NDMA formation potential removal in treated effluent by UV/H\textsubscript{2}O\textsubscript{2} process

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ABSTRACT

NDMA formation from treated wastewater is one of the concerns in water reuse. This study focused on NDMA formation potential (NDMAFP) removal in wastewater treated effluent by UV/H\textsubscript{2}O\textsubscript{2} technology. A UV/H\textsubscript{2}O\textsubscript{2} system was tested for the removal performance on both organic precursors and NDMAFP. The system consisted of a low pressure ultra-violet (LPUV) with an intensity of 2 mW/cm\textsuperscript{2} and a H\textsubscript{2}O\textsubscript{2} dosage of 100 ppm. Reaction time was 60 minutes. Two types of wastewater treated effluents were collected: activated sludge process (ASP) effluent and membrane bio-reactor (MBR) effluent. Results showed efficient dissolved organic carbon (DOC) removal (70%). Dissolved organic nitrogen (DON) removal was less efficient (20–30%). Eighty per cent of NDMAFP in ASP effluent was removed within 1 hour. However, no NDMAFP removal was discovered in MBR effluent. This indicated that the effect of the UV/H\textsubscript{2}O\textsubscript{2} system on NDMAFP removal was water specific. A generation of intermediate NDMA precursors was observed in the ASP effluent. Results indicated that sufficient oxidation should be provided to reduce intermediate NDMA precursors and to achieve NDMAFP removal.

Key words | DOC, DON, NDMAFP, treated effluent, UV/H\textsubscript{2}O\textsubscript{2}

INTRODUCTION

A clean drinking water supply is a challenging issue for society. Currently, water shortages and pollution problems are affecting human health and development. With population increase and urbanization, the problem is becoming more severe. One of the strategies to face the problem is to look for alternative water supplies from water reuse and reclamation (Fujikawa et al. 2012). However, due to the complex composition of wastewater, it is important to ensure reclaimed water quality. In current practice, treated water is discharged into the natural environment before consumption to reduce contamination levels (National Research Council 2012). A future approach is leading to directly restoring treated wastewater to potable quality (Shannon et al. 2008). Both current and future situations require stringent regulation and reliable engineering systems to ensure drinking water quality.

NDMA is one of the compounds of emerging concern affecting drinking water quality (Mitch et al. 2005; Richardson 2005). This carcinogenic compound poses a health threat to humans at very low concentrations: according to USEPA, 0.7 ng/L NDMA in drinking water yields 10\textsuperscript{-6} lifetime cancer risk. The California Department of Public Health (CDPH) established an interim action level of 10 ng/L (CDPH 2011). Moreover, the Ontario Ministry of the Environment (MOE) in Canada set an Interim Maximum Acceptable Concentration for NDMA as 9 ng/L (MOE 2000). The World Health Organization (WHO) established a guideline value of 100 ng/L (WHO 2006). With stringent regulation on NDMA, it is important to study and control NDMA formation in treated wastewater during water reclamation.

NDMA is formed mainly through chlorination and chloramination. Dissolved organic matter (DOM) is the
main precursor. Studies discovered dimethylamine (DMA) to be the most effective organic nitrogen precursor (Choi & Valentine 2002; Mitch & Sedlak 2002). Organic nitrogen compounds with a DMA and DMA functional group in wastewater also contribute to NDMA precursors. However, DMA is not the only source (Mitch et al. 2005b). Other precursors reported include dithiocarbamate and nitrogen-containing cationic polyelectrolytes (Weissmahr & Sedlak 2000). However, studies report that the majority of NDMA precursors in treated effluent are unknown compounds other than DMA (Mitch & Sedlak 2002; Deeb et al. 2006).

NDMA control includes NDMA removal and NDMA precursor removal. Many studies have addressed the issue of NDMA removal. Ultraviolet (UV) photolysis is one established method, where UV light cleaves the N-N bond and breaks NDMA into nitrite and DMA (US EPA 2008). Other techniques include reverse osmosis, nanofiltration, ozonation and chlorine dioxide (Lee et al. 2005; Plumlee et al. 2008). In comparison, fewer studies have investigated the treatment process for NDMA precursor removal in wastewater treated effluent. To measure the quantity of NDMA precursors in water samples, NDMAFP is introduced as the maximum amount of NDMA formed. Microfiltration demonstrates moderate removal efficiency for NDMAFP. Reverse osmosis can reduce NDMAFP by one order. Results are not available for UV’s effect on NDMAFP removal (Deeb et al. 2006).

The advanced oxidation process (AOP) is a powerful method to reduce and remove organic contaminants. It generates a hydroxyl radical, which is a strong oxidant. In particular, one of the AOP processes, UV/H₂O₂, has been applied in drinking water treatment since the 1990s (Hofman-Caris & Beerendonk 2011). It has also been studied to treat industrial wastewater (Rodríguez et al. 2007). Preliminary research results have shown the effect of UV/H₂O₂ on NDMAFP removal (Chen et al. 2010). With laboratory synthetic water (surface water combined with biologically treated wastewater), the UV/H₂O₂ process achieved NDMAFP removal of 50%. However, the performance may be overestimated for wastewater treated effluent, due to experiments being performed on synthetic water. Only one UV/H₂O₂ condition was chosen, different UV/H₂O₂ conditions and various treated wastewaters were not studied. A more recent study applied medium pressure ultra-violet (MPUV)/H₂O₂ and LPUV/H₂O₂ to six selected nitrogenous organic compounds (Chen et al. 2011). Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) removal were evaluated. Removal performances differed among compounds. A larger degree of DOC removal compared to DON removal was achieved for compounds with complicated structures. NDMAFP removal was tested on a DMA solution. However, the results were compound-specific, and organic content in the treated wastewater environment is more complicated. Therefore, studies on treated wastewater were needed.

There is limited research on UV/H₂O₂ removal efficiency for NDMAFP in treated wastewater, especially NDMAFP removal kinetics. This study aimed to evaluate UV/H₂O₂ performance for NDMA precursor removal in treated wastewater. In this study, a bench scale experiment was conducted to understand removal kinetics and efficiencies and to assess the feasibility of applying UV/H₂O₂ to remove NDMAFP in treated wastewater.

**MATERIAL AND METHODS**

**System set up**

A batch system was tested. One LPUV lamp (Trojan UV Max Model B lamp) was placed in the center of a 1 L beaker with a magnetic stirrer at the bottom (Figure 1). The UV lamp produced a UV intensity of 2 mW/cm² at

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**Figure 1** | Schematic diagram of UV/H₂O₂ system.
254 nm. The UV lamp was heated for 10 minutes before each batch experiment to ensure a steady UV output. The magnetic stirrers provided vigorous mixing.

**Water sample collection**

Two types of wastewater samples were collected from a local water reclamation plant: secondary effluent from an activated sludge process (ASP), and secondary effluent from a membrane bioreactor (MBR) process. All water samples were collected in 10 or 20 L jerry cans. They were transported by laboratory vehicle and stored at 4°C in a cold room. Effluents were filtered through a 0.45 μm filter to remove particles before reaction in photoreactor. Water quality parameters are presented in Table 1.

**Experiment design**

The batch reaction time was set as 60 minutes. H₂O₂ dosages of 50 and 100 ppm were chosen to examine the effect of H₂O₂ dosage. During each batch experiment, a 1 L water sample was dosed with H₂O₂ and treated by UV irradiation. A 100 mL sample was collected at a specific time for organic precursor analysis. H₂O₂ was stopped immediately by adding 27 units/mL catalase. The H₂O₂ in the remaining 900 mL sample was stopped by adding 100 mL 20 mM monochloramine stock. This sample was then used for NDMAFP detection. The precursor removal profile and efficiency were evaluated by total DOC/DON removal and DOC/DON removal in each organic fraction defined in liquid chromatography–organic carbon detector–organic nitrogen detector (LC-OCD-OND) results.

The NDMAFP measurement followed the method described by Mitch et al. (2003). A 900 mL water sample was dosed with 100 mL 20 mM monochloramine. Reaction was at room temperature for a period of 7 days. NDMAFP was measured at the end of the reaction by applying solid phase extraction (SPE) followed by an LCMS-8030 triple quadrupole mass spectrometer (Shimadzu, Japan) analysis. Organic precursors were analyzed by LC-OCD-OND (DOC-LABOR, Germany) which provided information on molecular weight distribution of both DOC and DON. LC-OCD-OND separates DOM into major fractions: biopolymers (BP), humic substances (HS), building block (BB), low molecular weight (LMW) acids and neutrals, and hydrophobic organic carbon (HOC). It estimates the quantity of organic carbon in each fraction and the quantity of organic nitrogen in biopolymer and humic substances fractions. Manual integration was applied to estimate the nitrogen content in LMW and the total nitrogen content. Nitrogen in BB was then calculated by subtracting the nitrogen content in other fractions out of the total nitrogen content:

\[
N_{in \ BB} = Total \ N - N_{in \ BP} - N_{in \ HS} - N_{in \ LMW} \tag{1}
\]

Total organic carbon and total nitrogen were measured by a TOC and TN analyzer (Shimadzu, Japan). Inorganic ions NO₃⁻ and NO₂⁻ were measured by Dionex ion chromatography (USA). Ammonium was measured using a Hach Nitrogen-Ammonia Reagent Set. UVT was measured using a DR 5000 UV-Vis spectrophotometer (Hach, USA). pH was measured by a pH meter (ITS Science & Medical, Singapore).

**RESULTS AND DISCUSSION**

**DOC removal kinetics**

DOC removal was linearly related to reaction time. Within 60 minutes, DOC decreased continuously with constant degradation rates (Figure 2). For 100 ppm and 50 ppm
H$_2$O$_2$ dosage, degradation rates were 0.08 ppm and 0.07 ppm DOC/min, respectively. Removal efficiencies of DOC were 65 and 55%. Similar results were observed in a previous study, when an LPUV/H$_2$O$_2$ system with a UV intensity of 40 mW/cm$^2$ and a H$_2$O$_2$ dosage of 11.2 ppm was applied to selected organic compounds. A continuous decreasing trend and constant oxidation rate for DOC was observed during 60 minutes’ reaction time. For histamine and caffeine, degradation rates were 0.05 ppm and 0.04 ppm DOC/min, respectively. Removal efficiencies of DOC were 70% and 50%, respectively (Chen et al. 2011).

Figure 3 shows that DOC removal kinetics in each fraction was different from that of total DOC. No linear relation was observed. Removal kinetics also differed among the fractions. BP contains molecules with high MW (20,000–100,000 Da). The initial DOC concentration in BP was 894.1 ppb. The DOC in BP decreased continuously and achieved 92% removal. The DOC degraded quickly from 0 to 20 minutes, with an average degradation rate of 33.4 ppb DOC/min; the degradation slowed down afterwards with an average degradation rate of 3.8 ppb DOC/min. The BP fraction contains mainly polysaccharide, proteins and amino sugars, with polysaccharide as the dominating component (Huber et al. 2011). Polysaccharide contains aliphatic chains which are easily oxidized (Chen et al. 2011). This may contribute to the significant removal of BP.

HS contains molecules of MW around 1,000 Da. HS was dominant in the ASP effluent, with an initial DOC concentration of 2,636.9 ppb. The DOC in HS degraded continuously, and total removal was 81%. The average degradation rate was 35.2 ppb DOC/min. In a previous study (Wang et al. 2006) when 108.8 ppm H$_2$O$_2$ was dosed in the UV system treating a humic substance ([DOC]$_0$ = 5 ppm), the degradation rate was 71.9 ppb DOC/min. However, the HS was dosed in DI water in that study. The higher degradation rate may be due to the less complicated water matrix. The HS solution was less complicated than ASP effluent, therefore UV transmittance was better and the hydroxyl radical was more efficient.

BB comprises molecules of MW from 300 to 500 Da. Its initial DOC concentration was 1,438.9 ppb. A fluctuating pattern and low degree of removal (9%) were observed in this fraction, with an average DOC degradation rate of 2.1 ppb DOC/min. This may be due to the generation of intermediate compounds in the BB fraction from HS breakdown (Huber et al. 2011). LMW compounds (acids and neutrals) are of MW less than 350 Da. Its initial DOC degradation rate was 15.2 ppb DOC/min. In a previous study (Wang et al. 2006) when 108.8 ppm H$_2$O$_2$ was dosed in the UV system treating a humic substance ([DOC]$_0$ = 5 ppm), the degradation rate was 71.9 ppb DOC/min. However, the HS was dosed in DI water in that study. The higher degradation rate may be due to the less complicated water matrix. The HS solution was less complicated than ASP effluent, therefore UV transmittance was better and the hydroxyl radical was more efficient.

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Concentration was 1,596.0 ppb. Significant removal (64%) was achieved. The concentration increased in the first 5 minutes, which may result from the fast breakdown of some of the BP compounds, such as polysaccharides. After 5 minutes, the LMW concentration decreased, with an average degradation rate of 22.7 ppb DOC/min.

**DON removal kinetics**

DON degradation was less efficient than that of DOC. Thirty per cent removal was achieved (Figure 4). DON increased in the first 5 minutes and then decreased. This increase of DON at the beginning may be due to the oxidation of macro organic matter (Chen et al. 2010). No linear relation was observed between DON removal and reaction time. In wastewater, approximately 0.6–13% DOM is in the form of combined amino acid and 14–25% is from protein (Manka & Rebhun 1982; Dignac et al. 2000). Hydroxyl radicals can break down these substances and result in the decrease in DON. However, for complex organic structures, in particular when nitrogen atoms are located in the centre of molecules, more oxidation capacity is required (Chen et al. 2011).

DON degradation in each fraction (Figure 5) shows the most removal was in BP, HS and BB (63%, 74% and 76%, respectively). However, there was a significant increase in DON in the LMW fraction with time. With an H₂O₂ dosage of 100 ppm (Figure 5(a)), the initial DON concentration in the BP was 192.7 ppb, which was dominant among the four fractions. The DON in the BP degraded quickly from 0 to 20 minutes, with an average degradation rate of 7.4 ppb DON/min; the degradation slowed down afterwards with an average degradation rate of 0.09 ppb DON/min. The initial DON concentration in the HS was 161.1 ppb, which was the second highest among the four fractions. The average DON degradation rate was 2.2 ppb DON/min. The BB fraction contained an initial DON of 73.2 ppb. Its average degradation rate was 0.7 ppb DON/min. The initial DON concentration in the LMW was the lowest (41.1 ppb), however, it increased with an average rate of 2.8 ppb DON/min. DON degradation kinetics were distinct from that of DOC. This indicates that removals of DOC and DON in ASP effluent were not directly related under UV/H₂O₂ treatment.

The increase in DON in LMW was observed in a previous study when UV/H₂O₂ was applied to synthetic...
wastewater containing melanoidins (Dwyer & Lant 2008). The increase was significant, from 29% of initial nitrogen to 46%. It was reported that DON associated with small molecular weight molecules (<1,000 Da) cannot be chemically oxidized easily, unlike the associated DOC (Dwyer & Lant 2008). Therefore, the increase in DON in LMW may be because of the accumulation in DON in smaller molecules broken down from larger molecules.

Comparison of organics removal in ASP and MBR effluents

ASP effluent and MBR effluent were tested to assess the effect of organics composition on DOM removal. MBR effluent had lower DOC and DON concentrations (Table 1). It also had lower DOC and DON contents in both BP and HS fractions (Table 2).

Figure 6 shows similar DOC removal kinetics for both ASP and MBR effluents. However, less DON was removed in the MBR effluent. A significant increase in DON was observed in the MBR effluent within 5 minutes.

DOC and DON increased significantly in the BP fraction at 5 minutes of reaction (Figure 7). These increases were not expected in the UV/H₂O₂ process. Within 5 minutes, the DOC increased from 258 to 316 ppb and the DON increased from 17 to 129 ppb. After 5 minutes, the DOC was degraded with average rates of 15.5 ppb DOC/min from 5 to 20 minutes and 1 ppb DOC/min from 20 to 60 minutes. The DON dropped from 129 to 40 ppb from 5 to 10 minutes at a rate of 17.8 ppb DON/min, and stayed relatively constant afterwards. Except for the difference in the BP fraction, DOC and DON removal trends in the other three fractions were similar for MBR and ASP effluents (Figures 3, 5 and 7).

The observation indicates the formation of large molecules in MBR effluent at the initial stage of UV/H₂O₂ treatment. This may be caused by UV irradiation, under which small organic molecules can be polymerized to form large polymers. For example, in UV polymerization technology, monomer was formed into polymer under UV irradiation (Hu et al. 2009).

NDMAFP removal kinetics

Figure 8 shows the result of NDMAFP removal. For both 100 and 50 ppm H₂O₂ dosages, humps were observed in NDMAFP profiles. NDMAFP decreased at the beginning, then increased significantly after 5 minutes, and finally decreased. With a 100 ppm H₂O₂ dosage, NDMAFP reached the highest value of 404 ng/L at 20 minutes; 80% NDMAFP removal was achieved after 60 minutes of treatment. With a 50 ppm H₂O₂ dosage, NDMAFP reached a higher value of 739 ng/L later, at 40 minutes. No NDMAFP removal was achieved within 60 minutes. The peak NDMAFP for a 50 ppm dosage was 1.89 times of the initial NDMAFP.

NDMA per DON profiles (Figure 9) were similar to that of NDMAFP. One mg/L DON yielded the highest NDMAFP of 2.979 ng/L (2.979 μg/L) at 40 minutes with a 50 ppm H₂O₂ dosage. This is smaller than the value tested with diltiazem under UV/H₂O₂ (Chen et al. 2011), where 1 mg/L DON yielded 59 μg/L NDMA. An H₂O₂ dosage of 50 ppm yielded more NDMA compared with a 100 ppm dosage. This is consistent with the finding that an inadequate quantity of oxidant yielded the maximum NDMA (Chen et al. 2011).

| Table 2 | Comparison of DOC and DON composition in ASP and MBR effluents |
|----------|-----------------------------|-----------------------------|
| **DOC, ppb** | ASP | MBR |
| % DOC | BP | HS | BB | LMW | BP | HS | BB | LMW |
| 894.06 | 2,636.88 | 1,438.93 | 1,596.03 |
| 14% | 40% | 22% | 24% |
| 258.32 | 1,950.81 | 1,337.38 | 1,508.72 |
| 5% | 59% | 26% | 30% |

| **DON, ppb** | ASP | MBR |
| % DON | BP | HS | BB | LMW | BP | HS | BB | LMW |
| 192.66 | 161.12 | 73.23 | 41.11 |
| 41% | 34% | 16% | 9% |
| 16.60 | 114.73 | 90.17 | 43.20 |
| 6% | 43% | 34% | 16% |
The similarity in NDMAFP removal profiles of 50 and 100 ppm dosages in Figure 8 may be because of the same organics removal kinetics, as shown in Figures 2–5. With an H2O2 dosage of 100 ppm, NDMAFP increased at a constant rate of 12.9 ng/L/min between 5 and 20 minutes. For 50 ppm dosage, NDMAFP increased at a constant rate of 10.4 ng/L/min between 5 and 40 minutes. These NDMAFP increases infer that at the beginning of the UV/H2O2 reaction, some organics were degraded to form intermediate NDMA precursors; as a result the amount of NDMA precursors increased. However, with the longer reaction time, the total amount of NDMA precursors could be decreased. NDMAFP removal profiles may be H2O2 dosage dependent. In this study, a higher H2O2 dosage resulted in a higher increase in a shorter period, and a larger degree of removal. In a similar study, when NDMAFP of diltiazem was tested under UV/H2O2 treatment, a comparison was made between a single H2O2
dosage of 220 ppm and an initial H₂O₂ dosage of 108 ppm with an 88 ppm addition every 10 minutes. Results from both conditions showed increases in NDMAFP followed by decreases; however, it later showed a lower increase rate in a longer period and a larger degree of removal (Chen et al. 2011). The continuous H₂O₂ dosing reduced the NDMAFP increase rate, this may be because with continuous dosing, the H₂O₂ concentration in the water sample at each time was relatively lower, which leads to slower oxidation and therefore a reduced increase rate for intermediate NDMA precursors.

Better NDMAFP removal efficiency with a higher H₂O₂ dosage may be due to faster DOM removal. With 100 ppm H₂O₂, DOC removal was faster, and more DOC was removed in each fraction (Figure 10). In terms of DON, although total DON removal was similar for both H₂O₂ dosages, the 100 ppm H₂O₂ system had a faster DON increase in LMW (Figure 11). This indicates a faster oxidation effect on DON with a higher H₂O₂ dosage.

During UV/H₂O₂ treatment, there was generation of intermediate NDMA precursors. Depending on the treatment condition, NDMAFP could increase up to 1.89 times the initial NDMAFP (at an H₂O₂ dosage of 50 ppm). In another study, NDMAFP increased up to 2.3 times with UV/H₂O₂ treatment of diltiazem (Chen et al. 2011). With a stronger oxidation effect, intermediate NDMA precursors could be further degraded. These results indicate that during UV/H₂O₂ treatment, it is preferable to use the DOM concentration as an indicator for NDMAFP...

![Figure 9](https://example.com/figure9.png)

Figure 9 | NDMAFP per DON of ASP effluent by UV/H₂O₂ process.

![Figure 10](https://example.com/figure10.png)

Figure 10 | Comparison of the DOC of four DOM fractions in ASP effluent with different H₂O₂ dosages.
removal. Alternatively, one potential suitable parameter to indicate NDMAFP removal would be the DON concentration in LMW, since the increase of DON in LMW indicates the degree of nitrogen associated organics oxidation. Caution should be taken to remove intermediate NDMA precursors by dosing sufficient oxidant (100 ppm H₂O₂ in this study) and providing adequate reaction time (60 minutes in this study).

Comparison of NDMAFP removal in ASP and MBR effluents

Within 60 minutes, unlike for ASP effluent (Figure 8), there was no hump presented in the NDMAFP profile for MBR effluent (Figure 12). NDMAFP reached a plateau after 20 minutes. Further comparison of H₂O₂ dosage showed no
NDMAFP removal at 60 minutes with 75, 100, 125 and 150 ppm dosage (Figure 13). This may be explained by the potential formation of large nitrogen-rich molecules at the initial stage of UV/H2O2 treatment (Figure 7). This formation may increase the required oxidation capacity to degrade NDMA precursors. It was reported that continuous H2O2 addition could achieve more DON removal (Chen et al. 2011). As reported in another study, NDMAFP correlated with DON fractions (Pehlivanoglu-Mantas & Sedlak 2008), therefore the method of continuous H2O2 dosing may be used to improve NDMAFP removal for MBR effluent. The difference between NDMAFP removal kinetics in ASP and MBR effluents indicates that UV/H2O2 treatment for NDMAFP is water specific. Further research is needed to evaluate UV/H2O2 performance on different wastewaters with different organics compositions.

CONCLUSIONS

UV/H2O2 treatment was proved to be able to remove DOC efficiently (up to 70%) and remove DON with less efficiency (up to 30 or 20%) in ASP and MBR effluents. UV/H2O2 removed NDMAFP in ASP effluent at up to 80%. This indicates the potential usage of UV/H2O2 as a means of removing DOM and NDMAFP in treated effluent. However, under the experimental conditions, no NDMAFP removal was achieved in MBR effluent. This shows that using the UV/H2O2 process to remove NDMAFP may be water specific. DOM removal in each fraction exhibited distinct kinetics. During the UV/H2O2 treatment on ASP effluent, DOC was degraded in all four fractions (biopolymers, humic substance, building block and low molecular weight compounds); DON was decreased in the first three fractions but increased significantly in the LMW fraction. This demonstrates the difficulty in treating DON in LMW, which is the challenge in DON removal and also in N-DBPs control. For MBR effluent, similar removal kinetics were observed except for the unusual increases in DOC and DON in the biopolymer fraction at the beginning. This indicates the potential formation of large molecules in MBR effluent at the initial stage of UV/H2O2 treatment. This may cause difficulty in UV/H2O2 treatment for MBR effluent. The results also indicated the generation of intermediate NDMA precursors during the treatment, where a high yield of NDMA was generated from insufficient oxidant dosing. Sufficient oxidant dosage should be applied to reduce the NDMA yield during the treatment and to achieve NDMAFP removal. In this study, 100 ppm H2O2 dosage with 60 minutes treatment time was proved to be suitable for ASP effluent.

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