TREATMENT TECHNOLOGIES
FOR THE REMOVAL OF NDMA FROM CONTAMINATED GROUNDWATER

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INTRODUCTION

N-nitrosodimethylamine (NDMA) is a contaminant of recent concern by drinking water regulators because of its discovery in contaminated groundwater supplies, in reclaimed water and treated drinking water from treatment plants where chlorination is the primary disinfection process. NDMA has been shown to cause cancer in laboratory animals such as rats and mice when the animals are exposed at high levels over their lifetimes.[1]. It is identified as a carcinogen by California's Proposition 65 and as a probable human carcinogen by USEPA.[1] Because NDMA historically has not been considered a common drinking water contaminant, it has no state or federal drinking standards. In April 1998, California Department of Health Services (DHS) established a drinking water action level (AL) for NDMA of 0.002 microgram per liter (µg/L)[1]. However, analytical capabilities did not enable detection at that concentration, so DHS's approach was to consider any detectable quantity as exceeding the DHS action level for NDMA. In November 1999, DHS temporarily revised the NDMA AL from 0.002 µg/L to 0.02 µg/L, while studies are taking place on the possible production of NDMA in drinking water treatment processes. The AL will revert to 0.002 µg/L once those investigations are completed.[2] Currently, only a small number of laboratories are able to detect NDMA at 0.002 µg/L.

The author recently conducted a wellhead treatment study for a private water purveyor whose groundwater supply is contaminated by NDMA. The treatment objective for NDMA is <0.002 µg/L. This paper presents a summary discussion of alternative treatment technologies for NDMA in drinking water.

TREATMENT TECHNOLOGIES FOR NDMA REMOVAL

NDMA is a polar, highly soluble compound with the following structure:

$$(CH_3)_2N\text{-}N{=}O$$

Due to its chemical nature, NDMA does not treat well by conventional water treatment processes such as air stripping, activated carbon adsorption or biodegradation. The three potential NDMA treatment methods include ultraviolet (UV) irradiation, UV/oxidation, and resin adsorption. These treatment technologies are discussed below.

UV Irradiation

UV irradiation has been shown to remove NDMA from water to very low levels in pilot- and full-scale systems.[3,4] NDMA absorbs UV light in a strong band centered at 228 nm and a weak band centered at 340 nm. Initial absorption of light at 228 nm results in cleavage of the N-N bond.[5] The resulting NO fragment is oxidized into nitrite, which can be further oxidized to nitrate. The organic fragment reacts with

dissolved oxygen leading to dimethylimine (CH_3-N=CH_2) which then oxidizes further eventually forming bicarbonate.

Photochemical (UV) destruction of NDMA is a relatively cost-effective treatment method for water contaminated with NDMA. Drinking waters typically have low UV absorbance values making direct photolysis of the NDMA feasible. The major byproduct of concern is nitrite. The main source of the nitrite is not from destruction of the NDMA due to the low contamination levels but from photolysis of any nitrate in the water. At typical nitrate levels found in drinking water (1–6 mg/L as N), the expected yield of nitrite is well below the USEPA drinking water standard of 3.3 mg/L nitrite (1 mg/L as N).[4]

The most comprehensive case history of study and full-scale application of UV irradiation for NDMA treatment in drinking water is in the Village of Ohsweken (Six Nations), Ontario, Canada.[3] NDMA was initially detected in the water supply in December 1989 during routine monitoring under the Ontario Ministry of Environment and Energy Drinking Water Surveillance Program. It was found regularly at levels above the Ontario Interim Maximum Acceptable Concentration of 0.009 µg/L. Laboratory studies demonstrated that this compound was formed by conventional drinking water treatment processes and was not a contaminant associated with the treatment chemicals. Although water quality improvements were achieved by process optimization, NDMA formation could not be completely suppressed by treatments using different oxidants, coagulants, physical treatment or chlorination strategies. UV irradiation was demonstrated to reduce NDMA to levels below detection during laboratory and pilot-scale studies. Full-scale UV treatment was installed at Ohsweken in December 1993 and has since been working successfully. The UV dosage required is approximately 1.3 kwh/m^3 (5 kwh/1000 gal). The full-scale UV system was supplied by Calgon Carbon (90 kW for 270 gpm). Comprehensive analysis of UV-irradiated water from Ohsweken indicates that harmful byproducts are not formed during treatment. However, reformation of NDMA after destruction by UV irradiation **MAY BE** possible **IF THERE ARE ORGANIC PRECURSORS IN THE WATER (IE. WASTEWATERS). TYPICALLY, THIS HAS NOT BEEN OBSERVED IN DRINKING WATER STUDIES WITH UV IRRAIDATION**. Chlorination following UV treatment to ensure disinfection in the distribution system was suspected of causing NDMA reformation. In practical application, all treatment chemical addition should, therefore, occur before UV treatment.

Calgon Carbon has supplied many other UV treatment systems for NDMA removal.[4] The groundwater treatment systems have included capacities from as low as 30 gpm to as high as 3,700 gpm. For NDMA applications, only UV has been used. When other contaminants such as VOCs are also present, UV/OXIDATION systems were installed. The Calgon Carbon Rayox (**TM- TRADEMARK**) System uses proprietary medium-pressure UV lamps that are specifically designed to emit UV light in the 200 to 300 nm absorbance spectrum range. Medium-pressure mercury lamps operate with more mercury in the bulb so they produce higher pressures and temperature than low-pressure lamps. The bulb temperature is typically in the range of 400-800°C. The lamps are mounted inside a **QUARTZ SLEEVE IN A** stainless steel tower. Low-pressure UV lamps are not **AS COST-**effective for NDMA destruction **DUE TO THE LARGE NUMBER OF LAMPS REQUIRED. A TYPICAL LOW PRESSURE LAMP HAS AN OUTPUT OF 40-80 W, WHERE AS CALGON CARBON'S MEDIUM PRESSURE LAMP HAS AN OUTPUT OF 20,000 W; THUS REQUIRING LESS LAMPS AND ASSOCIATED LABOR FOR LAMP CHANGEOUT.** However, flash lamps with pulsed-output were found to be effective for NDMA destruction.[6] Flash lamps operate at very high temperature (12,000^{o}C) and thus fewer lamps are required. However, the technology is not yet well established for commercial applications.

UV/Oxidation

UV/oxidation typically combines UV light with an oxidant, such as hydrogen peroxide. The process involves the generation of highly reactive hydroxyl radicals in sufficient quantity to affect water purification through a destruction process acting at near ambient or room temperatures. Bench- and full-scale UV/oxidation treatment of groundwater contaminated with 300 µg/L of NDMA was found routinely to remove NDMA to below a detection limit of 0.01 µg/L.[7] However, NDMA reacts only moderately fast with the hydroxyl radical ($k = 3.3 \times 10^8$ L mol^{-1} s^{-1}) which is an order of magnitude slower than most compounds that can be economically treated by hydroxyl radicals. In many cases, addition of hydrogen

peroxide can actually slow down photochemical treatment of NDMA since the peroxide can filter out UV light and block it from reaching the NDMA molecules.[3] Other water constituents that may interfere with UV/oxidation can include organics, nitrate, alkalinity and iron in high concentrations.

Ozonation or UV/ozonation was found to be ineffective to reduce NDMA in wastewater at an Army Ammunition Plant, but UV irradiation alone was effective.[7] Based on these studies, use of UV alone is better than UV/oxidation for treatment of NDMA. However, if other contaminants such as VOCs and pesticides have to be treated, the UV/peroxidation process can be used for combined treatment.

Resin Adsorption

Conventional GAC adsorption is not very effective in reducing NDMA to low levels. However, NDMA was found to be removed from groundwater most effectively by Ambersorb^R 572, a carbonaceous resin produced by Rohm and Hass.[8,9] The United States Army Corp of Engineers conducted bench-scale tests to evaluate various adsorbents for NDMA removal, including Ambersorb^R 572, Ambersorb^R 563, Calgon F-400 (a GAC), and Calgon CSC (a GAC). Liquid scintillation isotherm evaluations indicated that Ambersorb^R 572 was the most effective NDMA adsorbent at concentrations greater than 0.05 µg/L, achieving greater than 99percent reduction. Ambersorb^R 572 had the highest K (y-intercept) and 1/n (slope of the isotherm) values at 28.37 µg/g and 2.25, respectively, indicating that it is the optimal adsorbent in terms of adsorption capacity, but that the adsorption capacity for NDMA is the most affected of the adsorbents tested by changes in influent NDMA concentration. The results of the bench-scale isotherm studies indicate that application of modified adsorption systems to preexisting GAC systems may be an effective form of treatment. However, no pilot column testing results have been reported and there is presently no full-scale application of using this resin for NDMA removal.

RECOMMENDED NDMA TREATMENT TECHNOLOGY

UV irradiation is recommended for NDMA removal because it is the most technically effective and cost-effective process for the application. Other advantages of the UV process include: 1) no secondary wastes, 2) no off-gases, 3) quiet, compact and unobtrusive equipment, 4) low maintenance and operating requirements, and 5) flexibility if other organics are present (by adding hydrogen peroxide). Calgon Carbon's Rayox ™ uses proprietary medium-pressure UV lamps that are specifically designed to emit UV light in the 200 to 300 nm range and demonstrated to be effective for NDMA removal. The system includes a stainless steel reactor tower with UV lamps mounted horizontally inside the reactor but separated from the water by quartz tubes. An automated mechanical cleaner is located around the quartz tube and periodically removes solids and precipitates that form on the tube. Inside the reaction chamber internal baffles promote turbulent mixing. The medium-pressure lamps operate between 1,000 and 3,000 volts. PLCs control and monitor the system. Safety locks protect operators from the UV radiation and high voltage supply.[10] The Electrical Energy per Order (EE/O) for NDMA destruction in groundwater is generally in the order of 0.15 to 1.0 kWh/1000 gal/order (90 percent destruction). However, the presence of other UV-absorbing constituents such as nitrate ion may increase the EE/O.[4]

To date, most of the experience on NDMA removal has been acquired using the Rayox^R system. Calgon Carbon has supplied more than 300 RayoxTM systems worldwide for various applications and more than 11 installations in North America treating NDMA.[11] Calgon Corporation supplied Aerojet's 4,000 gpm RayoxTM system at their Rancho Cordova, California site and the LaPuente Valley County Water District, California's 2,500 gpm RayoxTM system.[12] Because of its specific experience on NDMA treatment, the RayoxTM UV system was recommended for implementation.

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