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# Capability of cation exchange technology to remove proven N-nitrosodimethylamine precursors

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## ABSTRACT

N-nitrosodimethylamine (NDMA) precursors consist of a positively charged dimethylamine group and a non-polar moiety, which inspired us to develop a targeted cation exchange technology to remove NDMA precursors. In this study, we tested the removal of two representative NDMA precursors, dimethylamine (DMA) and ranitidine (RNTD), by strong acidic cation exchange resin. The results showed that pH greatly affected the exchange efficiency, with high removal (DMA > 78% and RNTD > 94%) observed at pH < pK<sub>a</sub>-1 when the molar ratio of exchange capacity to precursor was 4. The exchange order was obtained as follows: Ca<sup>2+</sup> > Mg<sup>2+</sup> > RNTD<sup>+</sup> > K<sup>+</sup> > DMA<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup>. The partition coefficient of DMA<sup>+</sup> to Na<sup>+</sup> was 1.41 ± 0.26, while that of RNTD<sup>+</sup> to Na<sup>+</sup> was 12.1 ± 1.9. The pseudo second-order equation fitted the cation exchange kinetics well. Bivalent inorganic cations such as Ca<sup>2+</sup> were found to have a notable effect on NA precursor removal in softening column test. Besides DMA and RNTD, cation exchange process also worked well for removing other 7 model NDMA precursors. Overall, NDMA precursor removal can be an added benefit of making use of cation exchange water softening processes.

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## Introduction

Since N-nitrosodimethylamine (NDMA) was first detected in treated drinking water in Ontario, Canada in 1989 (Taguchi et al., 1994), nine kinds of main nitrosamines (NAs) have been identified as emerging disinfection by-products (DBPs) in drinking water, NDMA, N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitroso-di-n-propylamine (NDPA), N-nitroso-di-n-butylamine (NDBA), N-nitroso-di-phenylamine (NDPhA), N-nitrosopyrrolidine (NPYR), N-nitrosopiperidine (NPPI) and N-nitrosomorpholine (NMOR) (Mitch et al., 2003a; Zhao et al., 2006). Recent years,

some new nitrosamines also have been detected as DBPs (Wu et al., 2014). These NAs present much higher carcinogenicity than traditional DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Mitch et al., 2003a; Richardson et al., 2007; Wagner et al., 2012; Daniel et al., 2016). According to previous studies, NDMA is one of the most commonly detected nitrosamines and occurs in the highest concentration (Asami et al., 2009; Najm and Trussell, 2001; Charrois et al., 2007; Luo et al., 2012; Wang et al., 2012, 2015; Bei et al., 2016a). Moreover, the level of NDMA with a 10<sup>-6</sup> lifetime cancer risk is only 0.7 ng/L (USEPA, 2002), indicating that the carcinogenicity of NDMA is thousands of times higher than that of THMs. Because of this

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high toxicity, several countries and regions around the world have been setting standards for NAs in drinking water at the ng/L level. For example, the NDMA criteria in drinking water standards in Ontario, Canada were 9 ng/L, while the notification level in California in the United States was set at 10 ng/L. The forthcoming NA regulation has presented large challenges to water treatment plants (WTPs) worldwide, especially for those with high concentrations of NA precursors in source water (Krasner et al., 2013; Wang et al., 2013). Moreover, these NAs, especially NDMA, have a low molecular weight, with a strongly hydrophilic, stable structure that is uncharged, making their removal extremely difficult by conventional and advanced treatment processes.

As demonstrated in previous studies, one basic and effective strategy to control NA formation in drinking water is the removal and/or destruction of NA precursors (Liao et al., 2014, 2015a). To better understand NA precursors, many studies have been conducted to identify these chemicals in source water, wastewater and human consumptions over the last decade. Researchers have identified dozens of chemicals as NA precursors, including secondary amines (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Mitch et al., 2003b; Wang et al., 2011), water treatment coagulants (Krasner et al., 2013; Padhye et al., 2011), pharmaceutical and personal care products (PPCPs) (Shen and Andrews, 2011), pesticides (Bei et al., 2016b; Le Roux et al., 2011; Schmidt and Brauch, 2008), organic matter in effluent of wastewater treatment plants (EfOM) (Kosaka et al., 2010; Wang et al., 2014), certain industrial chemicals (Wang et al., 2014), algal organic matter (AOM) and natural organic matter (NOM) (Chen and Valentine, 2007; Gerecke and Sedlak, 2003). The long list of known NA precursor chemicals was site specific and continually updated every year.

A conclusion that could be drawn from previous investigations is that an NA precursor can be constructed with a protonated dialkylamine functional group and non-polar moiety (Chen et al., 2014; Liao et al., 2015b). This general structure inspired us to develop a targeted water treatment technology of cation exchange. Actually, the pKa of different NA precursors was usually higher than pH 7, indicating that these precursors will protonate and become positively charged under neutral pH (Chen et al., 2014). Thus, the cation exchange process could be used as a promising treatment technology to remove NA precursors before their reaction with chloramines or other disinfectants to yield NA. By far, the largest application of ion exchange in the water treatment industry is water softening, which is used to remove cations of calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ) and other polyvalent cations (Edzwald, 2011). Ion exchange has also been applied as an effective technology to remove trace levels of radionuclides, such as radium ( $^{226}\text{Ra}$  or  $^{228}\text{Ra}$ ) (Edzwald, 2011). The removal of positively charged NA precursors could be a new application of cation exchange technology.

There are some previous studies related with ion exchange and NDMA or its precursors. Gan et al. (2013) reported an increase in NDMA FP after the MIEEX® process but only for the effluent impacted waters. As a common chemical industry reagent rather than NDMA precursor, dimethylamine (DMA) has been investigated for its removal by ion exchange (Hu et al., 2011). This investigation reported the adsorption

capacity, kinetic, pH effect and some thermodynamic parameters by one cation exchange resin at high level of g/L.

This study was conducted to develop a targeted NA precursor removal technology of cation exchange. We tested the removal efficiency of two representative model NDMA precursors, DMA and ranitidine (RNTD), by one strong acidic cation exchange resin. We then evaluated the influence of pH, resin dosage and inorganic cation on this process. We also conducted a column test to understand the performance of NA precursor removal in a real application scenario. In the investigation, the basic parameters of cation exchange operation were determined, including the partition coefficient and kinetic rate constant. Besides the two representative chemicals, 7 other model NDMA precursors were also evaluated for removal efficiency by cation exchange resin treatment.

## 1. Materials and methods

### 1.1. Reagents

One commercial strong acidic cation exchange resin, Model 001 × 7 (similar to Amberlite IR-120 resin, Rohn & Haas Corp., Philadelphia, PA, USA), was purchased from NANKAI RESINCO Limited Corp., Shanghai, China. Its basic properties are summarized in Table 1. Following the manual, we used hydrochloric acid (HCl) and sodium hydroxide (NaOH) to clean the resin and convert it into a  $\text{Na}^+$  form.

DMA (Meryer Chemical Technology Co. Ltd., Shanghai, China) and RNTD (Sigma-Aldrich, Saint Louis, MO, USA) were used as the representative NA precursors in this study. DMA is the simplest NDMA precursor and RNTD is a very productive NDMA precursor, with a high molar yield over 80%. Other 7 model NDMA precursors, i.e., *N,N*-dimethylbutylamine (Sigma-Aldrich, Saint Louis, MO, USA), *N,N*-dimethyloctylamine (Sigma-Aldrich, Buchs, St. Gallen, Switzerland), *N,N*-dimethylisopropylamine (Tokyo Chemical Industry, Shanghai, China), *N,N*-dimethylaniline (Alfa Aesar, Tianjin, China), *N,N*-dimethylbenzylamine (Sigma-Aldrich, Munich, Bavaria, Germany), *N,N*-dimethylphenethylamine (Sigma-Aldrich, Saint Louis, MO, USA) and doxylamine (Sigma-Aldrich, Milan, Italy) were also used to evaluate the efficiency of ion exchange process. The properties of these compounds are summarized in the (Appendix A Table A1).

Stock solutions of nine precursor compounds were prepared with Milli-Q ultra-pure water. The pH of the solution

**Table 1 – Main properties of cation exchange resin.**

Properties	Model 001 × 7
Mode	Gel
Resin matrix	Styrene, divinyl benzene
Exchange groups	– $\text{SO}_3\text{H}$
Total exchange capacity (meq/g, dry)	4.7
Volume exchange capacity (meq/mL)	1.9
Moisture retention (%)	45–50
Specific gravity	1.24–1.28
Effective diameter (mm)	0.50–0.80
Uniformity coefficient ≤	1.7
Note: meq indicates mmol of electron equivalent.	

was adjusted by the addition of NaOH (Guaranteed reagent, GuangFu Corp., Tianjin, China) or HCl (Guaranteed reagent, GuangFu Corp., Tianjin, China) solution. Standard solutions of inorganic ions, such as  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  (1000 mg/L, ion chromatography level), were supplied by O2SI Smart Solution (Charleston, SC, USA).

## 1.2. Analyte detection methods

The RNTD concentration in Milli-Q water was detected by a UV–Visible spectrophotometer (UV-2700, Shimadzu, Kyoto, Japan) with a specific absorbance wavelength at 313 nm (Appendix A Fig. A1) as previously described (Chen et al., 2014). The detection limit of RNTD was 0.2  $\mu\text{mol/L}$ . The concentration of DMA in Milli-Q water was detected by a Total Nitrogen (TN) analyzer (TOC-V<sub>CPH</sub> with TNM-1 device, Shimadzu, Kyoto, Japan) since there was no interference by other organic materials observed in these experiments. The detection limit of DMA was 20  $\mu\text{mol/L}$ . The concentration of other 7 model NDMA precursors were also determined by TN analyzer.

Compared with the HPLC detection of RNTD (Arayne et al., 2010) and DMA (after pre-column derivatization with phenyl isothiocyanate) (Sacher et al., 1997), the detection methods used in this study performed much higher detection level. However, the basic exchange behaviors of cations, including pH effect, kinetic, partition coefficient and exchange sequence, were independent of their concentration. Thus, the detection method of spectrophotometer for RNTD and TN for DMA can also help us understand the efficiency of cation exchange for the removal of these NA precursors.

The concentration of inorganic cation ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) was determined using an ion chromatograph (ICS-5000, Dionex, Sunnyvale, CA, USA) with a Dionex IonPac™ CS12A chromatographic column (4 × 250 mm). The following chromatographic parameters were applied: eluent, 20 mmol/L methanesulfonic acid; eluent flow, 1.0 mL/min; injection volume, 25  $\mu\text{L}$ .

## 1.3. Experimental procedures

### 1.3.1. Effect of pH

Controlled varying amounts of resin were added into NDMA precursor (DMA or RNTD) standard solutions. The final concentrations of resin and DMA or RNTD were 2 mmol/L and 1 mmol/L, respectively. The pHs of DMA solutions were adjusted to pHs of 6–12, in range of DMA's  $\text{pK}_a$  of 10.64. The pHs of the RNTD solutions were adjusted to 5–11, in range of RNTD's  $\text{pK}_a$  of 8.2. Mixtures of resin and precursor solution were then put into a batch of 500 mL amber bottles (Schott, Mainz, Germany) and exchanged by continuous shaking at 60 rpm with a rotary shaking instrument for 24 hr at 25°C (Lin et al., 2015). The mixture was then filtered through a glass fiber membrane and the residual concentration of DMA or RNTD in the filtrate was measured.

### 1.3.2. Ion exchange kinetics

To evaluate the kinetics of ion exchange in this method, controlled doses of resin were added into 1 L of DMA solution (1 mmol/L) at pH 6.0 ± 0.2 or RNTD solution (1 mmol/L) at

pH 5.0 ± 0.2. The mixture was stirred with a jar tester (ZR4–6, ZhongRun Corp., Shenzhen, China) at 400 r/min to ensure the solution was mixed well. Aliquots of 10–20 mL were taken in (15–60 min) intervals, at which time DMA or RNTD concentrations were quantified.

### 1.3.3. Ion exchange isotherm

For the adsorption isotherm test, various dosages of cation exchange resin (0, 0.5, 1, 2, 3, 4, 6 meq/L) were added into 1 meq/L DMA<sup>+</sup> solution at pH 6.0 ± 0.2 or 1 mmol/L RNTD<sup>+</sup> at pH 5.0 ± 0.2 in a batch of 500 mL amber bottles. The optimum pH was determined by Experiment 1.3.1. The initial concentrations of Na<sup>+</sup> and DMA or RNTD were detected before ion exchange. The mixture was well exchanged by continuous shaking with a rotary shaking instrument at 60 r/min for 24 hr at 25°C. The resin was then filtered from the solution using a glass fiber filter, after which the residual concentrations of Na<sup>+</sup> and DMA or RNTD in the filtrate were detected.

The removal efficiency of cation exchange process for other 7 model NDMA precursors were also tested under one resin dosage. The initial concentration of each NDMA precursor was 1 mmol/L, the resin dosage was 2 mmol/L, and the pH was adjusted to  $\text{pK}_a - 1$  for each precursor, respectively.

### 1.3.4. Competitive effect of inorganic cations

To investigate the effects of inorganic cations on NA precursor removal, 1 meq/L resin was added into the solution with 1 meq/L of DMA<sup>+</sup> or RNTD<sup>+</sup> solution under a consistent pH and 1 meq/L of one individual inorganic cation. The pH was set at pH 6.0 ± 0.2 for DMA<sup>+</sup> or pH 5.0 ± 0.2 for RNTD<sup>+</sup>. The inorganic cations included 1 mmol/L of  $\text{NH}_4^+$ , 1 mmol/L of  $\text{K}^+$ , 0.5 mmol/L of  $\text{Mg}^{2+}$  and 0.5 mmol/L of  $\text{Ca}^{2+}$ . The mixture solution was well exchanged by continuous shaking with a rotary shaking instrument at 60 r/min for 24 hr at 25°C, after which the resin was filtered from the solution and the residual concentrations of Na<sup>+</sup> and DMA or RNTD in the filtrate were detected.

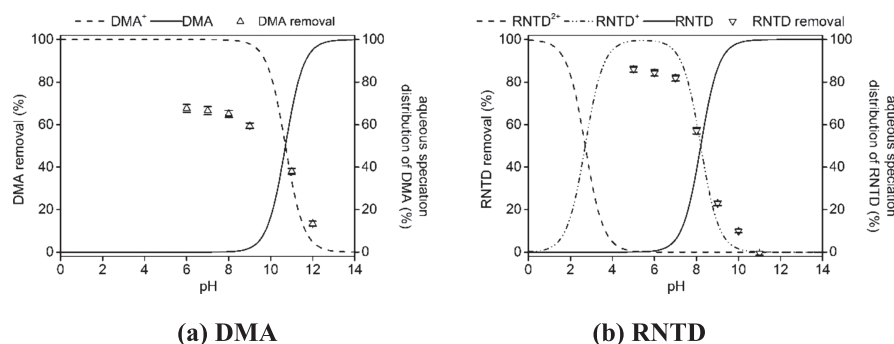
### 1.3.5. Water-softening ion-exchange column testing

To test the efficacy of NDMA precursor removal by water softening ion exchange column, a plexiglass column (diameter = 6 mm, height = 150 mm) filled with cation resin (Na<sup>+</sup> form) and a peristaltic pump (BT100–1 L, LanGe Corps., Baoding, Hebei Province, China) were used. Briefly, 3.1 meq/L RNTD<sup>+</sup> at pH 5.0 ± 0.2 with or without 1.55 mmol  $\text{Ca}^{2+}$  (3.1 meq/L) at pH 5.0 ± 0.2 were fed into the exchange column at a flow velocity of 15.4 m/hr according to normal operation of exchange process. The concentrations of RNTD in the effluent were detected after a prescribed time.

## 2. Results and discussion

### 2.1. Effect of pH on NDMA precursors removal by ion exchange

To investigate the effects of pH on the ion exchange process, controlled dose of resin was added into the prepared NDMA precursor solution at different pHs. The results are shown in Fig. 1.



**Fig. 1 – Removal of N-nitrosodimethylamine (NDMA) precursors under different pH and speciation distribution of precursor.** Precursor initial concentration = 1 mmol/L, resin dosage = 2 meq/L, ion exchange time = 24 hr, speed of rotary shaking instrument = 60 r/min, temperature = 25°C.

The removal of representative NDMA precursors (DMA or RNTD) by cation exchange resin is greatly influenced by pH. The DMA removal by a modest dosage of resin (2 mmol/L, two molar equivalents of NDMA precursor) reached over 60% at pH < 9, while it decreased rapidly to 13% at pH 12 (Fig. 1a). The RNTD removal reached over 80% at pH < 7, while the removal decreased completely to 0% at pH 11. It should be noted that the precursor removal was lower than the proportion of their cations, because not all the cations precursors can exchange onto the resin when considering ion exchange equilibrium, especially when the exchange capacity (2 times of precursor) was not sufficient.

The effect of pH on NDMA precursor removal is attributed to the protonation of these chemicals when pH < pK<sub>a</sub>-1. The removal of each NDMA precursor corresponded well with the proportion of cation molecule. As shown in Fig. 1b, at pH 5, over 99% of the RNTD presented as one valence cation (RNTD<sup>+</sup>) and a relatively high removal of RNTD by ion exchange was observed. At pH 11, all RNTD molecules exist as a neutral molecule; thus, there was almost no removal of RNTD. The same situation occurred for DMA.

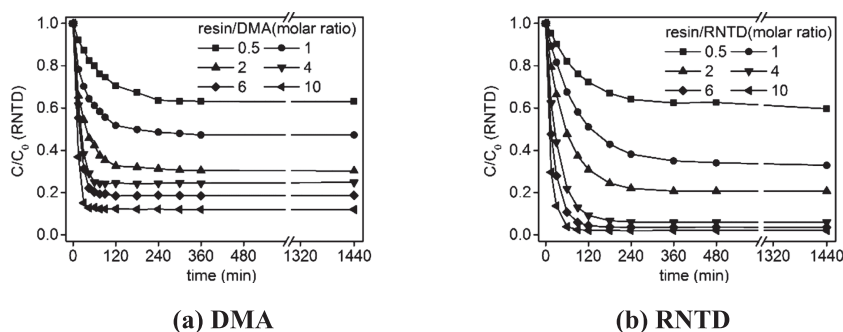
In the following studies, the optimum pH condition for ion exchange was set as 6.0 for DMA and 5.0 for RNTD when the precursors existed in the form of cations.

## 2.2. Kinetic study of removal of NDMA precursors by ion exchange

The kinetic curves of the removal of two NA precursors are shown in Fig. 2. The calculation of rate constant is shown in Appendix A Fig. A2.

The molar ratio of resin to NDMA precursor affects the equilibrium time greatly. The equilibrium time of the RNTD kinetic curves decreased from 360 to 60 min as the ratio of resin capacity to precursor increased from 0.5 to 10, while that of DMA kinetic curves decreased from 240 to 45 min as the ratio of resin capacity to precursor increased from 0.5 to 10. The DMA removal is faster than that of RNTD with the same ratio of resin capacity to precursor, which could be explained by the smaller DMA molecule diffusing faster in water than RNTD.

Both the removal of DMA and RNTD could be fit well by the pseudo second-order model, and the linear correlations coefficients were very strong (Table 2). The results of rate constant *k* from experiments with different ratios of resin capacity to precursor were quite similar, which also reinforces the accuracy of this model. The *k* of DMA (0.0088 L/mmol/min) was higher than that of RNTD (0.0074 L/mmol/min). The rate constant could be used to guide the exchange process.



**Fig. 2 – Kinetics curves of ion exchange process of the two nitrosamine (NA) precursors.** Precursor initial concentration = 1 meq/L, resin dosage = 0.5, 1, 2, 4, 6, 10 meq/L for both NDMA precursors, pH = 6.0 ± 0.2 for dimethylamine (DMA) and 5.0 ± 0.2 for ranitidine (RNTD), stirring rate of jar tester = 400 r/min, temperature = 25°C. The relative standard deviations of duplicate tests of each data were less than 5%. Error bars were not included to improve the readability of this figure.

**Table 2 – Parameters of pseudo second-order kinetic model.**

Precursor	Resin capacity to precursor	$C_{A0}-C_{B0}$ (meq/L)	Slope	$R^2$	Rate constant $k$ (L/mmol/min)	Average $k$ (L/mmol/min)
DMA	0.5	−0.500	−0.0048	0.96	0.0096	0.0088±0.0006
	2	1.000	0.0087	0.92	0.0087	
	4	3.000	0.0258	0.95	0.0086	
	6	5.000	0.0397	0.98	0.0079	
	10	9.000	0.0771	1.00	0.0086	
	1	–	0.0091	0.92	0.0091	
RNTD	0.5	−0.518	−0.0041	0.99	0.0079	0.0074±0.0004
	2	0.982	0.0067	0.97	0.0069	
	4	2.982	0.0230	0.99	0.0077	
	6	4.982	0.0377	0.98	0.0076	
	10	8.982	0.0656	0.98	0.0073	
	1	–	0.0073	0.99	0.0073	

Note: Calculation of rate constant  $k$  was introduced in Appendix A2.4 Data processing.  
The slope with negative value was because  $C_{A0}-C_{B0}$  is less than 0.

### 2.3. Effect of resin exchange capacity on removal and determination of partition coefficient

To study the effects of resin exchange capacity on NDMA precursor removal and calculate the partition coefficient, a batch of isotherm experiments was conducted with various resin dosages (Table 3 and Appendix A Fig. A3).

High removal of monovalent NDMA precursor (78% of DMA or 94% of RNTD) was observed when the resin exchange capacity to precursor was just over 4:1. The results confirmed that cation exchange could be applied as an efficient technology for NDMA precursor removal during water treatment.

The removal of RNTD was higher than that of DMA with the same capacity, as indicated by the calculated partition coefficients shown in Table 3. The  $K_{A^+B^+}$  of  $DMA^+$  to  $Na^+$  is  $1.41 \pm 0.26$ , and that of  $RNTD^+$  is  $12.1 \pm 1.9$ , which means the affinity of resin to  $RNTD^+$  is much higher than that of resin to  $DMA^+$  and that  $Na^+$  presents the least affinity. Therefore, the cation exchange resin in  $Na^+$  form can be applied to remove  $DMA^+$  and  $RNTD^+$ .

It should be noted that the concentration of NDMA precursors is in the trace level of nmol/L, while that of  $Na^+$  is approximately 1 mmol/L in actual source water. With sufficient

exchange capacity of resin, the background  $Na^+$  should have little effect on the ion exchange efficiency of NDMA precursors. To explain this, we assumed 1 volume of  $001 \times 7$  resin could treat 900 volumes of source water in the continuous stirring tank reactor, just as in the jar test. According to Hsu (2000), the common cation concentrations in China were listed as below:  $Na^+$  (1–4 mmol/L),  $Ca^{2+}$  (0.5–1 mmol/L). Given the concentrations of  $Na^+$  (1 mmol/L),  $Ca^{2+}$  (1 mmol/L), DMA (1 nmol/L) or RNTD (1 nmol/L) and absence of any other cations (their influence is discussed in the following sections) in this water, we can calculate that the removal of DMA was 49.8% and that of RNTD was 89.5%, based on their partition coefficients (calculation was included in the Appendix).

### 2.4. Competitive effect of inorganic cations

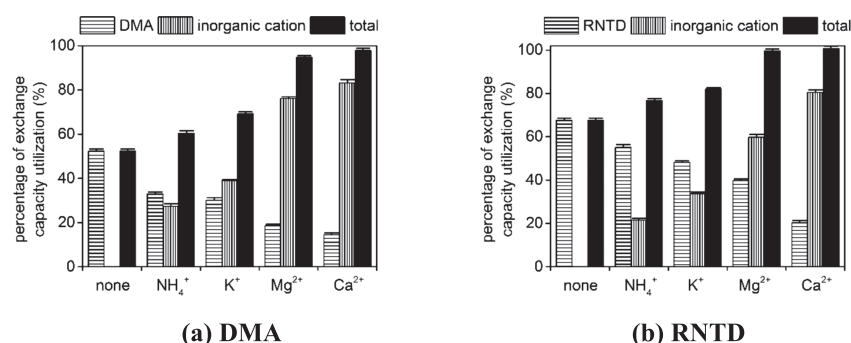
The impact of competitive inorganic cations on the removal of precursor by ion exchange was detected under the condition of limited capacity, as shown in Fig. 3.

The co-existence of inorganic cations impaired the removal of NDMA precursors to different extents when the resin dosage was limited. The removal of DMA decreased from 0.52 to 0.33 (37% reduction), 0.30 (42% reduction), 0.19 (63%)

**Table 3 – Partition coefficient of  $DMA^+$  or  $RNTD^+$  to  $Na^+$  with  $001 \times 7$  strong acidic cation exchange resin.**

Precursor	Resin capacity/ precursor	( $B^+$ ) (meq/L)	( $A^+$ ) (meq/L)	( $R^-B^+$ ) (meq/L)	( $R^-A^+$ ) (meq/L)	$K_{A^+B^+}$	$\bar{K}_{A^+}^{B^+}$
DMA	0.5	0.63	0.71	0.32	0.20	1.77	1.41 ± 0.26
	1	0.46	0.79	0.49	0.52	1.63	
	2	0.31	0.95	0.63	1.35	1.43	
	3	0.26	1.19	0.69	2.31	1.38	
	4	0.22	1.10	0.72	3.30	1.09	
	6	0.19	1.59	0.75	5.24	1.17	
RNTD	0.5	0.61	1.30	0.41	0.09	9.53	12.1 ± 1.9
	1	0.34	2.02	0.68	0.31	13.4	
	2	0.14	2.71	0.88	1.13	15.0	
	3	0.08	2.01	0.93	2.08	10.8	
	4	0.06	2.25	0.96	3.04	11.6	
	6	0.04	2.33	0.98	5.02	12.4	

Note:  $A^+$  is  $Na^+$  and  $B^+$  is the NDMA precursor cation. Initial concentration of DMA or RNTD was 1 mmol/L. temperature = 25°C, pH =  $6.0 \pm 0.2$  for DMA and  $5.0 \pm 0.2$  for RNTD. The calculation of  $\bar{K}_{A^+}^{B^+}$  was introduced in Appendix A2.4 Data processing.



**Fig. 3 – The effect of inorganic cations on the removal of NDMA precursor with limited capacity. Precursor cation initial concentration = 1 meq/L, inorganic cation concentration = 1 meq/L, resin dosage = 1 meq/L, pH = 6.0 ± 0.2 for DMA<sup>+</sup> and 5.0 ± 0.2 for RNTD<sup>+</sup>, ion exchange time = 24 hr, Speed of rotary shaking instrument = 60 r/min, temperature = 25°C.**

reduction) and 0.15 (71% reduction) meq/L without or with the impact of 1 meq/L of NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, respectively, while the removal of RNTD decreased from 0.68 to 0.55 (19% reduction), 0.48 (29% reduction), 0.40 (41% reduction) and 0.20 (71% reduction) meq/L. The divalent cations have a stronger affinity to resin, so they have a more notable impact on NDMA precursor removal. Moreover, the decrease of DMA removal was larger than that of RNTD with the same competitive cation, which agrees with the results in Section 2.2 showing that RNTD<sup>+</sup> presents higher affinity to resin than DMA<sup>+</sup>.

The exchange order of the two NDMA precursors and four common inorganic cations can be determined according to their removal (Fig. 3). The following exchange sequence was obtained: Ca<sup>2+</sup> > Mg<sup>2+</sup> > RNTD<sup>+</sup> > K<sup>+</sup> > DMA<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup>. There was also an increase in total consumption of the exchange capacity in Fig. 3 with co-existence of competing cation, which means more exchange sites of resin were occupied by the excessive cation. With the co-existence of Ca<sup>2+</sup> or Mg<sup>2+</sup>, the removal of precursor decreased greatly and the total consumption of exchange capacity was over 95%. Generally, the exchange sequence of different inorganic cations to strong acidic cation exchange resin is as follows: Fe<sup>3+</sup> > Al<sup>3+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> > K<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup>. Thus, the high valent cations have significant effects on NDMA precursor removal by the ion exchange process.

In addition to the ion exchange interaction, other weak interactions between precursor molecules and resin material, such as hydrogen bonds and van der Waals forces, may also contribute to precursor removal (Zagotodni, 2007). A previous study reported that hydrophobic interactions may be the main reason anionic proteins could be fixed by the zeolite despite the electrostatic repulsion (Matsui et al., 2001). When comparing RNTD and DMA, the former has a larger molecular weight and a larger non-polar moiety. Thus, the non-polar interactions or hydrophobic interactions between RNTD molecule and resin matrix are larger than that of DMA. As a result, the resin showed better removal of RNTD than DMA.

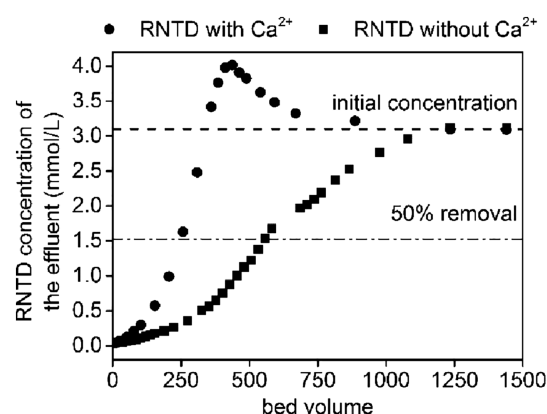
## 2.5. Column test of NDMA precursor removal by ion exchange

Softening is the most common application of cation exchange in water treatment. Therefore, we investigated NDMA

precursor removal by a cation exchange softening column, as shown in Fig. 4. When compared with aforementioned batch operation, column operation can remove the ion more completely and quickly by the successive ion exchange process from the top to bottom of the column.

The curve of the RNTD concentration in effluent presented complete breakthrough after about 1200 BV (bed volume) and 50% removal after about 600 BV. That with the co-existing Ca<sup>2+</sup> presented a complete breakthrough after about 350 BV and 50% removal after about 250 BV. As the exchange capacity got depleted, the adsorbed RNTD was eluted from the column by the co-existence of Ca<sup>2+</sup> in feeding water.

These results coincide with Section 2.4 that Ca<sup>2+</sup> has a higher affinity to cation exchange resin than RNTD<sup>+</sup>. When treating multiple cations in actual water samples, the following exchange order needs to be noted: Fe<sup>3+</sup> > Al<sup>3+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> > RNTD<sup>+</sup> > K<sup>+</sup> > DMA<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup> (Section 2.4). In other words, the working zone for RNTD removal is below



**Fig. 4 – Breakthrough curve of RNTD in column test. Column size: Φ 6 mm × h = 150 mm. Resin: 001 × 7, volume = 4.65 mL, capacity = 1.9 meq/mL. Flow velocity: 15.4 m/hr. pH = 5.0 ± 0.2, temperature = 25°C. Water samples: (1) 3.1 mmol/L of RNTD<sup>+</sup> and 1.5 mmol/L of Ca<sup>2+</sup> (2) 3.1 mmol/L RNTD alone. The relative standard deviations of duplicate tests of each data were less than 5%. Error bars were not included to improve the readability of this figure.**

that of hardness cations. If the working zone for RNTD is depleted, the adsorbed RNTD will be replaced by the continuous feeding of hardness cations.

It should be noted that the concentration of NDMA precursors was generally in nmol/L level in actual source water, while the RNTD concentration was set in mmol/L level in this column test. This level will benefit the direct comparison of removal of RNTD or  $\text{Ca}^{2+}$  in softening column operation and detection. More importantly, even under trace level of 1 nmol/L, according to the partition coefficients,  $K_{\text{Na}^+}^{\text{RNTD}^+} = 12.1$ , the RNTD<sup>+</sup> removal by the ion exchange resin can still approaching 63%–94% with 11%–84% of total ion exchange capacity (Calculation is shown in the Appendix A). Under such conditions, the consumed exchange capacity for NDMA precursors is very low and the cation exchange capacity will be consumed dominantly for hardness removal. That means, the NDMA precursor removal can be achieved as an added benefit of the cation exchange softening process. The similar situation occurred for the removal of trace level of  $\text{Ra}^{2+}$  or other radioactive nuclides (Edzwald, 2011), although  $\text{Ra}^{2+}$  present higher priority in the cation exchange sequence than  $\text{Ca}^{2+}$ . However, care must be taken to prevent depletion of the exchange capacity and avoid NDMA precursor elution during column operation.

The saturated ion exchange column could be regenerated by NaCl solution (80–100 g/L). Generally, the economic dosage of NaCl for regeneration of  $001 \times 7$  resin column in Chinese water treatment facilities is 100–120 g/mol, or about 2 mol NaCl/mol resin (Zhu, 2002).

## 2.6. Removal of other model NDMA precursors by cation exchange

Besides DMA and RNTD, we also tested the removal efficiency of cation exchange process on other model NDMA precursors, including *N,N*-dimethylbutylamine, *N,N*-dimethyloctylamine, *N,N*-dimethylisopropylamine, *N,N*-dimethylaniline, *N,N*-dimethylbenzylamine, *N,N*-dimethylphenethylamine and doxylamine. Many of them have been identified as the NDMA precursors (Shen and Andrews, 2011; Bei et al., 2016b; Selbes et al., 2013). The results were concluded in Table 4.

The results confirmed that cation exchange process also worked well for other model NDMA precursors. One reason that all NDMA precursors could be removed well by cation exchange is that all precursors tested contained a dimethylamine

structure that protonated at the pH tested. When the molar ratio of resin/precursor was 2:1, the removals were among 70%–93%. Increasing the resin dosage would further improve the precursor removal according to Section 2.

## 3. Conclusions and suggestions

Removal of several representative NDMA precursors by water softening strong acidic cation exchange resin was investigated in this study. The results confirmed that cation exchange is an efficient technology for removal of NDMA. Specifically, the following conclusions were obtained.

- (1) High removal (78% for DMA and 94% for RNTD) was observed under weakly acidic conditions when the molar ratio of resin/precursor was just over 4. pH had a dramatic effect on NA precursor removal, with the optimum condition being  $\text{pH} < \text{pK}_a - 1$ . DMA can be removed well at  $\text{pH} < 9$  and RNTD can be removed well at  $\text{pH} < 7$ . The removal decreased with higher pH, which was attributed to the deprotonation of NA precursor molecule under higher pH.
- (2) The presence of inorganic cation impaired the NA precursor removal greatly, especially polyvalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The order of the two NA precursors in the selectivity series for exchange of cation was as follows:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{RNTD}^+ > \text{K}^+ > \text{DMA}^+ > \text{NH}_4^+ > \text{Na}^+$ . The partition coefficient of  $\text{DMA}^+$  to  $\text{Na}^+$  was  $1.41 \pm 0.26$  and that of  $\text{RNTD}^+$  to  $\text{Na}^+$  was  $12.1 \pm 1.9$ .
- (3) The kinetic curves of DMA or RNTD could be well fitted by the pseudo second-order model. The reaction rate constant of DMA was  $0.0088 \pm 0.0006$  L/mmol/min and that of RNTD was  $0.0074 \pm 0.0004$  L/mmol/min. The higher rate constant of DMA compared with RNTD could be explained by the smaller size of former molecule, which helps it diffuse more rapidly in water.
- (4) The column test confirmed the applicability of cation exchange to remove NDMA precursors. However, care must be taken to prevent the capacity from being depleted and avoid NDMA precursor elution during column operation.

**Table 4 – Removal of 9 model NA precursors by cation exchange process.**

No.	Chemicals	MW	pKa	logP	Removal (%)
1	Dimethylamine	45.084	10.52	−0.43	69.7
2	<i>N,N</i> -dimethylbutylamine	101.190	9.79	1.66	75.5
3	<i>N,N</i> -dimethyloctylamine	157.296	9.79	3.78	93.2
4	<i>N,N</i> -dimethylisopropylamine	87.163	9.98	0.94	71.6
5	<i>N,N</i> -dimethylaniline	121.180	5.02	2.33	74.2
6	<i>N,N</i> -dimethylbenzylamine	135.206	8.99	1.98	86.8
7	<i>N,N</i> -dimethylphenethylamine	149.233	9.26	2.14	90.5
8	Doxylamine	270.369	8.87	2.37	91.0
9	Ranitidine	314.404	8.08	1.23	86.2

Note: Initial concentration of these NDMA precursors was 1 mmol/L. The molar ratio of resin/precursor was 2:1. temperature = 25°C,  $\text{pH} < \text{pK}_a - 1$  for these chemicals.  $\text{pK}_a$  corresponds to the protonation process of N atom in the dialkylamine functional group.



- (5) Besides DMA and RNTD, cation exchange process also works well for other 7 model NDMA precursors. The reason could be explained by all NDMA precursors tested here share the dimethylamine structure, which present positive charge under neutral pH.

Due to the limited budget and human resources, we only tested representative NDMA precursors in this study. In future studies, a field study will also be conducted to treat the actual source water, as well as domestic or industrial wastewater with high nitrosamine formation potential. The cost analysis will be given with more operation practice in the future. Besides the strong acidic cation exchange resins, other resins such as weak acidic cation exchange resins or chelating resins will be tested for their removal of NDMA precursors.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2017.04.007>.

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