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Removal of refractory compounds by ultraviolet and anodized TiO_2 metal membrane with reactive nano-sized cylindrical tubes on its surface

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ABSTRACT

We investigated the treatment performance of conventional membrane separation, UV irradiation, UV/O_3 system and UV/anodized TiO_2 membrane technology for the removal of *N*-Nitrosodimethylamine (NDMA) from water. The RO membrane did not prove to be effective for NDMA removal. The UV/anodized TiO_2 membrane process decomposed almost 100% of NDMA in the range of all NDMA concentrations. UV/A-Ti-M system was achieved the complete removal of NDMA within 20 mg l^{-1} of NDMA concentration, indicating that the UV/anodized TiO_2 membrane process is a promising treatment technology for treating NDMA contaminated water. With regards to by-products, DMA yield increased with an increase in initial NDMA concentration, whereas MA yield decreased.

Keywords: Anodization; NDMA; Reverse osmosis; TiO_2; UV irradiation; Ozone; By-products

1. Introduction

NDMA contamination of drinking water is of particular concern due to the minute concentrations at which it is harmful, the difficulty in detecting it at these low concentrations, and the difficulty in removing it from drinking water. Extensive research has been conducted on NDMA removal by means of physicochemical treatment options, such as adsorption on activated carbon (AC), hydrolysis, metal complexation, ozonation and UV photolysis [1–5]. Among these techniques, adsorption on granular activated carbon (GAC) and UV photolysis were reported to be the most effective in removing or degrading NDMA.

However, GAC adsorption involves challenges such as competitive adsorption by natural organic matter and the cost for such adsorbents. Also, the reformation of NDMA after destruction by UV irradiation may occur if there are organic precursors in the wastewater [6]. Membrane processes such as microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) are emerging technologies that can be used as alternative treatment processes for the removal of relatively low molecular weight organic contaminants from surface water and wastewater. However, RO is only able to remove approximately 50% of NDMA [7].

Authors’ lab has developed innovative hybrid technology which combines UV treatment with anodized TiO_2 membrane (A-Ti-M) technology. The anodized TiO_2 membrane showed dual function such as photocatalytic decomposition of organics and membrane filtration [8]. Several researchers reported that the hybrid membrane capable of dual function such as filtration and catalization [9–11]

The objective of this study is to compare NDMA removal efficiencies using conventional technologies (RO, UV treatment, UV/O_3 treatment) and innovative hybrid technology which combines UV treatment with

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anodized TiO_2 membrane (A-Ti-M) technology. In addition, in this study, we investigate the limiting concentration of NDMA removal and characteristics of by-product in different UV/A-Ti-M and UV/O_3 system.

2. Materials and methods

2.1. *Chemicals and solution preparation*

All experiments were conducted using deionized water produced from a Barnstead Nanopure II water purification system. NDMA, dimethylamine hydrochloride (DMA, 98%), methylamine (MA) and sodium nitrite (99%) were purchased from Sigma-Aldrich. Cambridge Isotope Laboratories (Andover, MA) NDMA-d_6 was used as an internal standard for NDMA analyses. Dichloromethane (98%; Cambridge Isotope Laboratories, Inc., Andover, MA) was used for liquid-liquid extractions of samples. All other chemicals used in these experiments are analytical-reagent grade.

2.2. *Experimental apparatus and procedure*

2.2.1. *Membranes*

RO membranes (AG–4040F) used in this study were purchased from Woongjin Chemical Co., Ltd. The spiral-wound RO membrane consisted of a polyamide thin-film composite and had 99.4% salt rejection and 8.9 $m^3 d^{-1}$ permeate flow flux. Also, effective membrane area and operating pH range were 8.4 m^2 and 4–11, respectively.

2.2.2. *UV/anodized TiO_2 membrane and UV/O_3 system*

A schematic of the setup for the UV/anodized TiO_2 membrane and UV/O_3 system is shown in Fig. 1. The UV/A-Ti-M system was composed of a 64 W UV lamp, pH meter and an A-Ti-M filtration device. Microporous tubular-type pure titanium filters (99.6 wt%, Fibertech, Co. Ltd., Korea), which had a 12-mm inner diameter and 100-mm length, were prepared for the anode materials. A 99.9% pure tantalum (Aldrich Chemical Company Inc., Milwaukee, USA) that had a thickness of 0.25 mm and surface area of 2,500 mm^2 was used as the counter electrode. After anodization, the specimens were rinsed immediately with deionized water and dried in a nitrogen stream [8]. The working volume of the photo-reactor was 8 l. UV illumination was provided by a 64 W Black-light lamp with a maximum light intensity output of 375 nm. A-Ti-M has an effective photo-reaction area of 4 × 58.4 cm^2. The solution temperature of the interior photo-reactor was maintained by a thermostatic water bath. The initial pH of the solution was adjusted ±0.2 by adding an appropriate amount of 0.1 N NaOH and 0.1 N H_2SO_4. The procedures for using UV treatment and an A-Ti-M were as follows. NDMA solution was prepared by adding a calculated amount of NDMA stock solution to distilled water. The initial pH was adjusted after addition of the NDMA stock. The prepared solution in the reactor was placed in a thermostat to maintain the solution temperature at 20 ± 1°C. Photolysis of the A-Ti-M was initiated by exposing the reactor to UV irradiation. In the NDMA removal experiment using UV/O_3 system, ozone was produced by AZOCOZON (Labco Co., Ltd.). Oxygen flow rate was adjusted to 2 ± 0.1 l min^{-1}, obtaining an ozone production of 8 g h^{-1}. Dissolved ozone concentration in the system was controlled by varying the oxygen flux, the voltage of ozone production and the time at which ozone was introduced into the system. Every 100 min, the sample was withdrawn for NDMA, DMA, MA, NO_2^- and NO_3^- analysis. Cellulose nitrate membrane filters (Whatman Plc., England) with a pore size of 0.2 μm was used to remove solid particles from the samples.

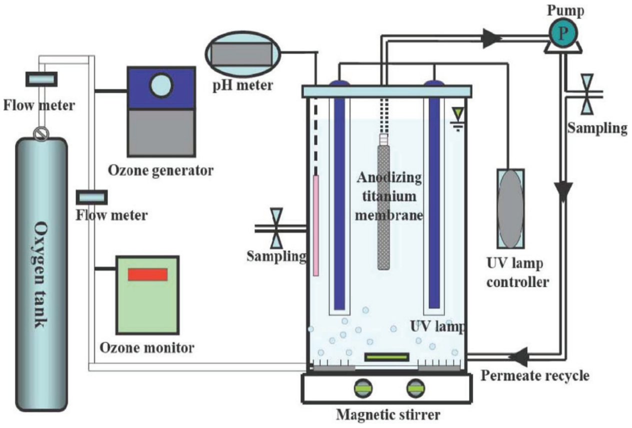

Fig. 1. Schematic of the UV/anodized TiO_2 membrane system.

2.3. *Analyses*

The Gas Chromatography/Mass Spectrometer (GC/MS; Agilent 6890 GC/5973 MS) with a chemical ionization option was used to determine the identity of the nitrosamines in the sample. A Supelco Equity TM – 1701 column (30 m × 250 μm 0.25 μm) and an uncoated retention gap was joined by a press-fit connector. The solvent-vent injection mode (typical injection volume of 5 μl) was used with a programmable temperature vaporization (PTV) based on a large volume injector (LVI) that is capable of a broad range of volume injections and pre-concentrations. A 100 μl syringe was used in the integrated automated liquid sampler HP 7683 injector for the 50 μl injection. The GC temperature program consisted of an initial temperature of 45°C, which was held for 3 min, followed by an increase in temperature to 180°C at 15°C/min and then to 250°C at 30°C/min. The GC/MS transfer line temperature and the mass spectrometer ion source temperature was maintained at 250°C. Helium gas was used as a carrier gas at 50 ml/min. NDMA was identified using an isotopic dilution method based on the mass detection of NDMA's molecular ion ($m/z = 74$) and the characteristic molecular ion of NDMA-d_6 ($m/z = 80$). The products of NDMA photolysis were identified and quantified using ion chromatography (IC; Dionex, DX-120) with a conductivity detector. DMA and MA were analyzed with an IonPac CS14 cationic column (4 mm × 250 mm) using 10 mM methansulfonic acid/ 0.3% acetonitrile solution as the eluent. NO_2^- and NO_3^- were analyzed with an IonPac AS14 anionic column (4 mm × 250 mm) using 8.0 mM Na_2CO_3/1.0 mM $NaHCO_3$ solution as the eluent.

3. Results and discussion

3.1. NDMA removal using membrane filtration and UV techniques

Experiments were conducted to examine and confirm the efficiency of NDMA removal using membrane separation and UV irradiation processes with previous researches [4,5,7]. The results from this comparison are shown in Fig. 2. For this experiment, about 40% of NDMA was rejected by the membrane when using RO, indicating that the small NDMA molecule easily passes through the membrane. It is reported RO rejection of NDMA of approximately 45 to 65% and 10 to 70%, respectively [7,12–14]. About 50% was required for thin-film composite RO membrane [7].

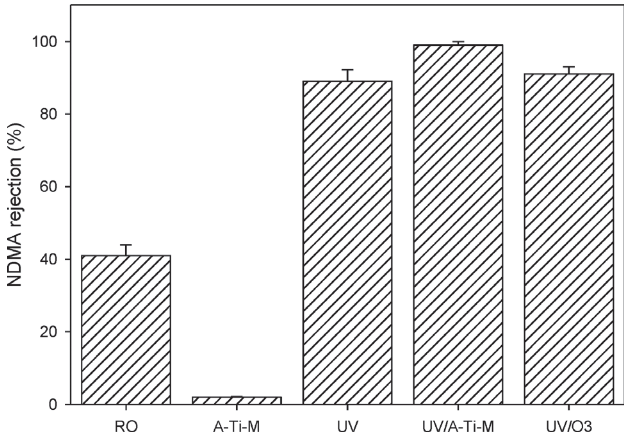

Fig. 2. Removal of NDMA using RO membrane (conditions: contact time 100 min, temperature 20 ± 1°C, NDMA 1 mg l^{-1}, initial pH 6 ± 0.2, UV intensity 64 W and ozone concentration 9.0 mg l^{-1}).

Efficiency of NDMA removal by UV irradiation was higher than that of membranes such as RO (see Fig. 2) and about 90% of NDMA was successfully removed by UV irradiation. Also, introducing ozone into the UV system did not enhance significantly the effectives of NDMA removal from water. This implies that UV acted as effective oxidants than ozone in NDMA removal by UV/O_3 system. However, the efficiency of NDMA removal using an anodized TiO_2 membrane in combination with UV irradiation was higher than that of only UV irradiation. The reason for this improvement is the production of hydroxyl radicals generated in a reaction between UV and A-Ti-M. Almost 100% of NDMA was removed within 100 min of operational time. Even though A-Ti-M can result in the increase of extra capitals and operating costs in order to improve 10% of removal efficiency, NDMA removal is significantly important because low concentration (nano-level) of NDMA can even be adversely influenced on human and environment. Therefore, UV irradiation alone was not a powerful enough tool to entirely remove NDMA from water. Using UV irradiation directly on an A-Ti-M surface proves to be an attractive method for removing NDMA.

3.2. Effect of initial NDMA concentration

Fig. 3 shows the effect of initial NDMA concentration on NDMA removal efficiency as a function of time in UV/A-Ti-M and UV/O_3 system. Fig. 3a shows the performance of the UV/A-Ti-M process for the removal of NDMA at various concentrations from 1 to 20 mg l^{-1}. The efficiency of NDMA removal using the UV/A-Ti-M process was about 100% in the range of 1 to 20 mg l^{-1} of initial NDMA. This finding implies that hydroxyl radicals were produced as a result of the photocatalytic reaction between UV and an A-Ti-M. As shown in Fig. 3b, when initial NDMA concentration reached to 10 mg l^{-1}, removal efficiencies gradually decreased. This result supposes that free radicals generated from UV/O_3 system are insufficient to remove NDMA completely from water and more effective removal can be achieved by the increase of ozone concentration or retention time in system.

3.3. Characteristics of by-product by UV/A-Ti-M and UV/O_3 system

Fig. 4a shows the effect of the initial NDMA concentration (from 1 to 20 mg l^{-1}) on the output of by-products such as MA and DMA. MA and DMA are known as the primary amino compounds produced by the two distinct pathways of NDMA photolysis [5].

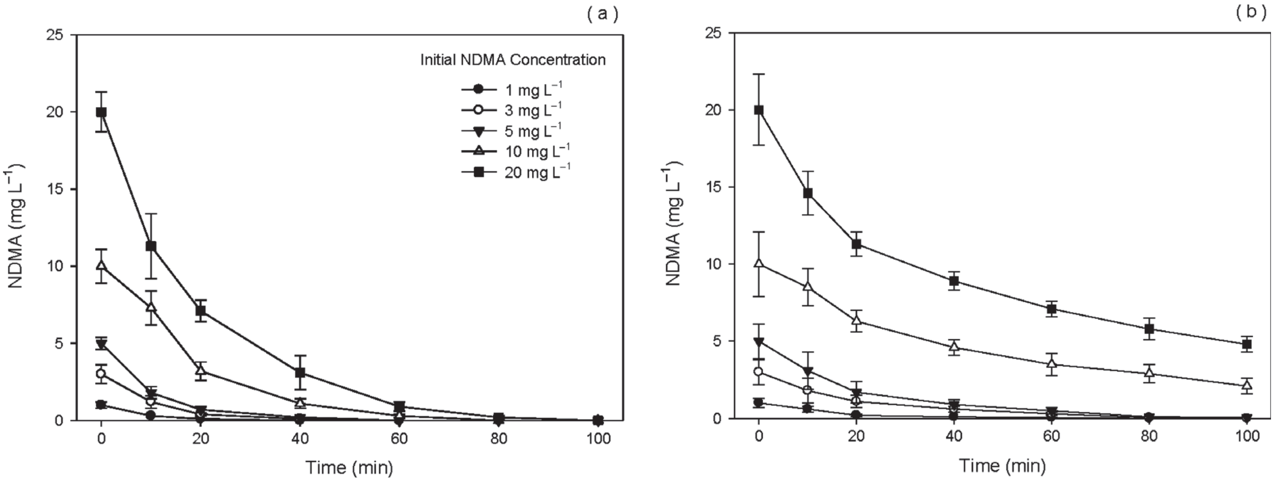

Fig. 3. Effect of initial NDMA concentration on NDMA removal using a) UV/A-Ti-M and b) UV/O_3 system (conditions: contact time 100 min, temperature 20 ± 1°C, initial pH 6 ± 0.2, UV intensity 64 W and ozone concentration 9.0 mg l^{-1}).

The yield rate of MA, DMA, NO_2^- and NO_3^- were calculated from the following equations:

$$\text{MA yield} = [\text{MA}]_{100}/[\text{NDMA}]_0 \quad (1)$$

$$\text{DMA yield} = [\text{DMA}]_{100}/[\text{NDMA}]_0 \quad (2)$$

$$NO_2^- \text{ yield} = [NO_2^-]_{100}/[\text{NDMA}]_0 \quad (3)$$

$$NO_3^- \text{ yield} = [NO_3^-]_{100}/[\text{NDMA}]_0 \quad (4)$$

where $[\text{MA}]_{100}$ and $[\text{DMA}]_{100}$ are the concentrations of MA and DMA produced by degrading NDMA after 100 min of operating time. Also, $[NO_2^-]_{100}$ and $[NO_3^-]_{100}$ are the concentrations of NO_2^- and NO_3^- produced by decomposing the NDMA after a 100 min of reaction time. We observed a variation in the production of by-products such as DMA, MA, NO_2^- and NO_3^-. As shown in Fig. 4a and 4b, with the increase of initial NDMA concentration, the production of DMA increased but that of MA decreased in both systems. The production of MA was higher than that of DMA in the range of 1 to 3 mg l^{-1} of NDMA but it decreased when the NDMA concentrations were greater than 5 mg l^{-1}. This can be explained by DMA decomposition, which easily reacts with the hydroxyl radicals produced at low concentrations of NDMA. However, these hydroxyl radicals react with NDMA more so than with NDMA decomposition intermediates at high NDMA concentrations. Especially, the yield of DMA during the NDMA oxidation reaction was higher than that of other

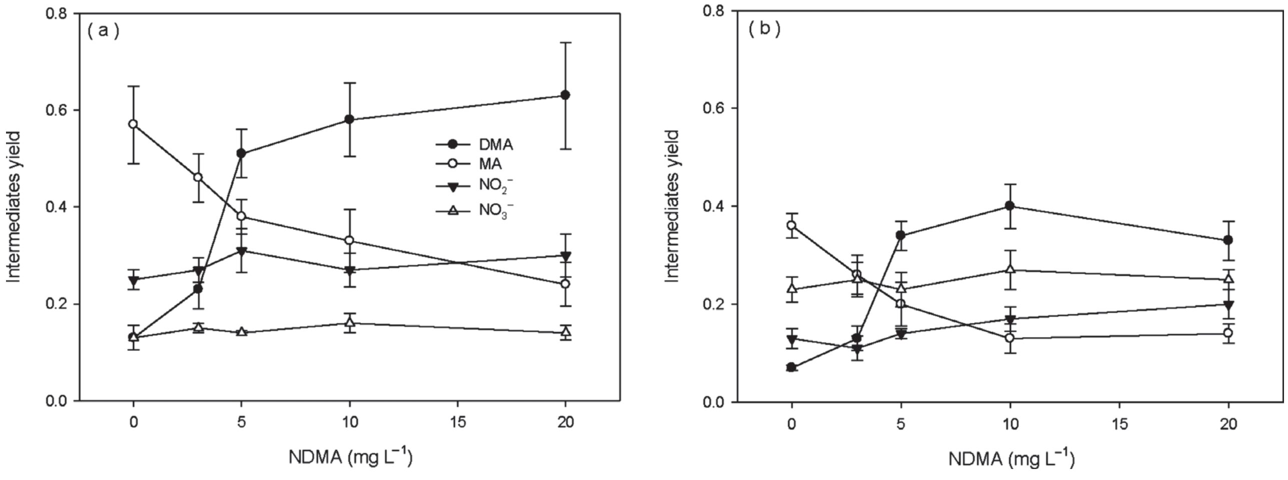

Fig. 4. The effect of initial NDMA on the output of NDMA intermediates using a) UV/A-Ti-M and b) UV/O_3 system (conditions: contact time 100 min, temperature 20 ± 1°C, UV intensity 64 W and ozone concentration 9.0 mg l^{-1}).

by-products. Therefore, UV/A-Ti-M system may be useful for preventing regeneration of NDMA induced by produced DMA.

In UV/O_3 system, the produced DMA and MA were lower than those in UV/A-Ti-M system. However, the yield of NO_3^- was greater than that of NO_2^-. As products generated from NDMA, DMA, MA, and NO_2^- were well known as the ubiquitous precursors of NDMA formation. Since their presence in water creates a significant potential of NDMA regeneration, UV/O_3 system also may be alternative treatment technology when NDMA concentrations below 5 mg/l in water is existed.

4. Conclusions

N-Nitrosodimethylamine (NDMA) is a disinfectant by-product shown to be carcinogenic, and mutagenic. Even through conventional membrane was ineffective in removing NDMA contents, efficiencies of NDMA removal by UV irradiation and UV/O_3 system were about 90% and 95%, respectively. UV irradiation used in combination with an anodizing TiO_2 membrane proposed in this study was achieved to remove NDMA completely from water. With the increase of initial NDMA concentration in the range of 1 to 20 mg l^{-1}, UV/A-Ti-M system was achieved the complete removal of NDMA but removal efficiencies of NDMA using UV/O_3 system decreased dramatically from 10 mg l^{-1}. Also, the production of DMA increased but that of MA decreased. The UV/A-Ti-M system may be useful for preventing regeneration of NDMA induced by produced DMA.

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