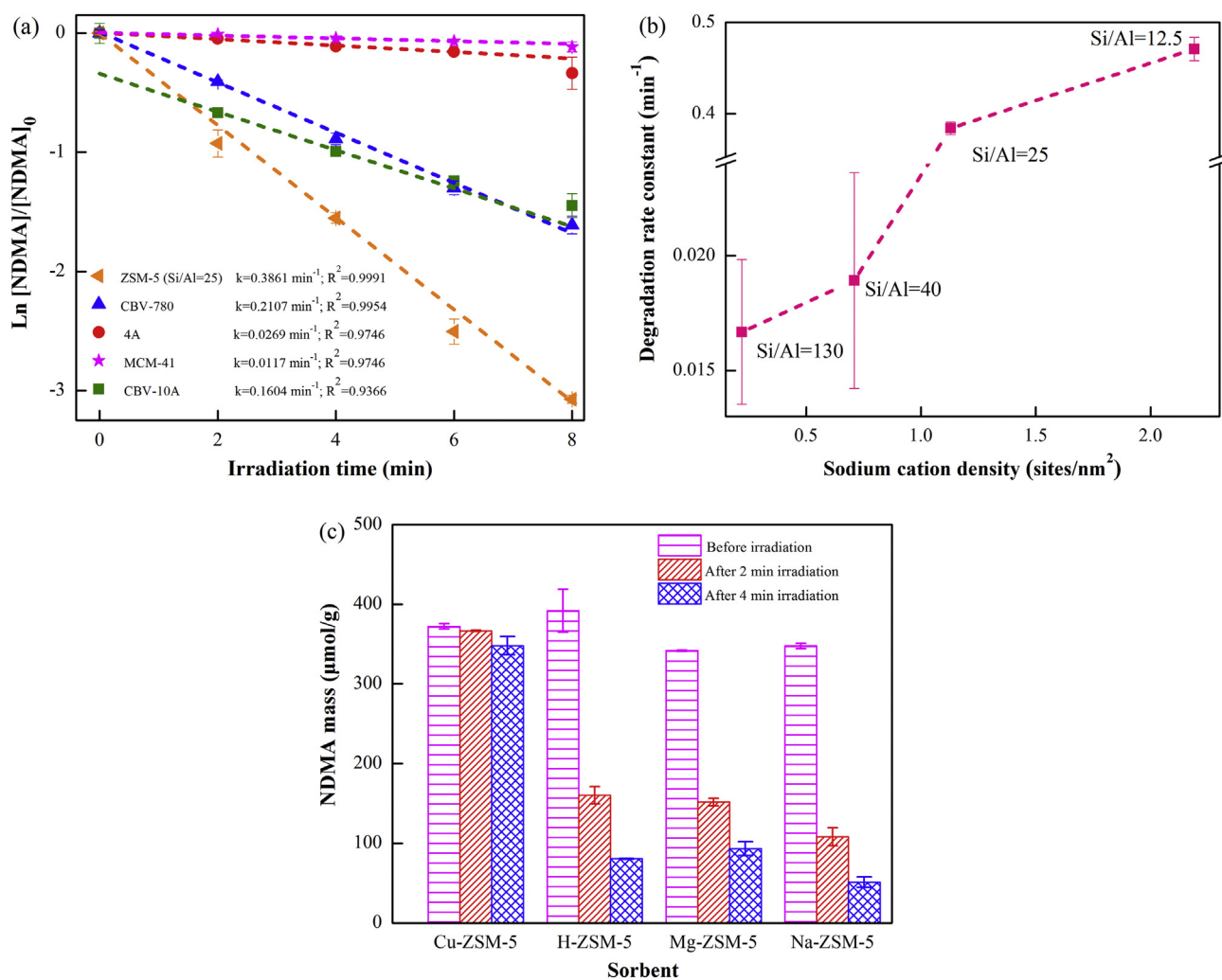


Fig. 2. Degradation of NDMA sorbed on porous minerals under microwave irradiation at 120 W: (a) Degradation of NDMA sorbed on Na-ZSM-5 (Si/Al = 25), CBV-780, MCM-41, 4A, and CBV-10A; (b) Impact of cation density on degradation of NDMA sorbed on dealuminated Na-ZSM-5 analogues (Si/Al = 12.5, 25, 40, and 130); and (c) Impact of surface cation type on microwave-induced degradation of NDMA sorbed on dealuminated ZSM-5 (Si/Al = 25) with different types of surface cations (Cu^{2+} , H^+ , Na^+ , and Mg^{2+}). The error bars represent standard deviations based on triplicated experiments.

formed induced degradation (presumably pyrolysis) of the sorbed NDMA molecules. The fastest degradation of NDMA occurred on Na-ZSM-5, which could be explained by the stronger confinement of NDMA molecules in its narrower micropores compared to the larger zeolitic channels and cages of CBV-780 and CBV-10A. These results clearly indicate that pore confinement is vital for the microwave-induced degradation of NDMA sorbed on porous minerals.

Fig. 2b shows that the pseudo-first-order degradation rate constant of NDMA sorbed on the dealuminated analogues of Na-ZSM-5 under microwave irradiation increased with the density of surface cations. NDMA molecules sorbed in the micropores degraded faster with more surface cations present in their surroundings, probably due to formation of more “hot spots” under microwave irradiation (Hu and Cheng, 2013a). It should be noted that although surface cations at higher densities can apparently accelerate the microwave-induced degradation of sorbed NDMA, they reduce the hydrophobicity of the zeolites and thus their NDMA sorption capacities. Overall, ZSM-5 with a Si/Al ratio of 25 (density of sodium cation at 1.13 sites/nm²) appears to have a high NDMA sorption capacity while allowing fast degradation of the sorbed NDMA under microwave irradiation.

Fig. 2c shows the degradation of NDMA sorbed in the micropores of ZSM-5 with a Si/Al ratio of 25 but exchanged with different types of surface cations after 2 and 4 min of microwave irradiation. The types of surface cations present in the micropores of ZSM-5 clearly affected the microwave-induced degradation of the sorbed NDMA, and the degradation rate decreased in the order of Na⁺, H⁺, Mg²⁺, and Cu²⁺. This could be attributed to the fact that more microwave energy was consumed in desorbing water molecules coordinated in the hydration shells of the surface cations with greater hydration free energies, reducing the fraction of microwave energy acted on formation of micro-scale “hot spots” (Hu and Cheng, 2013a). The hydration free energy of Na⁺ (−96.3 kcal/mol) is much lower compared to those of H⁺ (−252.6 to −262.5 kcal/mol), Mg²⁺ (−447.2 kcal/mol), and Cu²⁺ (−509.0 kcal/mol) (Bryantsev et al., 2008; Tawa et al., 1998; Yu et al., 2010), which explains the faster degradation of NDMA when sorbed on Na-ZSM-5 compared to H-, Mg- and Cu-ZSM-5. Based on the above results, Na-ZSM-5 with a Si/Al ratio of 25 appears to be the best mineral sorbent for removing NDMA (along with DMA) from aqueous solution followed by destruction of the sorbed NDMA by microwave irradiation.

The “hot spots” formed by the polar species (surface cations and hydroxyls, and the sorbed water and organic molecules) in the mineral micropores due to selective dielectric heating of microwave is on the molecular scale, and are thus difficult to detect (Serpone et al., 2010). Nonetheless, they could lead to gradual heating of the mineral sorbents under continuous microwave irradiation. Fig. 3a shows the evolution of bulk sorbent temperature for different porous minerals (with sorbed NDMA) during the course of microwave irradiation. The temperatures for most minerals rose quickly at the beginning of microwave irradiation, and then gradually plateaued off. The initial rapid heating of mineral sorbents was attributed mainly to the absorption of microwave energy by the residual water molecules on these sorbents (after being freeze-dried), which brought heating of the bulk minerals. Once most of the water molecules evaporated out of the porous minerals, the heating effect was primarily associated with the surface cations, as well as remaining water and NDMA (including some of its degradation products), as the zeolite framework is essentially transparent to microwave (Table S1). It appears that the degradation rates of NDMA were faster on the porous minerals exhibiting relatively higher “stable” temperatures under microwave irradiation (i.e., those with more effective microwave

absorption), except for 4A and CBV-10A. Due to the relatively strong microwave absorption of its framework (Table S1), the temperature of 4A quickly exceeded the upper limit set to protect the instrument (180 °C), even with the cooling of a stream of air (at flow rate of approximately 25 L/min). After that, the magnetron was actually operated at reduced power output (which was variable to maintain the temperature of the reaction vessel at ~180 °C) instead of 120 W. Thus, the degradation of NDMA sorbed on 4A proceeded slowly. Although the “stable” temperature of MCM-41 was relatively high, the degradation rate of sorbed NDMA was an order of magnitude lower than those observed on the zeolites except for 4A, due to the poor confinement effect of its much larger pores, as discussed above. The temperature of CBV-10A rose continuously during the course of microwave irradiation, and did not exhibit apparent plateau by 8 min. This could be explained by the retention of more water molecules in its micropores after freeze-drying due to its high density of surface cations (Table S8).

To further demonstrate the relationship between NDMA degradation and the bulk sorbent temperature, we conducted degradation experiments at 100, 120, and 150 W of microwave irradiation, while using a stream of compressed air (20–40 psi) to cool the reaction vessel once the bulk temperature of the irradiated sorbent exceeded the preset point during continuous microwave irradiation. Fig. 3b indicates that the degradation rate of NDMA sorbed on Na-ZSM-5 (Si/Al = 25) depended linearly on the bulk sorbent temperature at all three microwave power levels. By cooling the irradiated Na-ZSM-5, the stream of compressed air reduced the temperatures of the micro-scale “hot spots” formed in the zeolite micropores and thus slowed down the overall degradation of sorbed NDMA. Fig. 3b also shows that the degradation rate of NDMA increased significantly with the level of microwave energy at a given temperature. This is not surprising as greater energy input could result in the formation of more micro-scale “hot spots” and/or “hot spots” with higher temperatures, which accelerate pyrolysis of the NDMA molecules sorbed in their vicinity. Together, these results consistently suggest that the degradation of NDMA sorbed on microporous minerals was controlled by the formation of micro-scale “hot spots” within the mineral micropores, which is influenced by the microwave power, the type and density of surface cations, and the amount of water molecules in the micropores.

3.3. Pathway and mechanism of NDMA degradation

Fig. 4a shows the degradation of NDMA sorbed on Na-ZSM-5 (Si/Al = 25) under microwave irradiation at 120 W, and the corresponding formation of degradation products. NO₃[−] and HCOOH were found as the major degradation products of NDMA, and minor quantities of NH₄⁺ and CH₃COOH were also detected. The mass of NO₃[−] built up during the course of degradation while that of HCOOH accumulated initially and then dropped off. Previous studies on UV photolysis of NDMA and its metal-catalyzed reduction had found DMA, HCOOH, NO₃[−], and NH₄⁺ as the degradation products (Davie et al., 2006; Lee et al., 2007; Lv et al., 2013). The occurrence of CH₃COOH was unexpected, and could be attributed to the combination of formic acid radicals and methyl radicals generated during the pyrolysis of NDMA by the micro-scale “hot spots” formed under microwave irradiation (Lovas et al., 1975; Hill et al., 1996). The mass balance for nitrogen exhibited a small drop (approximately 7%) in the early stage of NDMA degradation, while that for carbon decreased gradually, with up to 68% lost after 9 min. The nitrogen on NDMA was primarily converted to NO₃[−], with a minor fraction converted to NH₄⁺. Thus the loss of nitrogen could only result from volatilization of ammonia (NH₃) transformed from NH₄⁺ and incomplete extraction of NH₄⁺ from the micropores of ZSM-5. In

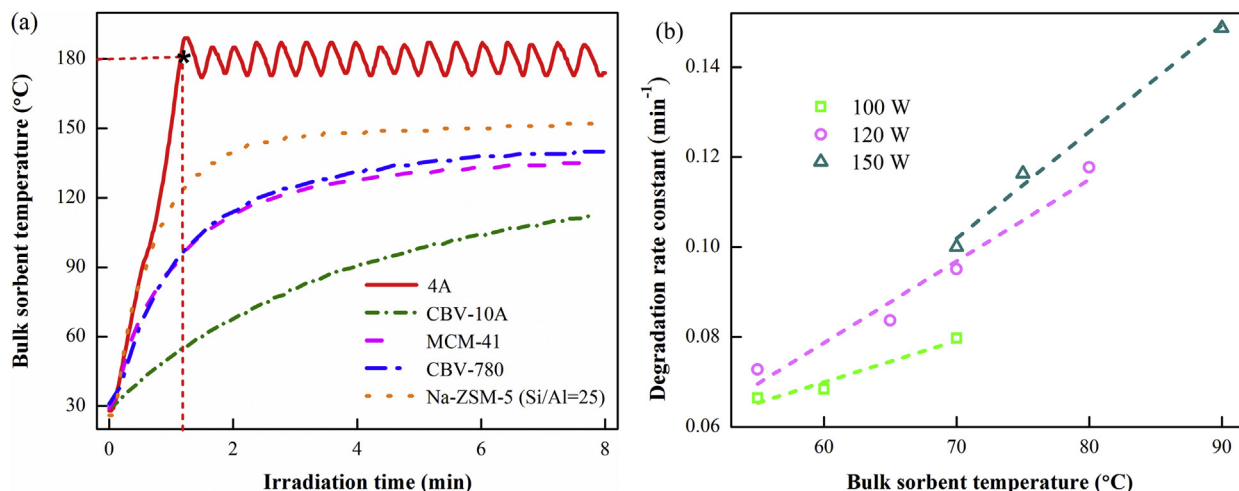


Fig. 3. Heating of mineral sorbents (with NDMA sorbed) under microwave irradiation and dependence of NDMA degradation rate on bulk sorbent temperature and microwave power: (a) Temperature profiles of the porous minerals (Na-ZSM-5 (Si/Al = 25), CBV-780, 4A, MCM-41, and CBV-10A) during 120 W microwave irradiation (For 4A, “*” denotes the point after which the magnetron operated at reduced power output to maintain the bulk sorbent temperature at below 180 °C); and (b) Degradation rate of NDMA sorbed on Na-ZSM-5 (Si/Al = 25) under controlled maximum bulk sorbent temperatures (by cooling with a stream of pressurized air) irradiated by microwave at 100, 120, and 150 W.

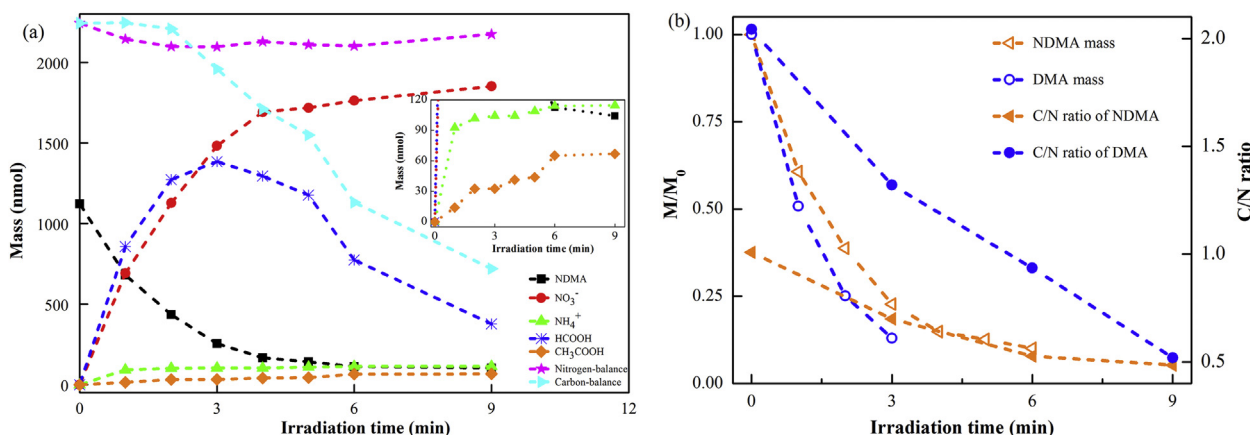


Fig. 4. Evolutions of NDMA degradation products, and degradation of NDMA and DMA, along with the changes in C/N ratio, when sorbed on Na-ZSM-5 (Si/Al = 25) during the course of 120 W microwave irradiation: (a) Degradation of NDMA and formation of degradation products; and (b) Degradation of sorbed NDMA (1.122 μmol/g) and DMA (0.482 μmol/g) represented by the ratio of mass remaining (M/M_0) and C/N ratio. The data points represent the mean values determined from triplicated experiments.

contrast, further degradation of HCOOH (and CH₃COOH) to carbon dioxide (CO₂, which was not analyzed for) under continuous microwave irradiation could significantly reduce the mass of measurable carbon. It should be noted that DMA and methylamine, which are important precursors of NDMA and are commonly found in the treatment of NDMA by UV direct photolysis, ozonation, advanced oxidation by O₃/H₂O₂, and metal-catalyzed reduction (Stefan and Bolton, 2002; Davie et al., 2006; Lee et al., 2007; Lv et al., 2013), were not detected in any samples of this study.

Fig. 4b shows the degradation of NDMA and DMA sorbed on Na-ZSM-5, along with the corresponding changes in C/N ratios, during the course of microwave irradiation. While 90% of the sorbed NDMA degraded by the end of 6 min, it took only 3 min of microwave irradiation for approximately 90% of the sorbed DMA to degrade. The faster microwave-induced degradation of DMA (1.01 Debye) compared to NDMA (4.22 Debye) was attributed primarily to its simpler structure. The C/N ratios of both NDMA and DMA sorbed on the Na-ZSM-5 decreased continuously over time, reaching approximately 0.5 in 9 min. Most of the nitrogen on NDMA and DMA molecules was converted to NO₃⁻ during degradation, with small fractions converted to NH₄⁺ (retained strongly on

the cationic sites in the zeolite micropores) and NH₃ (easily lost during post-irradiation sample handling). Thus, nitrogen content could be considered approximately conservative in the micropores of ZSM-5 during degradation. The significant reduction in C/N ratios clearly indicates the mineralization of sorbed NDMA and DMA (e.g., conversion of organic carbon to CO₂), which is consistent with the highly oxygenated organic species (HCOOH and CH₃COOH) detected among the organic degradation products of NDMA. It is expected that full mineralization of the sorbed NDMA and DMA could be achieved with prolonged microwave irradiation (>9 min). With the NDMA-laden mineral sorbent irradiated by microwave after being separated from the solution phase, the degradation products formed resided in the micropores of ZSM-5, instead of the treated solution. Nonetheless, once the sorbed NDMA is fully mineralized, releases of the inorganic degradation products back into the treated solution are not expected to cause significant concern (Table S9).

Fig. 5 depicts the proposed pathway for degradation of NDMA and DMA sorbed in mineral micropores under microwave irradiation based on the degradation products detected in this study. Upon heating above approximately 500 K, nitrosamines encapsulated

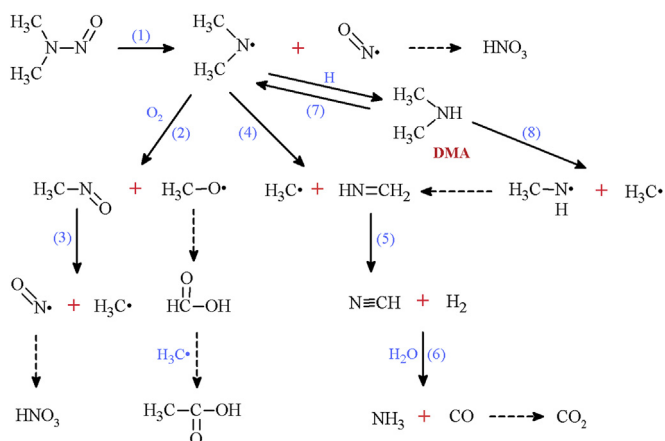


Fig. 5. Degradation pathway of NDMA and DMA sorbed in mineral micropores under microwave irradiation based on the degradation products identified in this study and relevant pyrolysis reactions reported in the literature: (1) Radical reaction reported in Wu et al. (2008); (2) Oxidation of DMA radical by oxygen reported in Li et al. (2015); (3) Thermal decomposition pathway reported in Pratt and Purnell (1961); (4) Pyrolysis reaction reported in Hill et al. (1996); (5) Pyrolysis reaction reported in Lovas et al. (1975) and Mulcahy et al. (2000); (6) Thermal decomposition pathway reported in Pratt and Purnell (1961); (7) Radical reaction reported in Hill et al. (1996); and (8) Unimolecular decomposition of DMA reported in Li et al. (2015). It should be noted that many more complicated reactions are probably involved due to the existence of multiple radicals and reactive species under the pyrolytic conditions, and these simple reactions are shown to illustrate that degradation of NDMA and DMA could yield the major products detected in this study.

inside the channels of basic zeolites (e.g., Na-ZSM-5 and NaY) were found to decompose through radical reaction process, similar as pyrolysis (Wu et al., 2008). In the vicinity of “hot spots” of cations, pyrolysis of the sorbed NDMA appears to occur first via the cleavage of the N–N bond in the N–NO group, which is the weakest one in nitrosamine structures (Wu et al., 2008). The N–N bond most probably undergoes homolytic cleavage, producing DMA radical and nitric oxide radical, as it has been shown that the homolysis energies of Y–NO bonds (where Y is a relatively large organic moiety) are 24–65% smaller compared to the corresponding heterolysis energies for *N*-nitrosoureas, *N*-nitrososulfonamides, and *N*-nitrosophosphoramides (Cheng et al., 1998). The nitric oxide radical is subsequently oxidized to HNO₃, while the DMA radicals can further degrade through two reaction paths. When oxidized, the DMA radical can eventually yield HNO₃ and HCOOH, while H₂, NH₃, and CO are produced when it undergoes pyrolysis in the absence of oxygen. Degradation intermediates, such as nitromethane (CH₃NO₂) and methyleneimine (HN=CH₂), were not detected in this study, probably because they decomposed readily under the pyrolytic conditions. The radicals and other fragments produced in the pyrolysis can further react with each other to form complex products, such as CH₃COOH. Nonetheless, the organic products (e.g., HCOOH and CH₃COOH) can be eventually mineralized under continuous microwave irradiation. DMA and DMA radical can interconvert between one another, while DMA can also undergo unimolecular decomposition to yield methyleneimine radical and methyl radical. This explains why DMA was not detected as a stable degradation product, which is also consistent with the quick degradation of sorbed DMA in mineral micropores under microwave irradiation. Among the stable degradation products detected, only NO₃⁻ is regulated as a drinking water contaminant (WHO: 50 mg/L; USEPA: 10 mg/L). Thus, there is negligible health risk from the degradation products generated from microwave-induced degradation of NDMA.

Current treatment technologies for NDMA are rather ineffective at removing its precursor, DMA, which can form NDMA through

reacting with monochloroamine and nitrosation by nitrite. Furthermore, the formation of DMA as a stable degradation product compromises the treatment performance of some of these technologies, such as direct UV photolysis, advanced oxidation processes, and catalytic reduction. In contrast, DMA, along with NDMA, can be efficiently sorbed onto hydrophobic microporous minerals from water, and both compounds decompose rapidly, and can be fully mineralized, under continuous microwave irradiation. Unlike the widely used UV photolysis treatment, in which the UV light is irradiated directly upon very large volumes of water to cause degradation of NDMA present at trace levels, NDMA is first enriched onto the microporous mineral sorbents before being destructed by microwave irradiation. Even though the energy level of the microwave can be rather intense, the volumes of sorbents to be irradiated can be reduced by 7 orders or more. Thus, this process is expected to be much more energy efficient compared to treatment of dilute solution. Although the performance of microporous mineral sorption coupled with microwave-induced degradation was evaluated in batch mode (sorption, separation of solution, followed by microwave irradiation) in the present study, the treatment process could be easily modified for continuous treatment of drinking water or wastewater in a dual-column configuration (Fig. S3). That is, while the microporous mineral packed in one column adsorbs NDMA (and its precursor DMA) from the aqueous stream, NDMA (along with DMA) sorbed in the other column can be destructed and the sorption capacity of the spent microporous mineral can be regenerated with microwave irradiation (Supplementary data). The fast *in situ* regeneration of the microporous mineral sorbents packed in the columns makes this treatment more advantageous compared to activated carbons adsorption. Because of the challenges with detection of NDMA and its degradation products, the concentrations of NDMA evaluated in this study was much higher than those typically occurred in water and wastewater. Nonetheless, the surface chemistry of ZSM-5 (and other microporous minerals as well) can be easily modified (e.g., loading of metal cations that can complex with NDMA molecules) to further improve their sorption capacities for NDMA, which can greatly improve the feasibility of the proposed treatment method.

4. Conclusions

The results of this study demonstrate that NDMA in water could be effectively sorbed on microporous mineral sorbents and then efficiently destructed by microwave irradiation. Furthermore, the precursor of NDMA, DMA, could be removed and destructed even more efficiently in these processes. The NDMA sorption capacities of dealuminated ZSM-5 analogues (e.g., at an initial aqueous concentration of 1 mg/L) are an order of magnitude higher than those of activated carbons reported in the literature (Fleming et al., 1996; Dai et al., 2009). Thus, microporous minerals can be used to control NDMA levels in drinking water with performance comparable or better than activated carbons. With the essentially microwave-transparent framework of dealuminated ZSM-5 zeolites, most of the irradiated microwave energy is absorbed by the surface cations and hydroxyls, and the polar molecules (water, NDMA, DMA, and their degradation products) sorbed in the micropores. The formation of micro-scale “hot spots” is responsible for the degradation of the sorbed NDMA and DMA, while the bulk temperatures of the mineral sorbents stay at relatively low temperatures (<160 °C) during the relatively short microwave irradiation treatment (about 10 min or longer). Once NDMA and DMA are fully mineralized, the mineral sorbents can be readily reused, as the microwave irradiation barely affects their microwave-transparent framework. Together, the promising laboratory results indicate that microporous mineral sorption coupled with microwave-induced

degradation could be a novel treatment alternative for removing NDMA and other nitrosamines from water and wastewater.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.02.065>.

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