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Simultaneous removal of ammonia and N-nitrosamine precursors from high ammonia water by zeolite and powdered activated carbon

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ABSTRACT

When adding sufficient chlorine to achieve breakpoint chlorination to source water containing high concentration of ammonia during drinking water treatment, high concentrations of disinfection by-products (DBPs) may form. If N-nitrosamine precursors are present, highly toxic N-nitrosamines, primarily N-nitrosodimethylamine (NDMA), may also form. Removing their precursors before disinfection should be a more effective way to minimize these DBPs formation. In this study, zeolites and activated carbon were examined for ammonia and N-nitrosamine precursor removal when incorporated into drinking water treatment processes. The test results indicate that Mordenite zeolite can remove ammonia and five of seven N-nitrosamine precursors efficiently by single step adsorption test. The practical applicability was evaluated by simulation of typical drinking water treatment processes using six-gang stirring system. The Mordenite zeolite was applied at the steps of lime softening, alum coagulation, and alum coagulation with powdered activated carbon (PAC) sorption. While the lime softening process resulted in poor zeolite performance, alum coagulation did not impact ammonia and N-nitrosamine precursor removal. During alum coagulation, more than 67% ammonia and 70%–100% N-nitrosamine precursors were removed by Mordenite zeolite (except 3-(dimethylaminomethyl)indole (DMAI) and 4-dimethylaminoantipyrine (DMAP)). PAC effectively removed DMAI and DMAP when added during alum coagulation. A combination of the zeolite and PAC selected efficiently removed ammonia and all tested seven N-nitrosamine precursors (dimethylamine (DMA), ethylmethylamine (EMA), diethylamine (DEA), dipropylamine (DPA), trimethylamine (TMA), DMAP, and DMAI) during the alum coagulation process.

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Introduction

Many drinking water treatment systems, particularly small water systems that treat ground water, are facing issues of naturally-occurring high ammonia (NH_3 and NH_4^+) in their source water. When ammonia is present in high concentration, it reacts with free chlorine to form chloramines which have lower disinfection capacity (Blute et al., 2012). When a higher dose of chlorine is applied to reach the breakpoint chlorination, high levels of toxic disinfection by-products (DBPs) will form (Blute et al., 2012). On the other hand, ammonia can also be consumed by nitrifying bacteria to form nitrite and nitrate, and high nitrite would pose an acute health hazard (Blute et al., 2012). Thus, control and removal of ammonia in drinking water treatment is important. N-nitrosamines are a class of potential mutagenic and carcinogenic DBPs that form during drinking water or wastewater disinfection by chlorine or chloramines (Mitch et al., 2003) with N-nitrosodimethylamine (NDMA) as the predominant product. There are several hypotheses regarding their formation including the oxidation of intermediate formed by the reaction of dichloramine and dimethylamine (DMA) (Schreiber and Mitch, 2006), the formation of highly reactive nitrosating intermediate in water containing organic nitrogen precursor during chlorination (Choi and Valentine, 2003), and the reaction between monochloramine with either DMA (Selbes et al., 2013) or secondary amines (Zhou et al., 2014), or certain tertiary amines (Mitch and Sedlak, 2002a; Selbes et al., 2013). Several major precursors have been identified including DMA, ethylmethylamine (EMA), diethylamine (DEA), dipropylamine (DPA), trimethylamine (TMA), 4-dimethylaminoantipyrine (DMAP) and 3-(dimethylaminomethyl)indole (DMAI), all of which can be detected by a simple and rapid method developed using ultra-fast liquid chromatography–tandem mass spectrometry (UFLC–MS/MS) (Wu et al., 2015a).

Several methods have been used for ammonia removal including membrane distillation (Qu et al., 2013; Rezakazemi et al., 2012), air stripping (Yuan et al., 2016), breakpoint chlorination, biological treatment (Peng and Zhu, 2006), electrochemical oxidation (Li and Liu, 2009), and microwave radiation (Lin et al., 2009). However, since the ammonia concentration in source water varies and the risk of forming high levels of DBPs increases when using breakpoint chlorination, less expensive and less-DBP forming methods are needed. A UV/chlorine process has recently been developed for ammonia removal, which lowers chlorine demand and the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). However, more haloacetonitriles (HANs) are formed (Zhang et al., 2015). In addition, the expense of the use of this UV/chlorine process is also another important factor that needs to be considered. There are also several methods developed for the removal of N-nitrosamines including reverse osmosis (RO) membranes (Fujioka et al., 2012), membrane bioreactor (Wijekoon et al., 2013), sand filtration (Krauss et al., 2009), and nanofiltration (Miyashita et al., 2009). Research has demonstrated that NDMA formation is attributable to the reaction between monochloramine and organic nitrogen-containing precursors (Gerecke and Sedlak, 2003; Krasner et al., 2013; Mitch and Sedlak, 2002a, 2002b). Therefore, a practical way to reduce the concentration of N-nitrosamines in water system is to remove their nitrogen-containing precursors.

Ion exchange is a promising ammonia and N-nitrosamine precursor removal method due to its low energy input and ease of operation (Demir et al., 2002; Gendel and Lahav, 2013; Lin and Wu, 1996). However, using organic resin exchangers is costly (Huang et al., 2010), thus, the use of natural zeolite is considered to be a competitive and effective treatment due to its relatively less cost and simplicity of application and operation (Englert and Rubio, 2005; Huang et al., 2010; Karadag et al., 2006; Zhou and Boyd, 2014). Zeolite has also been used to remove ammonia during waste water treatment (Almutairi and Weatherley, 2015; Markou et al., 2014) and landfill leachate (Couto et al., 2016). Combined with alum and polyaluminum chloride, clinoptilolite zeolite can remove total organic carbon (TOC) in surface runoff significantly (Murnane et al., 2016). Zeolites are mainly composed of aluminosilicates (Englert and Rubio, 2005) with a three-dimensional structure formed by AlO_4 and SiO_4 tetrahedra that are connected by a shared oxygen atom (Englert and Rubio, 2005; Huang et al., 2010; Šiljeg et al., 2010). This open and stable structure contributes to high cation exchange capacity, cation selectivity, higher void volume and great affinity for cation ions like $NH_{4(aq)}^+$ and other types of organic ions with positive charge (Farkaš et al., 2005; Huang et al., 2010; Rožić et al., 2000; Saltalı et al., 2007; Šiljeg et al., 2010; Wang and Peng, 2010; Wang et al., 2007). In a recent study, Mordenite zeolite has been shown to be an effective adsorbent to effectively remove most of the seven N-nitrosamine precursors previously identified in laboratory reagent water and untreated surface water (Wu et al., 2015b). However, the dual removal efficiencies of ammonia and N-nitrosamine precursors by zeolite have never been attempted in the drinking water treatment.

Powdered activated carbon (PAC) has been used for the removal of a wide range of emerging contaminants in water treatment (Bhatnagar et al., 2013; Mailler et al., 2015), usually at the step of alum coagulation. It shows low adsorption capacity on ammonia due to its non-polar surface (Halim et al., 2010), while can remove N-nitrosamine precursors (Beita-Sandí et al., 2016; Hanigan et al., 2012; Wu et al., 2015b). The effect of PAC on the ammonia and N-nitrosamine precursor removal during alum coagulation was also investigated.

We hypothesize that zeolite can effectively remove ammonia and N-nitrosamine precursors simultaneously, and by combination of zeolite and PAC, all the polar and less polar N-nitrosamine precursors can be well controlled during the drinking water treatment. The objectives of this study are to (1) identify the most effective zeolite for ammonia removal; (2) test the suitability of N-nitrosamine precursor removal by zeolite in combination with PAC; (3) apply zeolite and PAC in drinking water treatment processes by simulation of drinking water treatment steps of lime softening (add $Ca(OH)_2$ to reduce water hardness) and alum coagulation (add $Al_2(SO_4)_3{\cdot}14.3\ H_2O$ to destabilize water colloidal suspensions) through jar test. This aims to find out how to incorporate the zeolite and PAC in real drinking water treatment process.

1. Materials and methods

1.1. Chemicals and materials

Three types of zeolite including Bear River zeolite, Mordenite zeolite, and Zeolite Y used in the study were purchased from Bear River Zeolite Co. (Preston, ID, USA), Fisher Scientific (Pittsburgh, PA, USA), and Sigma Aldrich (St. Louis, MO, USA), respectively. Modified Bear River zeolite was prepared by mixing Bear River zeolite with 2 mol/L NaCl solution at 120 r/min and 36°C for 72 hr, then washing with ultra-high purity water three times and drying in an oven at 100°C (Šiljeg et al., 2010). HydroDarco B PAC was purchased from Cabot Norit Americas Inc. (Marshall, TX, USA). The characteristics of each adsorbent (zeolites and PAC) are listed in Table 1.

Seven N-nitrosamine precursor standards including DMA (40 wt.% in H_2O), TMA (25 wt.% in H_2O), DMAI (99%), DMAP, EMA (97%), DEA (≥99.5%), DPA (99%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ammonium hydroxide standard solution (trace metal grade, 20%-22% as NH_3) and LC–MS grade methanol was purchased from Fisher Scientific (Pittsburgh, PA, USA). Formic Acid (LC–MS grade) was purchased from Sigma Aldrich (St. Louis, MO, USA). Ultra-high purity water was generated by a Millipore Elix 3 water purification system (Millipore, Billerica, MA, USA). Lime ($Ca(OH)_2$, >95%) and Alum ($Al_2(SO_4)_3 \cdot 14.3\ H_2O$, >98%) used in the simulated drinking water treatment process were purchased from Fisher Scientific (Pittsburgh, PA, USA).

1.2. Water sample collection

Several types of water samples were used in this study including ultra-high purity water, surface (river) water, ground (well) water, and ground (well) water after certain treatment. Surface water was collected from the Missouri River (near Jefferson City, MO, USA). Ground water was collected from a shallow well (100 ft deep) near the Missouri River (MO, USA) that was influenced by the river water. The well water samples were collected at two different treatment steps, (1) after aeration but before lime softening (well water 1) and (2) after lime softening before recarbonation (well water 2) from a drinking water treatment facility.

All the water samples were collected in pre-cleaned 4-L amber bottles, placed in coolers filled with ice and transported to lab within 12 hr. The samples were stored in the refrigerator at 4°C unfiltered before use, then returned to room temperature before experiments were conducted.

1.3. Analytical techniques

The water sample characterization was performed by following the standard methods for examination of water & wastewater (Eaton and Franson, 2005) and using commercially available HACH test kits (HACH, Loveland, CO). Ammonia concentrations were detected using HACH TNT 830 kits with a detection range of 0.015 to 2.00 mg/L NH_3-N (HACH, Loveland, CO). HACH DR 2800 spectrophotometer was used for ammonia detection (HACH, Loveland, CO). Dissolved organic carbon (DOC) was tested by using a TOC-L analyzer with ASI-L liquid autosampler with detection limit of 0.20 mg/L (Shimadzu, Columbia, MD, USA). pH was measured with a Thermo Orion 3 Star pH meter (Thermo Fisher Scientific, Waltham, MA, USA). Turbidity was measured using a TB200 Portable Turbidimeter (Orbeco-Hellige, Sarasota, FL, USA) and UV_{254} absorbance was monitored with a Cary 50 UV–Vis Spectrometer (Agilent, Santa Clara, CA, USA). Seven N-nitrosamine precursors were analyzed using a UFLC-MS/MS method with method detection limits ranging from 0.02 to 1 μg/L, except for EMA (5 μg/L) (Wu et al., 2015a). Briefly, a Shimadzu LC-20ADXR UFLC system (Columbia, MD) coupled with 4000Q Trap mass spectrometer (AB Sciex, Concord, ON, CA) was used. The analysis was under positive electrospray ionization (ESI+) with multiple reaction monitoring (MRM) mode. Phenomenex polar-RP C18 column (Phenomenex, Torrance, CA) with dimensions of 150 × 2.0 mm i.d., particle size of 4 μm was used. Mobile phase A was ultra-high purity water with 0.1% formic acid and mobile phase B was methanol with 0.1% formic acid.

1.4. Water treatment procedures

1.4.1. Investigate ammonia removal efficiency by different types of zeolites

The ammonia removal efficiencies of Bear River (untreated and treated to improve adsorption), Mordenite, and Zeolite Y was tested and compared in untreated well water with naturally occurring ammonia concentration of 1.19 mg/L in small-scale tests. During this small-scale tests, water sample was added into 40 mL amber vials with addition of 1000 mg/L of specific type of adsorbent. Then the mixtures were shaken for 90 min. Afterwards, the water samples were filtered through 0.45 μm nylon membrane filter for ammonia analysis and 0.22 μm nylon membrane filter (both types of filters were purchased from LabTech America, Inc., Hopkinton, MA, USA) for N-nitrosamine precursor analysis.

1.4.2. Investigate the impacts of dosage, contact time, pH, and temperature on the removal of ammonia by the most effective zeolite

The most efficient zeolite was chosen to study the effects of dosage, contact time, pH and temperature on the removal of

Table 1 – Characteristics of zeolites and powdered activated carbon (PAC) tested for ammonia and N-nitrosamine precursor removal.

Adsorbent	Source	Type	BET surface area (m^2/g)	Composition	Si/Al molar ratio
Bear River Zeolite	Natural zeolite	Clinoptilolite	375	K-Ca-Na-Al-Si	~15:1 to 20:1
Mordenite	Natural zeolite	Mordenite	425	(Ca, Na_2, K_2) $Al_2Si_{10}O_{24} \cdot 7H_2O$	13:1
Zeolite Y	Synthesized zeolite	Synthesized zeolite	450	$(Na_2,Ca,Mg)_3.5[Al_7Si_{17}O_{48}] \cdot 32(H_2O)$	200:1
Powered activated carbon	Lignite coal	PAC	510	Carbon	N/A

ammonia. Untreated well water (contains naturally occurring 1.19 mg/L ammonia) was used for all the following tests. The treatment procedures were same with those described in Section 1.4.1.

(1) During dosage test, three dosages including 100, 1000 and 5000 mg/L were used with contact time of 4 hr.
(2) During exposure time test, the adsorbent was allowed to contact for 5, 10, 30, 60, 120, 240, 1440 min. The dosage of adsorbent during exposure time test was decided during dosage tests.
(3) During pH test, pH was adjusted to 6, 7, and 8 using a 10 mmol/L phosphate buffer. Then the most efficient absorbent at the concentration decided during dosage tests was added and the mixture was agitated for 4 hr.
(4) During temperature tests, three temperatures, 2°C, room temperature, and 40°C, were investigated. The dosage and contact time in the temperature tests were determined during dosage tests and exposure time tests.

1.4.3. Investigate simultaneous removal of ammonia and N-nitrosamine precursors by small-scale test

The simultaneous removal of ammonia and N-nitrosamine precursors was first tested in small-scale with 40 mL vials. Ultra-high purity water dosed with 8 mg/L ammonia and 25 μg/L N-nitrosamine precursors was used. The most effective Mordenite zeolite was used and the dosage was 1000 mg/L with contact time of 30 min. The treatment procedures were same with Section 1.4.1.

1.4.4. Investigate simultaneous removal of ammonia and N-nitrosamine precursors by simulation of drinking water treatment process using jar test

For practical application of the studied adsorbents to remove ammonia and N-nitrosamine precursors in drinking water treatment system, it is important to establish which water treatment step is the ideal step for adding these adsorbents. Simultaneous removal of ammonia and N-nitrosamine precursors was then tested through a simulated drinking water treatment process using a six-gang stirrer with 2-L square beakers (Phipps & Bird, Richmond, VA, USA). Three types of water were used for the simulation study, including well water 1 and 2 and Missouri River water. The concentrations of ammonia and N-nitrosamine precursors in water samples were adjusted to be 1.5 mg/L and 20 μg/L, respectively. Two commonly used drinking water treatment steps, lime softening and alum coagulation, were simulated. PAC was added at the step of alum coagulation to study its effect on the removal of ammonia and N-nitrosamine precursors.

During lime softening, excess lime was added to remove both Ca and Mg at pH 11; For alum coagulation, 50 mg/L $Al_2(SO_4)_3{\cdot}14.3\ H_2O$ was added; For alum coagulation with PAC sorption, 50 mg/L $Al_2(SO_4)_3{\cdot}14.3\ H_2O$ and 20 mg/L PAC was added. The chemicals were dosed into the water samples in specific reaction beakers of the six-gang stirring system. Mordenite was added into specific beakers simultaneously with lime, alum, or alum with PAC, followed by rapid mixing (30 sec at 300 r/min), flocculation (10 min each at 58, 42 and 28 r/min) and sedimentation (180 min at 0 r/min). After treatments, samples were filtered with 0.22 μm nylon membrane filters for N-nitrosamine precursor analysis and 0.45 μm the same type of filter for UV_{254} absorption and ammonia analysis. pH and turbidity were tested in unfiltered samples.

1.5. *Quality assurance and control*

US EPA quality control and assurance guideline was closely followed during this study. All the analytical methods have been validated to make sure certified performance before used for sample analysis. Method detection limits, reproducibility, calibration curve linearity, and matrix effect were all been tested to make sure they meet the performance criteria. During sample analysis, continuing quality control, including blank sample, duplicates of selected samples, and spiking recovery of samples, were performed for every batch or every 10–15 samples.

2. Results and discussion

There were four types of water samples used in this study and their basic chemical and physical parameters were measured at room temperature (~20°C) and are listed in Table 2. Untreated well water was used for the study of ammonia removal by zeolites in small scales. Well water 1, well water 2 and Missouri River water were used for the study of simultaneous ammonia and N-nitrosamine removal through jar tests. Missouri River water contained high DOC (5.76 mg/L) and non-detectable NH_3-N, while in well water, the DOC level was relatively low and it contained around 1 mg/L of naturally occurring NH_3-N. Before lime softening, the hardness in well water samples was high.

2.1. *Ammonia removal by zeolites*

The ammonia removal efficiencies by different zeolites in untreated well water (naturally occurring ammonia concentration of 1.19 mg/L) were compared. The ammonia removal

Table 2 – The basic parameters of tested water samples at 20°C.

Water sample	pH	DOC	NH_3-N (mg/L)	UV_{254} absorption	Calcium hardness as $CaCO_3$ (mg/L)	Total hardness as $CaCO_3$ (mg/L)	Alkalinity as $CaCO_3$ (mg/L)	Turbidity (NTU)
Missouri River water	7.40	5.76	<0.015	0.1335	149	222	149	324
Well water (source water)	7.40	2.87	1.19	0.2040	410	570	603	142
Well water 1 (after aeration before lime softening)	7.72	2.80	1.02	0.0824	397	546	568	129.5
Well water 2 (after lime softening before recarbonation)	9.55	2.37	1.18	0.0516	69	186.5	161	2.31

results are shown in Fig. 1. Ammonia removal efficiency was as follows: Mordenite > Modified BRZ > Zeolite Y > BRZ. Mordenite had the best removal efficiency (68%). This result can be explained by its low Si/Al molar ratio (Si/Al = 13:1) and moderate surface area (425 m^2/g) which contribute to a high cation-exchange capacity. For Bear River zeolite and Zeolite Y, although the former has higher Si/Al ratio, Bear River zeolite has lower surface area (375 m^2/g for Bear River zeolite and 450 m^2/g for zeolite Y), thus resulted in lower ammonia removal efficiency than that of Zeolite Y (Wu et al., 2015b). Modified BRZ showed better removal efficiency on ammonia than BRZ, which agrees with the previous published data and is because that the stability of NH_4^+ on Na-form of zeolite (modified BRZ) is higher than that on ordinary form of zeolite (Lin et al., 2013; Šiljeg et al., 2010; Soetardji et al., 2015).

Zeolite dosage, exposure time, pH, and temperature impacts on the ammonia removal efficiency were evaluated in untreated well water (naturally occurring 1.19 mg/L ammonia) using the most efficient absorbent, Mordenite zeolite. Ammonia removal was 17%, 72% and 86% when 100, 1000, and 5000 mg/L Mordenite were added, respectively. Compared to that with 100 mg/L zeolite applied, the ammonia removal efficiency increased drastically with 1000 mg/L zeolite applied, but increased slowly when further increasing the zeolite concentration to 5000 mg/L. When adding higher concentration of zeolite, the solid/liquid ratios increases, the potential of aggregation or particles precipitation increases (Huang et al., 2010; Saltalı et al., 2007) which would affect the zeolite adsorption efficiency. This might be the reason why the removal of ammonia did not increase linearly with the increase of zeolite dosage from 100 to 5000 mg/L. Therefore, dosage of 1000 mg/L was selected for the following study.

Exposure time dependence was investigated by allowing Mordenite to contact for 5, 10, 30, 60, 120, 240, 1440 min. The removal kinetics were fast, with 66% of ammonia removed after 5 min of contact time but only 5% increased removal at the longest time point. Similar results have been obtained by other studies (Huo et al., 2012; Lin et al., 2013). The fast ammonia adsorption might result from excess adsorption sites on the zeolite at the beginning of the interaction (Du et al., 2005). Meanwhile, the adsorption of N-nitrosamine precursors by Mordenite is rapid, which reaches equilibrium within 10 min of contact (Wu et al., 2015b).

For pH and temperature dependence tests, no significant difference in ammonia removal was found for all the tested pHs (shown in Fig. 2), and all the tested temperatures (shown in Fig. 3).

2.2. Simultaneous removal of ammonia and N-nitrosamine precursors in ultra-high purity water by Mordenite zeolite in small-scale tests

The most effective ammonia removal zeolite, Mordenite, was selected to determine the simultaneous removal efficiency of ammonia and N-nitrosamine precursors because of its high performance in ammonia removal. Mordenite effectively removed more than 95% of all the tested N-nitrosamine precursors, except DMAP, and 75% of the ammonia in ultra-high purity water in small-scale tests (Table 3). DMAP is aromatic amine which is less ionic and has weaker electrostatic interactions with zeolites, resulting in lower removal efficiency by Mordenite compared to the other precursors (Wu et al., 2015b).

2.3. Simultaneous removal of ammonia and N-nitrosamine precursors by Mordenite zeolite during simulated drinking water treatments through jar test

For practical applications, it is important to evaluate the removal efficiency of ammonia and N-nitrosamine precursors by Mordenite when combined with other drinking water treatment processes. The practical zeolite application for real drinking water treatment process should be coagulation processes including lime softening and alum coagulation. Alum has been used in the wastewater treatment and shows a great effect on the removal of dissolved phosphorus and total phosphorus (Brennan et al., 2012; O'Flynn et al., 2013) PAC is usually added during the step of alum coagulation in drinking water treatment plant. Using a six-gang stirrer, lime softening and alum coagulation with and without PAC sorption, were

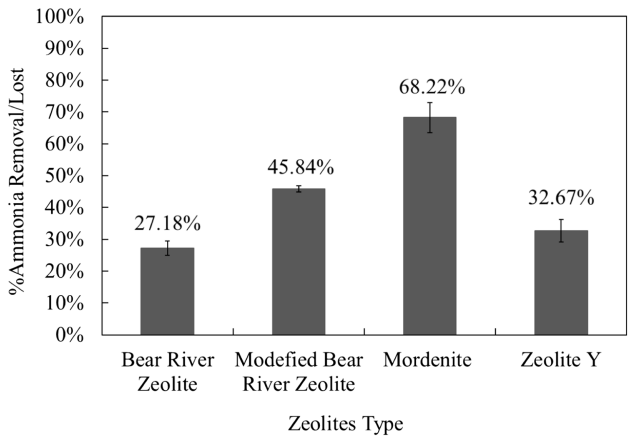


Fig. 1 – Ammonia removal efficiencies by different types of zeolites at a dosage of 1000 mg/L in well water sample (ammonia concentration of 1.19 mg/L) after 4 hr contact time (*n* = 2, error bars represent the percent difference).

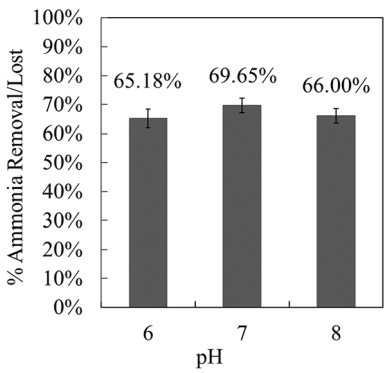


Fig. 2 – Ammonia removal efficiencies by 1000 mg/L Mordenite zeolite in well water sample (ammonia concentration of 1.19 mg/L) at different pHs after 4 hr contact time (*n* = 2, error bars represent the percent difference).

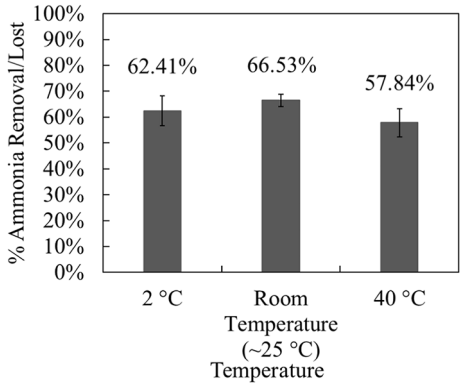


Fig. 3 – Ammonia removal efficiencies by 1000 mg/L Mordenite zeolite in well water sample (ammonia concentration of 1.19 mg/L) at different temperatures after 5 min contact time (n = 2, error bars represent the percent difference.

simulated with addition of 1000 mg/L Mordenite to evaluate the simultaneous removal of ammonia and N-nitrosamine precursor.

2.3.1. Ammonia and N-nitrosamine precursor removal by Mordenite zeolite during simulated lime softening treatment

Lime softening is a common early step in the drinking water treatment process. Thus, the removal of ammonia and N-nitrosamine precursors was first tested during lime softening. Well water 1 was used for the study after adjusting the concentration of ammonia and N-nitrosamine precursors to be 1.5 mg/L and 20 μg/L, respectively. In the first experiment, Mordenite with concentration of 1000 mg/L was added to the water samples and allowed to contact for 10 min. After 10 min, the removal efficiencies of ammonia and N-nitrosamine precursors were tested. Lime was then added without removing the Mordenite. After rapid mixing, flocculation and sedimentation, samples were taken for ammonia and N-nitrosamine precursor detection. In the second experiment, 1000 mg/L Mordenite was added together with lime and subjected to rapid mixing, flocculation, and sedimentation.

When mordenite was added before lime and allowed to contact for 10 min, 68% ammonia was removed. However, after adding lime, the removal of ammonia decreased to 29%, indicating that the ammonia was being replaced on the adsorbent during lime softening. In the samples dosed with Mordenite and excess lime simultaneously, only 15% ammonia removal was observed. This indicated that lime softening had a negative effect on ammonia removal by Mordenite zeolite. N-Nitrosamine precursor removal was largely unchanged between the two experiments, resulting in more than 95% removal except for TMA (60%), DMAI (8%) and DMAP (no removal) in each case.

During the softening process, the pH increased to 11. Ammonia has a pK_a of 9.4; above this pH, ammonia exists in molecular form rather than ionic. Thus, it was hypothesized that ammonia removal was pH dependent and that when pH above ammonia pK_a, ammonia removal would be minimal due to the ammonia equilibrium in water shifting to the molecular form. The effect of pH on ammonia and N-nitrosamine precursor removal was investigated by adjusting the pH of well water 1 to 6, 7, 8, 9, 10, and 11 using 1 mol/L sodium hydroxide and 10% sulfuric acid, with adjustment of ammonia and each precursor to be 1.5 mg/L and 20 μg/L, respectively, and contacting with 100 mg/L Mordenite for 30 min. The results can be seen in Table 4. Ammonia removal was between 12%–14% in samples at pH 6, 7, 8, decreased to 5% removal in samples at pH 9, and was not removed in samples at pH 10 and 11. N-nitrosamine precursor removal increased slightly as pH increased, most likely due to the relatively high pK_a values for most of the precursors ranging from 9.8–11 and less competition for ion exchange sites under basic conditions (Wu et al., 2015b).

2.3.2. Ammonia and N-nitrosamine precursor removal by mordenite during alum coagulation with and without PAC

Six-gang stirrer simulations were conducted to determine the effects on ammonia and N-nitrosamine precursor removal when alum and Mordenite were added simultaneously with and without PAC sorption. Three types of water were evaluated including well water 1, well water 2 and Missouri River water. The concentrations of ammonia and N-nitrosamine precursors in water samples were adjusted to 1.5 mg/L and 20 μg/L, respectively. During alum coagulation, pH was adjusted to around 7 from initial pH values of 7.72, 9.55, and 7.40 for well water 1, well water 2, and Missouri River water, respectively. Since the optima pH range for alum coagulation is 6–7, in general acid is used in addition of the coagulant during drinking water treatment process to reduce the amount of coagulant needed and effectively lower chemical costs. Turbidity decreased significantly after coagulation for well water 1 and Missouri River water, indicating an efficient coagulation process. The detailed results of pH, UV_{254} absorption, and turbidity change before and after each treatment are shown in Table 5.

Table 3 – Ammonia and N-nitrosamine precursor removal in ultra-high purity water (spiked with 8 mg/L ammonia and 25 μg/L each of N-nitrosamine precursors) by Mordenite zeolite (1000 mg/L). Contact time for the removal was 30 min.

Sample ID	Mordenite (mg/L)	% Removal/lost							
		DMA	EMA	TMA	DEA	DPA	DMAI	DMAP	Ammonia-N
Control	0	2.1	8.5	5.9	8.7	16.4	10.7	3.4	24.9
Sample	1000	100.0	97.1	95.9	100.0	98.3	98.5	0.0	75.1
Sample duplicate	1000	100.0	97.3	95.7	100.0	98.3	98.6	0.0	75.1

DMA: dimethylamine; EMA: ethylmethylamine; TMA: trimethylamine; DEA: diethylamine; DPA: dipropylamine; DMAI: (dimethylaminomethyl)indole; DMAP: dimethylaminoantipyrine.

Table 4 – Ammonia and N-nitrosamine precursor removal efficiency by Mordenite zeolite (100 mg/L) in well water 1 (after aeration but before lime softening) with ammonia (1.5 mg/L) and N-nitrosamine precursor (20 μg/L each) at different pHs.

Sample ID	pH	Mordenite (mg/L)	% Removal/lost							
			Ammonia	DMA	TMA	EMA	DEA	DPA	DMAI	DMAP
Well water 1–control	8.08	0	0.0	0.0	0.0	21.7	7.2	7.0	1.2	1.9
Well water 1–6	6.02	100	11.8	26.2	15.5	36.1	22.9	56.4	3.1	1.2
Well water 1–7	6.93	100	13.5	26.0	11.5	30.9	24.8	50.8	5.1	8.2
Well water 1–8	8.08	100	13.5	45.0	16.2	40.2	25.3	59.8	5.4	5.3
Well water 1–9	8.96	100	4.7	34.8	17.7	58.1	29.2	75.2	9.5	6.8
Well water 1–10	9.96	100	0.0	55.1 (0.3)	23.1 (1.1)	65.9 (7.3)	34.5 (2.7)	65.2 (9.3)	21.5 (2.6)	7.6 (9.1)
(%RPD[a], n = 2)	(0.0)		(N/A[b])							
Well water 1–11	10.97	100	0.0	51.4	47.2	72.3	42.4	68.5	21.3	7.8

[a] RPD means relative percent difference of duplicated samples.
[b] N/A means not applicable.

Ammonia and N-nitrosamine precursor removal after the different treatments in each type of water is shown in Table 6. In the experiment with well water 1, duplicates were conducted for samples with the addition of alum and Mordenite, or alum, PAC and Mordenite. In the experiment with well water 2 and Missouri river water, four replicates were conducted for the above mentioned samples. Acceptable reproducibility for the removal of ammonia and N-nitrosamine precursors was achieved in all three types of water matrices with the percent of relative standard deviation ranging from 0.0 to 21.3%. Without Mordenite addition during alum coagulation, no ammonia removal was observed and less than 25% of the precursors were removed except for DMAI and DMAP in samples treated with PAC. When Mordenite was added during alum coagulation without PAC addition, more than 67% ammonia and 70%–100% precursors were removed except DMAI and DMAP, indicating that the addition of alum did not affect the ion exchange sites on the zeolite.

During alum coagulation with PAC sorption process, more than 67% of ammonia was removed when Mordenite was added. N-nitrosamine precursor removal was similar to the test results without PAC addition, except for DMAI and DMAP. When PAC was added, more than 73% DMAI and 40% DMAP were removed. PAC is a highly porous material with a large surface area to which natural organic matter can adsorb, especially hydrophobic compounds (Nam et al., 2014). Therefore, DMAI and DMAP were removed when PAC was added, similar to results from a previous study (Wu et al., 2015b). Due to its non-polar surface, PAC did not have much adsorption of ammonia (Halim et al., 2010). In the samples dosed with alum, PAC, and Mordenite, more than 75% precursors were removed except DMAP (43% removal). This demonstrated that the combination of Mordenite and PAC was an efficient way for the control of both ammonia and N-nitrosamine precursors. Alum coagulation did not show negative effect on the adsorption process of both Mordenite zeolite and PAC.

Table 5 – Values of pHs, UV_{254} absorption, turbidity of water matrices tested after different treatments.

Water samples	Treatments[a]	[c]pH (%RSD[b])	UV_{254} absorption (%RSD)	Turbidity (NTU) (%RSD)
Well water 1	No treatment (n = 1)	7.72	0.0824	129.5
(after aeration before lime softening)	Alum (n = 1)	7.68	0.0552	0.4
	Alum + PAC (n = 1)	7.56	0.0455	0.2
	Alum + Mordenite (n = 2)	7.45 (0.7)	0.0575 (8.0)	2.4 (12.2)
	Alum + PAC + Mordenite (n = 2)	7.40 (0.5)	0.0488 (3.1)	2.4 (11.3)
Well water 2	No treatment (n = 1)	9.55	0.0516	2.3
(after lime softening before recarbonation)	Alum (n = 2)	7.07 (0.7)	0.0421 (1.0)	0.4 (2.6)
	Alum + PAC (n = 2)	7.04 (0.4)	0.0332 (8.4)	0.3 (7.4)
	Alum + Mordenite (n = 4)	7.06 (0.7)	0.0452 (6.0)	1.9 (18.4)
	Alum + PAC + Mordenite (n = 4)	7.02 (0.1)	0.0372 (4.3)	1.4 (15.9)
Missouri River water	No treatment (n = 1)	7.40	0.1335	324.0
	Alum (n = 2)	6.95 (1.2)	0.0929 (6.1)	0.5 (8.7)
	Alum + PAC (n = 2)	7.06 (0.4)	0.0808 (6.8)	0.7 (14.5)
	Alum + Mordenite (n = 4)	7.16 (0.3)	0.0999 (1.2)	2.2 (20.6)
	Alum + PAC + Mordenite (n = 4)	7.16 (0.2)	0.0904 (2.9)	2.0 (17.3)

PAC: powdered activated carbon.
[a] Water treatments included alum (50 mg/L) coagulation, alum (50 mg/L) coagulation with PAC (20 mg/L) addition, alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L), and alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L) and PAC (20 mg/L).
[b] RSD means relative standard deviation of replicated samples.
[c] pHs for all three types of water matrix were adjusted to be around 7 with sodium hydroxide or sulfuric acid after the addition of alum.

Table 6 – Percent removal/lost of ammonia and N-nitrosamine precursors in different water matrices after different types of water treatments.

Water samples	Treatment[a]	% Removal/lost (%RSD[b])							
		Ammonia	DMA	TMA	EMA	DEA	DPA	DMAI	DMAP
Well water 1	No treatment (n = 1)	0.0	0.3	0.5	0.0	0.0	0.0	0.0	0.5
(after aeration before lime softening)	Alum (n = 1)	0.0	6.0	0.7	0.0	0.0	0.0	1.4	3.1
	Alum + PAC (n = 1)	0.0	0.5	1.4	6.6	0.0	0.0	77.9	42.9
	Alum + Mordenite (n = 2)	67.7 (0.8)	100.0 (0.0)	82.1 (1.3)	92.2 (4.6)	91.9 (1.0)	100.0 (0.0)	0.0 (N/A)	0.2 (6.1)
	Alum + PAC + Mordenite (n = 2)	67.2 (1.2)	100.0 (0.0)	83.4 (1.2)	87.3 (1.4)	88.1 (3.1)	100.0 (0.0)	79.1 (1.8)	43.4 (0.3)
Well water 2	No treatment (n = 1)	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
(after lime softening before recarbonation)	Alum (n = 2)	0.0 (N/A[c])	12.3 (7.6)	3.2 (7.4)	1.9 (1.0)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	1.4 (9.5)
	Alum + PAC (n = 2)	0.0 (N/A)	18.9 (11.2)	3.6 (20.0)	15.5 (0.6)	1.1 (7.0)	17.9 (3.0)	83.7 (5.0)	55.3 (12.3)
	Alum + Mordenite (n = 4)	74.2 (0.3)	99.1 (13.5)	86.6 (0.9)	98.0 (1.8)	95.0 (2.1)	100.0 (0.0)	8.4 (8.9)	0.0 (N/A)
	Alum + PAC + Mordenite (n = 4)	74.0 (0.5)	94.9 (11.0)	85.2 (2.1)	95.9 (7.5)	95.7 (0.6)	100.0 (0.0)	86.5 (0.8)	56.4 (5.1)
Missouri River water	No treatment (n = 1)	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.6
	Alum (n = 2)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	6.4 (7.8)	0.0 (N/A)	3.6 (0.9)
	Alum + PAC (n = 2)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	0.0 (N/A)	10.6 (18.3)	72.6 (20.3)	39.7 (14.4)
	Alum + Mordenite (n = 4)	69.8 (8.4)	97.5 (2.0)	85.5 (1.2)	78.0 (12.2)	94.5 (0.5)	100.0 (0.0)	5.3 (21.3)	3.3 (19.7)
	Alum + PAC + Mordenite (n = 4)	67.2 (2.4)	98.1 (1.9)	85.1 (2.0)	92.2 (3.0)	95.1 (1.2)	100.0 (0.0)	83.8 (5.8)	44.1 (5.3)

[a] Water treatments included alum (50 mg/L) coagulation, alum (50 mg/L) coagulation with PAC (20 mg/L), alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L), and alum (50 mg/L) coagulation with Mordenite zeolite (1000 mg/L) and PAC (20 mg/L).

[b] RSD means relative standard deviation.

[c] N/A means not applicable.

3. Conclusions

In this study, ammonia removal efficiencies by using different types of zeolites including Bear River zeolite, modified Bear River zeolite, Mordenite zeolite, and Zeolite Y was investigated in high ammonia water. Mordenite zeolite was demonstrated to be the most efficient adsorbent for ammonia removal. The removal of ammonia by Mordenite was very fast and reached equilibrium in about 5 min. pHs lower than the pKa value of ammonia (6, 7, and 8) and temperature (2°C, room temperature, 40°C) did not show significant effects on the removal efficiencies. Mordenite zeolite was subsequently used to study the simultaneous removal of N-nitrosamine precursors and ammonia in ultra-high purity water spiked with ammonia and N-nitrosamine precursors during small-scale tests, and in real water samples with concentration adjustment of ammonia and N-nitrosamine precursors during simulated drinking water treatments. The simulated drinking water treatments included lime softening and alum coagulation with and without PAC addition. The lime softening process had negative effects on the removal of ammonia by Mordenite zeolite due to increased pH (up to 11) and the low pK_a (9.4) of ammonia. Above pH 9.4, ammonia existed in molecular form and seemed to be no longer participating in ion exchange. Mordenite zeolite efficiently removed most of the ammonia and N-nitrosamine precursors (except DMAI and DMAP) during alum coagulation without PAC. PAC showed a good removal efficiency for aromatic and less hydrophilic amines DMAI and DMAP. Therefore, the combination of two types of adsorbents is a good choice for removal of ammonia and N-nitrosamine precursors from drinking water system.

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