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Effects of UV/H_2O_2 on NOM fractionation and corresponding DBPs formation

Hui-Chuan Lin, Gen-Shuh Wang *

Institute of Environmental Health, National Taiwan University, 17 Xu-Zhou Road, Room 734, Taipei, Taiwan 10055

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ABSTRACT

In this study, UV/H_2O_2 treatment was used to evaluate its efficacy for control of natural organic matter (NOM) in different water sources in Taiwan and the results were compared with the conventional water treatment process. The NOM fractions analysis showed that compositions of NOM could be very different between the various water sources, and the raw water quality in Kin-Men (an off shore island of Taiwan) was characteristic when compared to other water sources. Raw water taken from Kin-Men generally had high dissolved organic carbon (DOC) concentrations and ~50% of the NOM in the raw water was hydrophilic. After UV/H_2O_2 treatment, a portion of the hydrophobic fractions of NOM in raw waters were transformed into hydrophilic ones. In conventional water treatment process, coagulation and slow filtration treatments have better efficiency to reduce the NOM in water especially for the hydrophobic portion. However, the pre-chlorination treatment for raw water increased the DOC concentration due to the lysis of algae cells. This study concluded that hydrophobic acids portion is the most sensitive portion of NOM to UV/H_2O_2 and conventional treatment processes. Trihalomethanes formation potential (THMFP) tests showed that hydrophobic acids portion is also the main contributor to THMs formation after chlorination process.

1. Background

Natural organic matter (NOM) is a complex heterogeneous mixture and is the major precursor of disinfection byproducts (DBPs). In drinking water treatments, methods for controlling DBPs through removal of NOM have been extensively investigated. In conventional water treatment processes, NOM can be removed by alum or ferric coagulation. Alternative treatment technologies such as advanced oxidation processes (AOPs) have also shown their effectiveness to remove NOM in water. Due to their complicate compositions, however, different fraction of NOM may have different reactivity to various treatment processes and have different potential to form DBPs.

The aqueous NOM is a very complex mixture in its entirety. It is made up of organic matters of different molecular sizes, molecular weight, structures, functional groups, and hydrophobicity. The variation of NOM fractionations and its characteristic also depend on the origins of water sources. Other factors that affect the NOM compositions are season, climate, microorganisms, type of human activities and the eutrophication status of the water. Past study has divided the aqueous NOM into four major parts: colloidal organic matter, hydrophobic organic matter, transphilic organic matter, and hydrophilic organic matter [1]. Each part of the NOM could be subdivided into more homogeneous portion by different properties.

Several methods have been developed for the isolation of NOM in water. Resin adsorption (RA) and ultrafiltration (UF) techniques are two fractionation methods in common use for separation of NOM into various portions [2]. The incunabular fractionation method used three kinds of resins to isolate the dissolved organic matter into six portions: hydrophobic acid, hydrophobic base, hydrophobic neutral, hydrophilic acid, hydrophilic base and hydrophilic neutral [3]. Few years later, another kind of resin was used to divide the dissolved organic matter into four portions: very hydrophobic acids (VHoA), slightly hydrophobic acids (SHoA), hydrophilic charged (HiC), hydrophilic neutral (HiN) [4]. The conventional fractionation methods usually took lots of time and larger volume of sample, and a modification method was proposed to reduce the sample size (only need ~500 ml) and analysis time (~7 hours), made the NOM fractionation more convenient [5].

Removal of DBPs precursors is an appropriate strategy to reduce the DBPs formation in drinking water. Several alternative methods have been proposed for control of NOM, such as enhance coagulation, nanofiltration, reverse osmosis and AOPs [6,7]. Conventional treatment processes using alum or ferric coagulation is efficient in removing the hydrophobic portion of NOM with higher molecular weight. For hydrophilic materials, however, the conventional chemical coagulation is not very effective. Nanofiltration, ozonation and activated carbon adsorption were reported to be able to decrease the hydrophilic parts of NOM in water. Recently, more and more researches focus on using AOPs to mineralize NOM and other micropollutants in water. The AOPs contain UV oxidation, ozonation or combination of different catalytic reactions (such as UV/H_2O_2, UV/

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* Corresponding author. Tel.: +886 2 33668098; fax: +886 2 23940612.
E-mail address: gswang@ntu.edu.tw (G.-S. Wang).

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TiO_2, or O_3/H_2O_2) to reach a better oxidation efficiency [6,8]. UV/H_2O_2 process has its potential for removal of organic precursors by mineralizing the NOM in water. After UV/H_2O_2 treatment, the distribution of the molecular weight of NOM was changed, and the larger molecular weight matters were degraded into smaller ones [8–10].

Mathematical models describing the degradation of organic chemicals in water by UV/H_2O_2 process have been proposed [11,12]. In addition to the engineering models, several factors have also been found to affect the efficiency of UV/H_2O_2 process. Since the hydroxyl radical could also react with hydrogen peroxide, the concentrations of hydrogen peroxide in the system will affect the reaction rates of UV/H_2O_2 process. Selection of the optimum H_2O_2 dose in the UV/H_2O_2 process could provide the best NOM removal efficiency [8,13]. It has been shown that the hydrophobic parts of NOM especially the humic matters were the main contributor to trihalomethanes (THMs) formation [14]. However, some studies suggested that the hydrophilic portions can still play an important role on DBPs formation [15]. Further understanding of NOM fractionations in raw water will be helpful to adopt proper treatment technologies for control of NOM and reduction of DBPs formation.

The purposes of this study were to assess the treatment efficiency of UV/H_2O_2 process for control of NOM in different water sources and the results were compared with the conventional water treatment process. The correlations between the characteristics of different NOM portions and their contribution to DBPs formation were also studied.

2. Materials and methods

2.1. Water sources

Raw waters from three different water treatment plants in Taiwan were chosen for this study: Tai-Lake water treatment plant (WTP) in Kin-Men County, Chang-Hsin WTP in Taipei City, and Feng-Shan WTP in Kao-Hsiung County. For comparison, a synthetic humic acid stock solution was prepared from a commercial humic acids extract (Aldrich) to represent hydrophobic portion of NOM in water. The three water treatment plants were selected to represent water sources with different characteristics (Table 1). Both Tai-Lake and Feng-Shan Reservoir have eutrophication problems in their water sources. The chemical oxygen demand (COD) values of Tai-lake and Feng-Shan reservoir were quite high, and total phosphate also showed the same trends. The dissolved organic carbon (DOC) concentration in Tai-Lake water was specifically much higher than those observed in the other two raw waters. In Table 1, it also showed that the water quality condition of Tai-Lake was very complicated and composed of different kinds of constituents. Contrary to Tai-Lake and Feng-Shan reservoir, the raw water in Chang-Hsin treatment plant has much better water quality, and its COD and DOC in raw water were fairly low.

The raw water samples collected were stored in a 4 °C refrigerator for further uses. Prior to each experiment, the humic acid stock solutions were diluted to desired DOC concentrations for UV/H_2O_2 photolysis, NOM fractionation, and THMFP measurements. Due to the low DOC in the Chang-Hsin raw water (~1 mg/L of DOC), a reverse osmosis unit was used to concentrate the NOM in Chang-Hsin raw water to ~2–3 mg/L of DOC before the NOM fractionation and UV/H_2O_2 photolysis operations.

Table 1
Mean raw water quality characteristics in this study[a].

Parameters	Tai Lake WTP	Chang Hsin WTP	Feng Shan WTP
Location of WTP	off shore island	Northern Taiwan	Southern Taiwan
Secchi Disk Depth (m)	0.58 ± 0.13	–	0.43 ± 0.13
COD (mg/L)	34.5 ± 6.1	<4.0	15.8 ± 2.3
TOC (mg/L)	8.5 ± 1.4	0.9 ± 0.1	3.1 ± 0.4
Turbidity (NTU)	14.7 ± 5.9	2.3 ± 2.2	25.5 ± 12.0
S.S. (mg/L)	14.3 ± 8.0	1.7 ± 1.2	54.7 ± 45.8
Chlorophyll a (μg/l)	65.4 ± 30.3	2.8 ± 0.4	109.8 ± 114.2
NH_4^+-N (mg/L)	0.19 ± 0.29	0.04 ± 0.01	1.53 ± 0.82

[a] Based on 4 samplings in 2007.

2.2. NOM fraction

The rapid NOM fraction method developed by Chow et al. [5] was adopted in this study for separation of NOM constituents. For NOM fractionation, three contiguous glass columns were set up in serial. Each column was filled with different resin in order (DAX-8, XAD-4 and IRA-958, respectively). The resins were used to separate the NOM into four different portions: very hydrophobic acid (VHoA), slightly hydrophobic acid (SHoA), hydrophilic charged (HiC), and hydrophilic neutral (HiN).

2.3. UV/H_2O_2 treatment and conventional treatments

A 10-L stainless-steel batch reactor with a UV lamp inside was used in this study for UV/H_2O_2 treatment of NOM in the aqueous solution. The UV photolysis used a 450 W high pressure mercury vapor lamp (Hanovia, NJ). The UV lamp located at the center of the reactor was covered with a quartz sleeve. A water-cooling loop was used to prevent the lamp from overheating and the reactor was immersed in a water bath to maintain a constant temperature of 25 °C during the UV photolysis. In order to stabilize the UV energy, the UV lamp was turned on for 10 minutes before performing the experiment. Detail description of the UV/H_2O_2 treatment can be seen elsewhere [8].

In this study, water samples were also collected from each treatment unit in Tai-Lake Water Treatment Plant so that the treatment efficiency for NOM can be compared between conventional treatments and AOP. Tai-Lake WTP in Kin-men employ prechlorination, coagulation, flotation, rapid filtration, slow sand filtration, and post chlorination as treatment processes. The NOM fractionation of water sample taken from each treatment unit was carried out to evaluate the effects of different conventional treatment process on NOM fraction, and the THMFP of water samples after each treatment process were measured.

2.4. Analysis

The non-pergeable DOC (NPDOC) concentration was measured with a Total Organic Carbon analyzer (Shimadzu TOC 5000A), and the UV absorbance was measured by a high-precision, double-beam spectrophotometer (Shimadzu UV 160A). The THMFP measurement follows the procedures described in section 5710B of the Standard Methods. The four THMs were quantified by a purge and trap (Model 4560, OI Analytical, Texas, USA) and a GC/MS (Hewlett Packard 6890GC/5973MSD) which used a fused silica capillary column (RTX-VOC) for separation of the THM species. The method detection limits were 0.2 μg/L for the four THMs. Catalase purchased from Worthington Biochemical was used to decompose the residual H_2O_2 prior to the THMFP experiments.

3. Results and discussion

3.1. NOM fractionation in raw waters

Fig. 1 gives the results of the NOM fractionation for the humic acids solution and the three water sources used in this study. In general, the NOM fraction compositions in different water sources appeared in the order of: VHoA $\geqq$ HiN $>$ SHoA $>$ HiC (Tai-Lake: $42\% \geqq 42\% > 10\% > 6\%$; Chang-Shing: $55\% > 29\% > 10\% > 6\%$; Feng-Shan: $63\% > 26\% > 8\% > 3\%$, respectively). For the commercial humic acids solution, VHoA