JOURNAL OF
HAZARDOUS
MATERIALS

Removal of *N*-nitrosodimethylamine from waters using physical–chemical techniques

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Abstract

During the 1950s and 1960s, the Rocky Mountain Arsenal (RMA) was leased by the US Air Force for the purpose of producing rocket fuel, namely Aerozine 50, by blending hydrazine and unsymmetrical dimethyl hydrazine (UDMH). A product of the decomposition of UDMH is *N*-nitrosodimethylamine (NMDA). Bituminous coal granular activated carbon (GAC) systems located at the boundaries of the RMA are not highly effective at removal of NDMA. Modifications to the existing systems by adding additional adsorbents specific to NDMA removal vs construction of new facilities were evaluated. This paper summarizes the results of investigations into alternative adsorption technologies which might be more effective at removal of NDMA than bituminous coal GAC. The results were well described by the Freundlich adsorption isotherm model. Bench-scale isotherm and column studies revealed that a coconut shell GAC and carbonaceous resin were more effective at removal of NDMA than bituminous coal GAC.

1. Introduction

When the Titan Missile and Lunar Lander programs were ongoing in the 1950s and 1960s, the US Air Force engineered and constructed a building at the Rocky Mountain Arsenal (RMA), Denver, CO, for the purpose of producing rocket fuel, namely Aerozine

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50, by blending hydrazine and unsymmetrical dimethyl hydrazine (UDMH). N-Nitro-sodimethylamine (NDMA) is an intermediate in the production of Aerozine 50, which in some cases may have contained up to 0.1% NDMA as an impurity [1]. Due to activities surrounding the production of UDMH, groundwater at the RMA was contaminated with NDMA. In the 1970s and 1980s, several contaminant interception treatment systems containing bituminous coal carbon were constructed to remove contamination from the groundwater before it left the site, using granular activated carbon (GAC). Studies conducted on the containment systems indicate that NDMA is not being effectively removed from the extracted groundwater. Concentrations of NDMA in RMA groundwater generally range from 0.87 to $2.7 \mu g \, l^{-1}$.
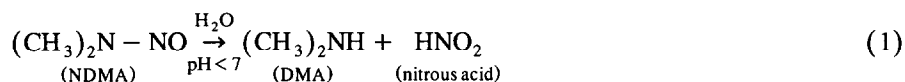
NDMA is a Class A carcinogen and is considered a hazardous waste under the Resource Conservation and Recovery Act definitions of ignitability, corrosivity and reactivity. The ambient water quality criteria (AWQC) is 1.4 parts per trillion (ppt) NDMA and the United States Environmental Protection Agency drinking water standard is 0.7 ppt NDMA. The RMA has adopted the AWQC as an applicable and appropriate requirement for cleanup of RMA groundwaters. No laboratory was available for this study with capability to analyze NDMA to the AWQC. At the initiation of the study, Datachem Laboratories, Salt Lake City, UT, had capability and was certified to analyze to 33 ppt NDMA according to methods described in UM 34 [2] using gas chromatography/mass spectroscopy (GC/MS) and were used for preliminary tests and to verify liquid scintillation (LS) results. After the study was initiated, Oak Ridge National Laboratories (ORNL), Oak Ridge, TN, became certified to analyze to 2 ppt NDMA using GC with chemiluminescent nitrogen detection methods. Samples analyzed by Datachem Laboratories and LS were reanalyzed at ORNL to determine whether NDMA had been reduced to below 33 ppt.

Three processes were evaluated for efficiency of removal of NDMA: adsorption, hydrolysis and metals complexation. The objectives of the evaluations were to reduce NDMA to the lowest possible level, to identify the most effective treatment for removal of NDMA, and to compare the removal of the three most effective treatments to the removal efficiency of the existing GAC systems. Another objective was to determine whether NDMA could be hydrolyzed to dimethylamine (DMA), a less toxic compound which might be more readily removed from RMA waters using ion exchange techniques.

There was no historical data available on removal of NDMA through metals complexation or efficiency data for hydrolysis of NDMA to DMA. There was limited data on adsorption capacities for removal of NDMA using carbons. Studies conducted by Kaplan and Kaplan [3] evaluated adsorption of NDMA onto granular activated coconut shell carbon (CSC) (6/14 mesh; Fisher). For their isotherms, NDMA concentrations of 5, 50, 500, 5000 and 10 000 mg l^{-1} NDMA were used. The results indicated that 110 mg of NDMA were adsorbed per g of carbon. Dobbs and Cohen [4] performed isotherm evaluations of NDMA and 127 other compounds and the results did not show the same degree of treatment described in the Kaplan study. However, a bituminous coal carbon (Calgon Filtrasorb 400) was used in the Dobbs and Cohen study and CSC was used in the Kaplan study. Isotherms were developed by spiking pure solutions for each test to prepare 128 isotherms. Of the 128 compounds studied, NDMA had the lowest adsorption capacity of 6.8×10^{-5} mg NDMA adsorbed per gram of Filtrasorb 300

carbon (a carbon which is the same as that used in the RMA contaminant interception systems but a smaller mesh size). Faust and Aly [5] performed NDMA adsorption isotherm studies with three different types of carbon (manufacturers were not provided). The results of adsorption capacity were similar to those obtained by Dobbs and Cohen [4] and were 6.8×10^{-5}, 4×10^{-5} and 9×10^{-6} mg per gram of carbon.

Adsorption involves attractions between the adsorbate and the adsorbent due to weak intermolecular forces known as van der Waals' forces. Van der Waals' forces consist of attraction–repulsion interactions which total to give the potential energy of the system [6]. Hydrolysis is the reaction of a chemical with water, or with the hydronium or hydroxide ions associated with water, to form a new compound. In the case of NDMA, hydrochloric acid was added in an attempt to convert NDMA to DMA, a less toxic, easier to remove compound than NDMA. If NDMA were effectively hydrolyzed to DMA, techniques for removal of DMA were to be considered. Acidic ion exchange resins ranging from weakly acidic to strongly acidic were also evaluated to determine their ability to hydrolyze NDMA to DMA and nitrous acid. The DMA could then be protonated to the amine salt that would be exchanged to the resin. The equation for DMA formation as the result of hydrolysis of NDMA is

$$(CH_3)_2N - NO \underset{pH < 7}{\overset{H_2O}{\rightarrow}} (CH_3)_2NH + HNO_2 \tag{1}$$
$$\text{(NDMA)} \qquad \text{(DMA)} \qquad \text{(nitrous acid)}$$

Metals complexation requires an ion or molecule (NDMA) that has one pair of unshared electrons for coordinate covalent bonding and a metal ion (Cu^{2+}, Fe^{2+}, Ni^{2+}) that has a sufficient attraction for electrons to form a coordinate covalent bond with the attaching group [5]. Through covalent bonding, NDMA is transferred to the metal-bound adsorbent and removed from the aqueous phase.

2. Materials and methods

2.1. Preliminary, isotherm and confirmation evaluations

Groundwater was collected from the RMA and shipped to the Waterways Experiment Station (WES) in five gallon pails. Upon arrival at the WES, the RMA water was placed in cool storage at $4\,^{\circ}C$ until needed for testing.

A series of batch studies were conducted to determine whether NDMA could be removed through adsorption, hydrolysis or metals complexation. The preliminary batch tests were used as a screening tool to select processes for further evaluation. The carbonaceous resins selected for the physisorption evaluations were Ambersorb® 572 and Ambersorb® 563, and the activated carbons selected for evaluation were Calgon CSC and Calgon Filtrasorb-400 (F-400). One resin, Rohm and Haas® XAD-7, was selected. Rohm and Haas® XAD-7 resin is an acrylic ester type resin that involves polar bonding between the hydrophilic portion of the adsorbate molecule and the aliphatic surface of XAD-7. The materials selected for evaluation of hydrolysis of NDMA to DMA were Y-zeolite, silica, hydrochloric acid, and Rohm and Haas Amberlyst® 15.

Evaluations of metals complexation involved treatment of the Y-zeolite, silica, and Rohm and Haas Amberlyst® 15 with Cu^{2+}, Fe^{2+} and Ni^{2+}.

Calgon CSC and F-400 were prepared for testing by oven-drying to constant weight at 150 °C according to procedures described in ASTM D 2867 [7]. Ambersorb® 563 was hydrated for four days prior to testing according to methods described by Rohm and Haas [8]. Ambersorb® 572 did not require pretreatment due to manufacturers' instructions, since it is the most hydrophilic of Rohm and Haas resins. In order to remove iron contamination that may have been introduced during manufacture of the silica, 500 g of silica was mixed with 500 ml each of 6 M HNO_3 and 6 M HCl, heated to boiling, the acids decanted, and the procedure repeated. The acid-treated silica was rinsed three times with 500 ml of 0.1 M HCl, then rinsed with 500 ml 2 M NaOH to remove amorphous silica, followed by four rinses of 500 ml of distilled water to remove excess base. The treated silica was dried at 110 °C to a constant weight and heated for 12 h at 450 °C to remove organic materials. Metals treatment involved dissolving 1000 g of the metal chloride (i.e. $CuCl_2$, $FeCl_2$, or $NiCl_2$) in 2000 ml of distilled water and adding 1000 g of Y-zeolite or Amberlyst® 15 to complex the metal onto the adsorbent. The metal–water–adsorbent mixture was contacted/tumbled for 24 h at 30 revolutions per minute (rpm), the metal-treated adsorbent filtered, rinsed three times with distilled water to remove excess salt, air-dried, and stored until needed for testing.

RMA water was spiked to 100 μg l⁻¹ NDMA in an attempt to ensure differentiation between volatilization and treatment and to aid in evaluation of removal efficiencies since actual concentrations at the site approach the analytical detection limit of 33 ppt. Twenty-one treatment scenarios were evaluated and are presented in Table 1. Samples were prepared and testing conducted in three 820 ml centrifuge bottles, which were sized to fill two 1 l sample bottles. Each adsorbent was tested at a 1:10 adsorbent:water ratio (AWR), by mass, i.e. 76 g of adsorbent in 760 ml groundwater. Displacement tests were conducted on each adsorbent to determine the volume of water displaced by the adsorbent at a 1:10 AWR so that corrections could be incorporated in the preliminary tests. Adsorbents were weighed and added alternately with the 100 μg l⁻¹ NDMA solution and the test bottles totally filled to eliminate headspace. The adsorbent/100 μg l⁻¹ NDMA solution was mixed using toxicity characteristic leaching procedure (TCLP) type tumblers for a period of 1 h, centrifuged for 30 min at 1200 rpm in an International Equipment Company model PR-7000 centrifuge, and filtered using in-line stainless steel filters. Samples were collected in 1 l precleaned amber bottles and analyzed for NDMA and DMA. Datachem Laboratories, Salt Lake City, Utah analyzed the samples for NDMA using UM 34 and Lockheed Environmental Systems and Technologies Company, Las Vegas, NV analyzed the DMA samples using ion chromatography methods.

Based upon the results of the preliminary tests, three adsorbents were selected as optimal for removal of NDMA and the results of the preliminary tests were confirmed by repeating the preliminary tests for the three optimal adsorbents. The three optimal adsorbents along with Calgon F-400 (the carbon currently used at RMA) were selected for further evaluation in the form of isotherm determinations.

Isotherm determinations were evaluated using radiolabeled ¹⁴C NDMA at a concentration of 5 μg l⁻¹ NDMA, a concentration more closely mimicking actual site water

Table 1
Results of screening tests on adsorption technologies for removal of NDMA from RMA waters

Test no.	Adsorbent	pH adjustment	Average [a] NDMA concentration ($\mu g l^{-1}$)	Average DMA concentration ($\mu g l^{-1}$)
Adsorption				
1	Ambersorb 563®	NA	0.62	NT [b]
2	Ambersorb 572®	NA	0.17	NT
3	Coconut shell carbon	NA	0.34	ND
4	XAD-7®	NA	81.6	0.8
5	Y-Zeolite	NA	84.7	1.8
6	Silica	NA	80.4	1.6
Hydrolysis				
7	NA	6	99.2	NT
8	NA	2	97.3	1.7
9	Amberlyst 15	NA	102.0	1.0
pH adjustment				
10	Coconut shell carbon	4	0.59	ND
11	XAD-7®	4	89.7	ND
Metals complexation				
12	Amberlyst 15/copper	NA	106.0	3.5
13	Amberlyst 15/iron	NA	95.6	1.0
14	Amberlyst 15/nickel	NA	103.5	2.4
15	Y-Zeolite/silica	NA	97.2	ND
16	Y-Zeolite/copper	NA	120.5	1.5
17	Y-Zeolite/iron	NA	104.0	ND
18	Y-Zeolite/nickel	NA	109.0	1.7
19	Y-Zeolite/copper/silica	NA	73.8	ND
20	Y-Zeolite/iron/silica	NA	99.1	1.2
21	Y-Zeolite/nickel/silica	NA	84.2	3.3

[a] Indicates not tested.
[b] Initial NDMA concentration was $100 \mu g l^{-1}$.
NA = not applicable.
ND = not detected.

concentrations, since it was determined that NDMA was not volatilizing in the preliminary tests. LS techniques were used for determining the concentration of NDMA in untreated and treated waters. LS analysis was used because it was a relatively inexpensive approach to predicting the relative effectiveness of the adsorbents using isotherms and comparing the relative performance of the three optimal adsorbents to Calgon F-400. LS data was used to determine whether alternative adsorbents may be a viable option for treatment of RMA waters, leading to more detailed evaluations using the RMA's contract laboratory, Datachem. A standard curve was prepared and method detection limit determined according to methods described in Chap. 1 of the Volume 40 Code of Federal Regulations, Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11 [9]. Two controls were

run with each set of tests, an adsorbent blank and a method blank. The adsorbent blank contained a 1:10 AWR of adsorbent and water, without radiolabeled NDMA, and the method blank contained $5 \mu g l^{-1}$ radiolabeled NDMA and water, without adsorbent. The adsorbent blank was used to determine whether the presence of adsorbents affects the LS counts of radiolabeled NDMA. The purpose of the method blank was to determine whether LS handling procedures caused losses of radiolabeled NDMA.

Equilibrium time determinations were conducted in triplicate using $5 \mu g l^{-1}$ radiolabeled NDMA at a 1:10 AWR in 25 ml centrifuge tubes and shaking the radiolabeled NDMA and adsorbents on a reciprocating shaker (180 excursions per minute) for 0.5, 1, 2, 8, 24 and 48 h. At the end of the contact time, the radiolabeled NDMA/adsorbent solutions were centrifuged, filtered, and 1 ml of the filtrate analyzed according to LS methods. Isotherm determinations were conducted at a concentration of $5 \mu g l^{-1}$ radiolabeled NDMA at 1:5, 1:10, 1:20, 1:30 and 1:50 AWRs and contacted for 8 h on a reciprocating shaker at 180 excursions per minute.

Adsorption isotherms were prepared according to the Freundlich equation:

$$\frac{x}{M} = K C_e^n \tag{2}$$

In Eq. (1), x/M represents the mass of NDMA adsorbed (μg) per mass of the adsorbent (g), C_e represents equilibrium concentration of NDMA remaining in solution, and K and n are constants. Linearizing Eq. (1) yields:

$$\log \frac{x}{M} = \log K + n \log C_e \tag{3}$$

Confirmation tests were conducted using the same materials and methods as described for the preliminary tests at a spiked concentration (nonradiolabeled) of $5 \mu g l^{-1}$ NDMA by Datachem Laboratories and ORNL.

3. Discussion of results

The average results of DMA and NDMA analysis of the preliminary tests are presented in Table 1. The results of NDMA removal in the preliminary tests indicated Ambersorb® 572 was the most effective adsorbent, followed by Calgon CSC, and Ambersorb® 563. Adsorption processes, including carbon and carbonaceous resins treatment, resulted in greater than 99% removal of NDMA in the preliminary tests. Y-zeolite and silica treatment, without the addition of metals (Cu^{2+}, Fe^{2+}, Ni^{2+}) resulted in approximately 15–20% reduction in NDMA concentrations and less than $2 \mu g l^{-1}$ DMA formation. XAD-7® reduced the NDMA concentration to $81.6 \mu g l^{-1}$, an approximately 18% reduction in NDMA. Acidic pH adjustment was evaluated in conjunction with XAD-7® and Calgon CSC to determine if DMA formation occurred, whether XAD-7® or Calgon CSC had an adsorption capacity for DMA. XAD-7® and Calgon CSC were not as effective after pH adjustment; DMA concentrations were not detected, indicating NDMA was not effectively hydrolyzed to DMA.

Neither the hydrolysis or metals complexation processes were effective at removal of

NDMA. pH adjustment to 2 was expected to be more effective at decomposing NDMA to DMA than pH adjustment to 6 since hydrolysis is more favorable under acidic conditions. Thus, a sample for DMA was tested at pH 2 and because the DMA concentration in this sample was $1.7 \mu g l^{-1}$, DMA was not analyzed for the pH 6 sample. Since metals complexation is dependent upon the formation of DMA from NDMA and NDMA was not effectively hydrolyzed to DMA, metals complexation was not an effective treatment option. The optimal metals complexation treatment was Y-zeolite/Cu^{2+}/silica with approximately 26% removal of NMDA. The DMA hydrolysis tests indicated that NDMA was not effectively hydrolyzed to DMA by any of the hydrolysis processes. Neither Amberlyst® 15 nor Y-zeolite in the presence of metals (Cu^{2+}, Fe^{2+}, Ni^{2+}) were sufficiently acidic to decompose NDMA; the treated concentration of NDMA was approximately equal to the spiked concentration. Addition of silica (which is more acidic than Y-zeolite) to Y-zeolite evaluations in the presence of copper and nickel, aided in removal of NDMA. However, DMA concentrations did not increase when silica was added to Y-zeolite evaluations, indicating DMA formation was not the mechanism for NDMA removal. Addition of iron (Fe) did not appear to aid in removal of NDMA; the treated NDMA concentration was approximately the same as the spiked NDMA concentration. Addition of silica to Y-zeolite, without the addition of a metal (Cu^{2+}, Ni^{2+}), showed little removal of NDMA. The mechanism fo NDMA removal is not clear and must be determined through further research, but the collective effect of Y-zeolite/(Cu^{2+}, Ni^{2+})/silica showed approximately 20–30% removal of NDMA. It may be difficult to hydrolyze NDMA to DMA, and thus difficult to remove NDMA through metals complexation, due to the stability of NDMA in water.

The preliminary tests were rerun to determine whether the results were repeatable and the results are presented in Table 2. NDMA was below the analytical detection limit of $0.033 \mu g l^{-1}$ for the Ambersorb® 572 and Calgon CSC tests and the average NDMA concentration for Ambersorb® 563 was $0.80 \mu g l^{-1}$. The results of the Ambersorb® 572 and Calgon CSC were approximately an order of magnitude or greater less than the results of the preliminary tests. The results of the Ambersorb® 563 confirmation tests were slightly higher than the results of the Ambersorb® 563 preliminary tests.

Table 2
Results of confirmation tests on sorption technologies for removal of NDMA from RMA waters

Sample	Sorbent	pH adjustment	NDMA concentration ($\mu g l^{-1}$)
RMA water (spiked)	NA	NA	99.9
Duplicate	NA	NA	106.0
Test	Ambersorb® 563	NA	0.79 (0.80)
Duplicate	Ambersorb® 563	NA	0.81
Test	Ambersorb® 572	NA	ND
Duplicate	Ambersorb® 572	NA	ND
Test	Coconut shell PAC	NA	ND
Duplicate	Coconut shell PAC	NA	ND

( ) indicates an average of test and duplicate samples.

Based upon the results of the preliminary tests, four adsorbents were selected for further evaluation through isotherm and column studies; Ambersorb® 572, Ambersorb® 563, Calgon F-400, and Calgon CSC. The results of equilibrium time determination and batch isotherm tests are presented in Figs. 1 and 2, respectively. According to Fig. 1, equilibrium was achieved in under approximately 2 h for each Ambersorb® 563, Ambersorb® 572, and Calgon CSC. One hour was selected as the equilibrium time required for removal of NDMA for the remainder of Datachem UM34 and ORNL testing. An 8 h equilibrium time was selected for LS tests for convenience in performing the tests.

The results of K (y-intercept at $C_e = 1.0\,\mu\mathrm{g}\,\mathrm{l}^{-1}$), $1/n$ (slope of the isotherm), and r^2 (variance) determinations for the liquid scintillation, Datachem UM 34, and ORNL analysis techniques are presented in Table 3. Among the analytical methods used during testing, there is considerable variability among K and $1/n$ values as presented in Table 3. The available data using Datachem UM 34 (Ambersorb® 563 and 572 concentrations were below the detection limit of 33 ppt) and ORNL GC methods are comparable. Although values of K and $1/n$ obtained using LS techniques vary from those obtained using Datachem Laboratory and ORNL analytical results, the purpose of the LS analytical evaluations was to provide a screening evaluation of performance of the adsorbents which was reevaluated using Datachem Laboratories, the certified analytical
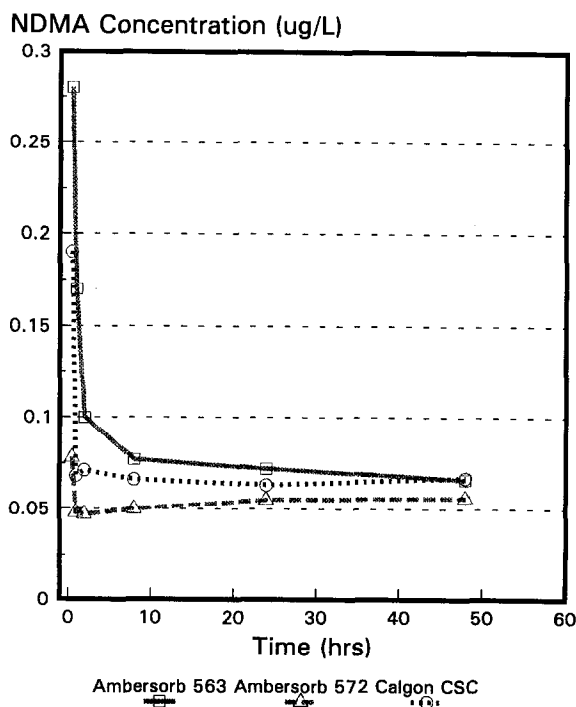

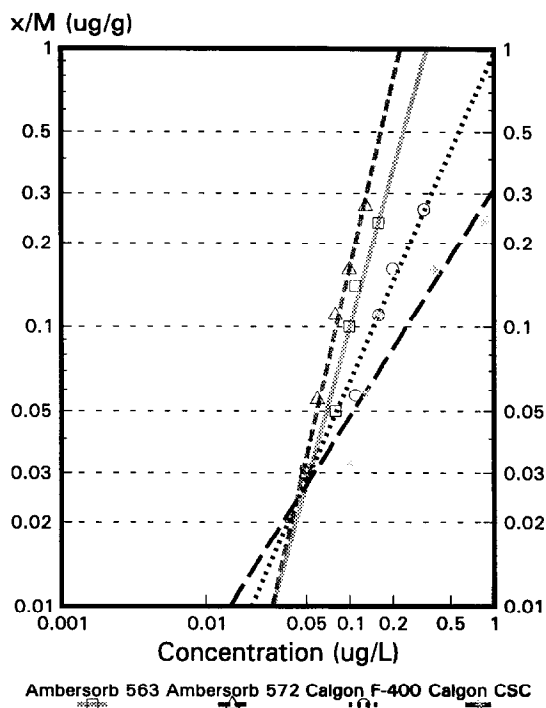Fig. 1. Equilibrium time determination using LS techniques.

x/M (ug/g)

Fig. 2. Isotherm data using LS techniques.

laboratory for NDMA analyses for the RMA. All three analytical methods consistently indicated that Ambersorb® 572 was the most effective adsorbent. Analysis of each of the phases of the adsorption tests using varying analytical techniques showed Ambersorb® 572 is more effective than the adsorbents currently in use in the RMA contaminant interception treatment systems.

Table 3
Results of K and $1/n$ determinations

Analysis technique	Adsorbent	K (μg g^{-1})	$1/n$	r^2
Datachem/UM34	Ambersorb® 563	NA	NA	NA
	Ambersorb® 572	NA	NA	NA
	Calgon F-400	1.16	1.04	0.98
	Calgon CSC	2.01	0.82	0.88
Liquid scintillation	Ambersorb® 563	7.35	1.87	0.96
	Ambersorb® 572	28.37	2.25	0.99
	Calgon F-400	0.96	1.18	0.97
	Calgon CSC	0.31	0.82	0.85
ORNL/GC	Ambersorb® 563	2.09	0.98	0.99
	Ambersorb® 572	9.65	1.17	0.88
	Calgon F-400	1.27	1.00	0.98
	Calgon CSC	2.57	0.93	0.97

The values of r^2 indicated the Freundlich equation was a suitable selection for analysis of the data for this adsorption study since the data formed a linear isotherm on a log–log scale plot. Values of K are used as an indicator of adsorption capacity. Values for K ranged from 0.31×10^{-3} mg g^{-1} for Calgon CSC to 28.37×10^{-3} mg g^{-1} for Ambersorb® 572. Small values for K (< 10 mg g^{-1}) indicate low adsorption capacity [2]. Although K values are low, for NDMA the range of K values, differing by two

Table 4
Results of adsorbent dosage evaluations of removal of NDMA analyzed by Datachem

Sample type	Solid:liquid ratio	Replicate	NDMA concentration (μg l^{-1})
Basin A neck effluent	NA	1	0.508
		2	0.518
		3	0.516
		4	0.517
		5	0.510
Spike	NA	1	4.9
Method blank	NA	1	5.4
Ambersorb® 563	1:5	1	b
	1:10	1	ND
	1:20	1	ND
	1:30	1	ND
	1:50	1	ND
Spike	NA	1	5.3
Method blank	NA	1	5.5
Ambersorb® 572	1:5	1	ND
	1:10	1	ND
	1:20	1	ND
	1:30	1	ND
	1:50	1	ND
Spike	NA	1	5.1
Method blank	NA	1	5.4
Calgon coconut shell carbon	1:5	1	ND
	1:10	1	ND
	1:20	1	0.034
	1:30	1	0.037
	1:50	1	0.087
Spike	NA	1	5.1
Method blank	NA	1	1
Filtrasorb 400	1:5	1	1
	1:10	1	0.048
	1:20	1	0.099
	1:30	1	0.14
	1:50	1	0.26

[a] Sample was not evaluated due to breakage.

orders of magnitude, provides a means of comparing adsorbent performance. According to Faust and Aly [5], when $1/n$ is close to or greater than 1, it indicates that high equilibrium concentrations yield high adsorption capacities which decrease sharply as concentration is reduced. The $1/n$ values ranged from 0.82 (Calgon CSC) to 2.25 (Ambersorb® 572), indicating the adsorption capacity is significantly affected by the concentration of NDMA in the influent waters, as indicated by Faust and Aly [5]. Values for K and $1/n$ could not be determined for Ambersorb® 563 or Ambersorb® 572 using Datachem Laboratory data since the NDMA concentrations in the treated water were less than the analytical detection limit of $0.033\ \mu g\ l^{-1}$.

Liquid scintillation isotherm evaluations indicated that Ambersorb® 572 was the most effective adsorbent at concentrations greater than $0.05\ \mu g\ l^{-1}$. The adsorbent effectiveness from most to least at concentrations greater than $0.05\ \mu g\ l^{-1}$ was:

Ambersorb® 572 > Ambersorb® 563 > Calgon F-400 > Calgon CSC

Ambersorb® 572 had the highest K and $1/n$ values at $28.37\ \mu g\ g^{-1}$ and 2.25, respectively, indicating that Ambersorb® 572 is the optimal adsorbent in terms of adsorption capacity, but that the adsorption capacity of Ambersorb® 572 for NDMA is the most affected of the adsorbents tested by changes in influent NDMA concentration.
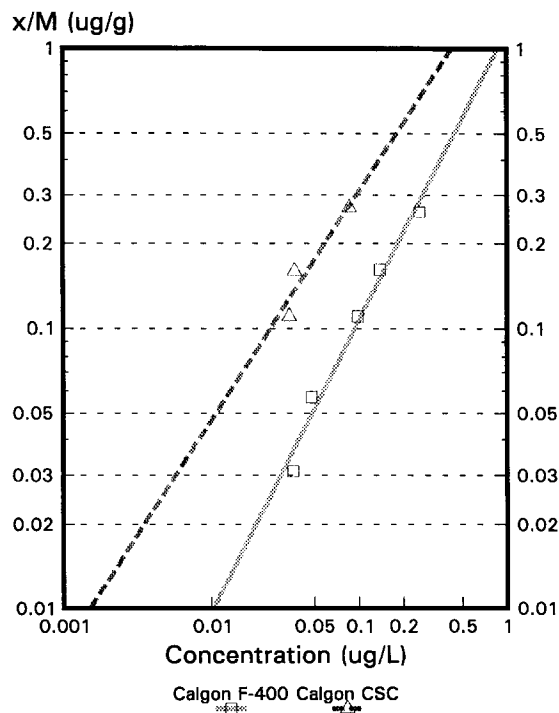

Fig. 3. Isotherm data using UM34.

Liquid scintillation isotherm tests were rerun using analytical methods by Datachem Laboratories and ORNL. The results of Datachem analyses are presented in Table 4 and Fig. 3 and the results of ORNL analyses are presented in Table 5 and Fig. 4. NDMA analyses results using Datachem Laboratories for Ambersorb® 563 and Ambersorb® 572 were less than the detection limit of 33 ppt NDMA. Based on K and $1/n$ values (see Table 5), Calgon CSC was more effective at removal of NDMA than Calgon F-400. According to isotherms prepared based on ORNL analysis, the order of effectiveness of the adsorbents from most to least was:

Ambersorb® 572 > Calgon CSC > Ambersorb® 563 > Calgon F − 400

Table 5
Results of ORNL analysis of adsorbent dosage testing

| Adsorbent	Adsorbent:water ratio	Average NDMA concentration (ppt)
Ambersorb® 563	Spike	4857
	Method blank	3369
	Adsorbent blank	3
	1:5	8
	1:10	18
	1:20	29
	1:30	51
	1:50	68
Ambersorb® 572	Spike	5686
	Method blank	5853
	Adsorbent blank	3
	1:5	7
	1:10	21
	1:20	24
	1:30	27
	1:50	46
Calgon F-400	Spike	4841
	Method blank	4842
	Adsorbent blank	5
	1:5	25
	1:10	40
	1:20	73
	1:30	98
	1:50	214
Calgon coconut shell PAC	Spike	3828
	Method blank	3661
	Adsorbent blank	1
	1:5	5
	1:10	13
	1:20	26
	1:30	30
	1:50	53

x/M (10-3 ug/g)
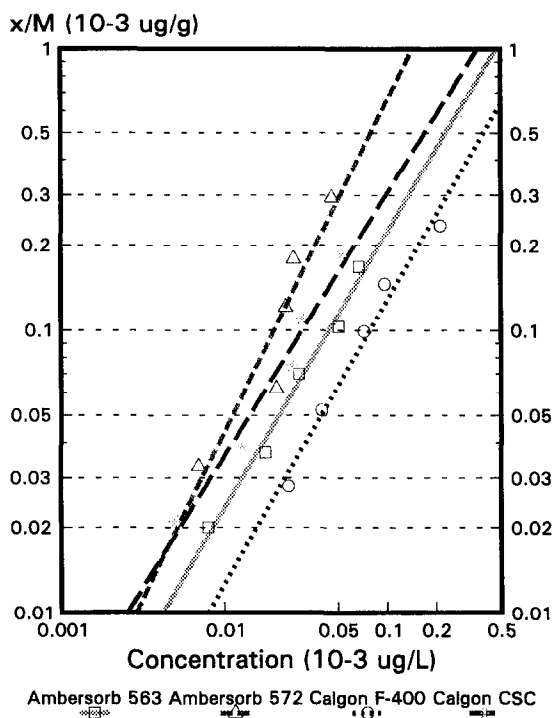
Fig. 4. Isotherm for NDMA using ORNL.

Based on ORNL data, Ambersorb® 572 had the highest K and $1/n$ values at 9.65 μg g^{-1} and 1.17, respectively, indicating Ambersorb® 572 had the highest adsorption capacity for NDMA, but that it also was the adsorbent whose adsorption capacity was most affected by changes in influent NDMA concentrations.

4. Conclusions and summary

NDMA was removed from RMA groundwater the most effectively by Ambersorb® 572, a carbonaceous resin produced by Rohm and Haas. Values for K were higher for Ambersorb® 572 than Ambersorb® 563, Calgon CSC, and Calgon F-400. Metals complexation and hydrolysis were not as effective at removal of NDMA as currently existing Calgon F-400 GAC systems.

The results of the bench-scale isotherm studies indicate that application of modified adsorption systems to the preexisting GAC systems may be an effective form of treatment. Further tests were performed in the form of column studies to further evaluate the efficiency of adsorption techniques for removal of NDMA.

Acknowledgements

Appendix A. Nomenclature

C_e equilibrium concentration of the adsorbate in solution ($\mu g \, l^{-1}$)

K constant, provides adsorption capacity of the adsorbent at unit equilibrium concentration

n constant, indicator of adsorption intensity

r^2 variance

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