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Photocatalysis of THM precursors in reclaimed water: the application of TiO_2 in UV irradiation

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ABSTRACT

In this study, ultraviolet (UV) irradiation followed by chlorination was employed for reclaimed water disinfection. In order to reduce trihalomethanes (THMs) from reclaimed water, suspended TiO_2 (10 mg/L) was added as photocatalyst in UV process to enhance the removal of THM precursors. Reduction of UV absorbance in 254 nm (UV_{254}), dissolved organic carbon (DOC), and THMs formation was analyzed under different experimental conditions (exposure time, pH, TiO_2 doses, and TiO_2 forms). Excitation–emission matrix spectra technology was also used to investigate the changes of dissolved organic matters properties during UV and UV-TiO_2 process. Expansion of irradiation time resulted in a remarkable decrease in UV_{254} and THM yields, but showed few influence on DOC removal. THMs yield decreased more than 50% with pH increased from 5 to 9 and rise in TiO_2 dosage also presented a positive effect on photocatalytic disinfection. In addition, a dramatic increase in removal rates of UV_{254}, DOC, and THMs was observed when TiO_2 doses were increased from 3 to 15 mg/L. In terms of TiO_2 form, suspended TiO_2 exhibited a better removal capacity on UV_{254}, DOC, and THMs by contrast with TiO_2 coated on granular active carbon.

Keywords: UV; TiO_2; THMs; Photocatalysis; Chlorination

1. Introduction

Continuous growth of population and economic development cause severe water scarcity issues. Traditional sources such as surface water and ground water can no longer meet future water demand [1]. Thus, reclaimed water is used as one of the most important resources in arid zones and urban areas to flush toilet, restore water channel, cool pavement, and irrigate plant to tackle water shortage [2]. However, wastewater contains plenty of bacteria, pathogens, natural organic matters (NOM), and other hazardous substances which make disinfection process indispensable to reduce transmission risk of waterborne infectious disease during water reuse.

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Recently, use of chlorination in reclaimed water draws increasing attention since it is inexpensive and efficient [3]. Sufficient residual chlorine can also prevent the regrowth of bacteria in reused water distribution system. However, chorine disinfection is found to be ineffective to some waterborne microbial pathogens in recent studies [4,5]. Thus, many researchers considered ultraviolet (UV) irradiation to be essential in predisinfection processes to inactivate microorganisms [6].

UV irradiation can interact with nucleic acids and other vital cellular compounds, such as proteins and lipids, and then effectively inactivate a wide range of pathogens [7,8]. Recently, UV irradiation has become a prevalent disinfection method because of its efficiency, safety, and economical advantage [9]. However, UV irradiation does not have residual disinfect effect which means bacteria could regenerate after UV process. As a result, UV irradiation coupled with other accesses was required in disinfection process [5]. Ballester and Malley used UV irradiation as the primary treatment combined with free chlorine as disinfectant in their study. They found both prevented microbial regrowth and synergetic effect in disinfection process [10].

In chorine disinfection process, dissolved organic matters (DOM) would be converted into hazardous byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs) [11]. It has been reported that THMs and HAAs could cause DNA damage in drinking water. HAAs were also demonstrated to be mutagenic in Salmonella and Chinese hamster ovary cells [9]. Furthermore, UV exposure at disinfection doses was speculated to split the NOM structure rather than destroy the aromatic matter [12]. NOM molecule is more likely to be split to lower molecular weight acids by UV irradiation, which means the reactivity of NOM with chlorine would be changed. Some researchers have reported that the employed UV would increase the DBPs in latter chlorination [13]. As a result, applications of UV exposure and chlorination hybrid process should be improved so as to avoid the increase in DBPs formation.

Recently, use of advanced oxidation process in removal of DBP precursors has undergone investigation processes such as photo-Fenton treatment, UV/H_2O_2, Ozone/UV, and UV/TiO_2 [14–17]. In UV/TiO_2 oxidation process, TiO_2 is added as a photocatalyst. An electron is excited from the valence band to conduction band when TiO_2 is illuminated at the wavelength of light less than 388 nm, leaving an electronic vacancy called the hole (h^+) in valence band. This hole could react with OH^- and H_2O molecules to produce hydroxyl radicals ($OH^\cdot$), which is proved to be one of the most powerful oxidants [18]. These generated $OH^\cdot$ radicals trigger the degradation of aromatic compounds by attacking aromatic rings directly. The h^+ may also initiate direct oxidation of molecular absorbed on the surface of TiO_2 and produce radical cations which subsequently interact with oxygen-containing species [19]. Therefore, UV/TiO_2 process has shown greater potential to degrade stubborn NOM compounds (e.g. trichloroethylene, THMs, pesticides, and polychlorinated biphenyls) into nontoxic compounds [20]. Kent and Montreuil used UV/TiO_2 treatment to induce photocatalytic oxidation of DBP precursors in surface water, and the results indicated that the formation of THMs and HAAs was greatly reduced [21].

It is well known that DBPs formation during chlorination after UV and UV/TiO_2 treatment in drinking water and surface water can be well explained [21,22]. However, the mechanism of DBPs formation in UV/TiO_2 of reclaimed water was still unclear, and a further investigation was required. Compositions of DOM in reclaimed water are more complex and distinctly different as compared with those in drinking water. The photocatalysis of DOM and reaction between chlorine and DOM in postchlorination of reclaimed water would be more complicated. Therefore, the objective of this work will be focused on (i) the effect of TiO_2 on DOM degradation and removal of DBPs precursors and (ii) the feasibility of sequential use of UV/TiO_2 and chlorination in reclaimed water. Effects of different photocatalysis factors on THMs removal were also evaluated in this work.

2. Materials and methods

2.1. Water sample

Samples were collected from the secondary effluent of Jinan urban wastewater treatment plant in which A^2/O and oxidation ditch were used as the principal treating process. In order to satisfy the requirement of reclaimed water, original water samples were prefiltered through 0.45-μm micromembranes before UV/TiO_2 photocatalytic oxidation experiment. UV_{254}, pH, and DOC of these samples were analyzed before/after UV/TiO_2 treatment, THMs formation during chlorination of UV/TiO_2-treated water was also detected, and the optimum condition for the DBP precursors degradation was evaluated.

2.2. Water quality analysis

Dissolved organic carbon (DOC) of those samples was analyzed using a Shimadzu TOC-VCPH analyzer, UV_{254} was measured by UV-754 UV/VIS spectrophotometer at 254 nm. The pH and bromide ion were measured by pH meter (Luoqite, China) and ion chromatogram (Dionex, USA), respectively. Raw water quality indexes including pH, UV_{254}, turbidity, DOC, SUVA, and bromide ion concentration were presented in Table 1.

2.3. TiO_2 coating procedures

Synergistic effect was observed when activated carbon was coupled with TiO_2 in photocatalytic process for female hormone degradation [23]. As a result, the degradation effect on DOMs by TiO_2 laden granular activated carbon (GAC) was investigated in this work. The coating procedures were as follows: 50 g GAC was added into boiled water for 5 min and then ultrasonic cleaning for 30 min. Thereafter, GAC was immersed into the diluted hydrochloric acid and suspended for 2 h to remove active groups on surface of GAC. GAC was then filtered and washed repeatedly until pH of filtrate achieved about 7. The clean GAC was dried at 105℃ for 2 h and stored in a desiccator for future use [24].

Precursor solution for TiO_2 coating was prepared as follows: 20 mL of tetrabutyl orthotitanate was dripping into 60 mL of ethanol and the mixture was stirred vigorously for 20 min after titrating with 4 mL of glacial acetic acid. Thereafter, 23 mL of prepared HNO_3–ethanol solution (2 mL HNO_3, 20 mL ethanol, and 1 mL deionized water) was gradually dripped into the tetrabutyl orthotitanate–ethanol mixture, stirring slowly for 1 h to form stable colloidal solution.

Dip-coating method was employed for film preparation. Twenty gram of pretreated GAC was immersed into 50 mL of newly prepared colloidal solution for 5 min. The mixture was then dewatered in a drying oven for 2 h at 105℃. These two steps were repeated for three times to ensure enough TiO_2 to be loaded on GAC. Afterward, this new mixture was put into a muffle at 500℃ for 4 h by purging with nitrogen. The composite catalyst (laden TiO_2) was then obtained on the surface of GAC, forming a white layer with mass percentage of 5.94%.

Table 1
Raw water quality used for UV/chlorine and UV-TiO_2/chlorine

Analyte	Units	Value
pH		7.54–7.96
UV_{254}	cm^{-1}	0.117–0.141
Turbidity	NTU	2.56–4.06
DOC	mg/L	4.78–6.21
SUVA	L/mg m	2.01–2.56
Br^-	mg/L	0.76–0.91

2.4. UV irradiation with the addition of TiO_2

UV irradiation experiment was conducted using standard collimate beam test. The photoreactor used in this study was custom-made in previous study with some minor modifications [25]. Suspension TiO_2 was applied in the whole study except the TiO_2 form experiment where two kinds of UV/TiO_2 treatments were applied. For suspension TiO_2 experiments, a stock solution was prepared by adding 1.0 g of anatase titanium oxide (Analytical Reagent) nanopowder into 200 mL of deionized water with continuously stirred.

The schematic diagram of the photocatalytic experimental rig in this study is shown in Fig. 1. The main component of the system was the reactor with a circulation water tank. Water in the system was driven by a peristaltic pump. The effective volume of the whole system was 4 L. A 15-W UV lamp positioned inside a quartz tube was placed in the middle of the reactor. The wavelength range and the peak wavelength of the UV lamp were 200–275 nm and 253.7 nm, respectively. Water sample (300 mL) was taken from the reactor after photocatalytic oxidation process in each experiment and filtrated through 0.45-μm membrane to remove suspension TiO_2.

2.5. Excitation-emission matrix fluorescence spectroscopy analysis

Excitation-emission matrix (EEM) spectra measurements were conducted using a luminescence spectrometry (F-4500 FL spectrophotometer, Hitachi, Japan). The EEM spectra were collected with corresponding scanning emission spectra from 250 to 550 nm at 5-nm increments by varying the excitation wavelength from 200 to 400 nm at 5-nm sampling intervals. The EEM spectra normalized to 1 mg/L DOC are plotted as contours.

Fluorescence regional integration (FRI) technique was used to quantify EEM data [26]. The EEM spectra were divided into five regions which represented specific components of DOM (Table 2). Fluorescence response of DOM with similar properties in each region was calculated as following equations:

$$\Phi_i = \int_{ex} \int_{em} I(\lambda_{ex} \lambda_{em}) d\lambda_{ex} d\lambda_{em} \quad (1)$$

Table 2
Excitation and emission wavelength boundaries and chemical descriptions used in FRI technique [26]

Region	Excitation (nm)	Emission (nm)	Description
Region I	200–250	250–330	Aromatic proteins I
Region II	200–250	330–380	Aromatic proteins II
Region III	200–250	380–550	Fulvic-like acids
Region IV	250–400	250–380	Soluble microbial-like products
Region V	250–400	380–550	Humic-like acids

$$\Phi_{i,n} = \mathrm{MF}_i \Phi_i \tag{2}$$

where, $\Phi_{i,n}$ is the normalized EEM volume at region i, $\Delta\lambda_{\mathrm{ex}}$ is the excitation wavelength interval, $\Delta\lambda_{\mathrm{ex}}$ is the emission wavelength interval, and $I(\lambda_{\mathrm{ex}}\lambda_{\mathrm{em}})$ is the florescence intensity of each excitation–emission wavelength pair; MF_i is the multiple factor applied to the secondary or tertiary responses at longer wavelengths.

2.6. Chlorination

In order to prevent photodegradation of chlorine and light-induced algal growth, chlorination of test water was conducted in dark brown bottles. Three-day reaction time (72 h) was selected for estimating the concentration of THMs precursors in water samples [27]. Before chlorination experiments, a chlorine demand preliminary study was conducted using a series of chlorine dosages (10, 15, 20, and 40 mg/L of Cl_2) to determine the 72-h chlorine demand of raw water. The average 72-h chlorine demand for raw water was evaluated to be 18.74 mg/L. Thus, the chlorine dosage in this study was selected as 20 mg/L. After 72-h chlorination, the average free chlorine residual in the raw water was 2.37 mg/L.

In the chlorination experiment, chlorine dosing solution (1 mL) with specific concentration was added into 200 mL of water sample to provide initial chlorine of 20 mg/L. These samples were then sealed with PTFE-lined screw caps and then kept in darkness for 72 h. After chlorination, 1 mL of sodium thiosulfate solution (0.1 mol/L) was added into each bottle to neutralize chlorine residue.

2.7. THMs analysis

THM concentration was analyzed for each sample according to headspace method by gas chromatograph, GC-ECD (Shimadzu, Japan). The GC-ECD operation conditions were as follows: (1) The condition of headspace bottle: the equilibrium temperature for 50℃, balance time for 30 min, take headspace gas for measurement, and sampling volume 100 µL. (2) Chromatographic column: RTX-1 (30 m in length, 0.32 mm in inner diameter, 0.25 µm in film thickness); detector temperature: 200℃, injector temperature: 120℃; carrier gas: high purity nitrogen, flow rate: 3 mL/min. THMs were measured in forms of chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), detection for $CHCl_3$, $CHCl_2Br$, $CHClBr_{2,}$ and $CHBr_3$ were 1.0, 1.50, 2.34 and 1.98 µg/L, respectively.

3. Results and discussion

3.1. Comparison of DOM properties after UV and UV/TiO_2 treatment

UV_{254} and DOC of water samples exposed to UV and UV/TiO_2 were shown in Fig. 2(a). It was obvious that both UV irradiation and UV/TiO_2 treatment could decrease UV_{254} of reclaimed water. Removal of UV_{254} by UV exposure was about 17% which was lower than that of UV/TiO_2 treatment (23%). However, removal efficiency of DOC with UV irradiation and UV/TiO_2 treatment were less than 5%. These results indicated that UV and UV/TiO_2 process could degrade polycyclic aromatic hydrocarbon into intermediates but play less roles in mineralization of DOC compounds [28]. This was consistent with former research investigating photocatalytic oxidation of DBPs precursors in surface water using UV with TiO_2 in low dose [21]. A high degree of removal of THMs precursor compounds was also achieved using higher TiO_2 doses [29]. Philippe indicated THMs precursors can be removed as a result of absorption using 1,000 mg/L TiO_2 [28].

THMs formation in chlorinated water samples which were treated by UV and UV/TiO_2 treatments was shown in Fig. 2(b). $CHCl_3$ was the major THMs in all water samples, whereas no $CHBr_3$ was detected due to the low bromide concentration in raw water (Table 1) [30]. TTHMs concentration in water samples with UV process was higher than that in raw water, indicating that UV irradiation process can increase

THM formation reactivity of DOM. Similar result was also observed in previous study, in which the DBPs formation in four organic waters was evaluated [13]. These results could be explained by the photochemistry fundamentals of UV irradiation. Many organic compounds—especially the compounds containing ring structures—were capable to absorb UV radiation at 254 nm (wavelength of radiation emitted by Hg lamp in water disinfection) [31]. UV irradiation could affect the character of organic substances through either direct or indirect reactions [32]. Magnuson et al. [33] found that UV irradiation resulted in the change of mass spectra of NOM at the UV dose ranged from 20 to 160 mJ/cm^2. These changes might alter the reactivity of NOM with chlorine and affect the formation of DBPs in subsequent chlorination. In addition, UVC irradiation can split large NOM molecules to lower molecular organic acids [34]; this might suggest that refractory compounds in original water sample would be degraded into more tractable one, and as a result, it was easier to react with chlorine to form THMs.

As shown in Fig. 2(b), THMs compounds were restrained by UV/TiO_2 treatment as compared to UV process. However, the THMs after UV/TiO_2 treatment were still higher than those in raw water. This result indicated the addition of TiO_2 in UV irradiation could offset the bad side effect caused by UV radiation. The difference on THMs yield between UV exposure and UV/TiO_2 can be explained by the extent of photodegradation. Hydroxyl radical, which was formed by the reaction between water molecules with light-formed electron–hole pair, was found capable to induce NOM degradation [4,35]. Therefore, more THMs precursors in UV/TiO_2 process were degraded than those in UV process; this was also consistent with the result of UV_{254} (Fig. 2(a)). As a result, the formation of intermediates that contributes to TTHMs was finally decreased [36].

3.2. *Effect of exposed time on TiO_2 photocatalysis performance and THMs formation*

A positive correlation has been found between UV dose and exposure time [37]. In this study, UV exposure time was ranged from 10 to 40 min for adjusting the UV dose. As shown in Fig. 3(a), the value of UV_{254} dramatically decreased when the exposure time was extended from 10 to 30 min; UV_{254} was then kept almost constant in 30–40 min. DOC concentration was practically unchanged with the variation of exposure time. Thus, it was presumably that polycyclic aromatic hydrocarbon was progressively degraded into intermediates by photocatalysis as the UV dose increased, resulting in the reduction of UV_{254}. We should point out that the slightly fluctuant of DOC concentration in these four selected exposed times was caused by systemic error. Therefore, there is no obvious mineralization of DOC compounds with extension of exposure time at relatively low TiO_2 dose.

Fig. 3(b) illustrated the formation of THMs during chlorination of samples treated by UV/TiO_2 with different radiation time. With the exposure time increased, THMs significantly increased in the first 20 min and then, they were gradually decreased. The initial increase of total THMs was based on the halogenations of intermediate degradating products that were formed in initial rapid breakdown of large NOM compounds. The DBPs formation potential of these degradating products was higher than that of original DOM. After the premier increase, there was a reduction in THMs possibly due to the further degradation of these intermediate products with UV dose increased [38]. In this process, the intermediate products were probably destructed and lost the high reactivity with chlorine. Other studies on transformation of DOM during ozonation showed similar trends with this study [39].

Considering the inactivation rate of bacteria and pathogens, UV dose used in municipal wastewater disinfection should not be less than 15 mJ/cm^2 (GB/T 18918-2002). In this study, the standard was met when UV exposure time was not less than 20 min with a 15-W Hg lamp (approximately 25 mJ/cm^2). As shown in Fig. 3(b), THMs reduction of reclaimed water by UV/TiO_2 treatment occurred when UV irradiation time was over 20 min. This means UV contact time above 20 min was required for UV/TiO_2 treatment to meet GB standard as well as decrease THMs formation. Soltermann found that DBPs (N-nitrosamine and chlorinated dimethylamine) increased dramatically when UV dose was lower than 500 mJ/cm^2 and a significant decrease in DBPs was obtained only at UV dose higher than 1,500 mJ/cm^2 [40]. Since UV dose was the major cost in UV exposure process, the addition of TiO_2 in UV irradiation may provide a more cost-effective and energy-saving way to disinfect reclaimed water.

3.3. *Effect of pH on TiO_2 photocatalysis and THMs formation*

Water pH is an important factor which influences the photocatalytic process [31]. In pH experiment, pH (range from 5 to 9) was adjusted by HCl (0.1 and 1 mol/L) and NaOH (0.1 and 1 mol/L) solutions. The water samples were readjusted to raw water pH value before chlorination. UV_{254} and DOC of water samples with different pH were plotted in Fig. 4(a). UV_{254} removal efficiency represents a downtrend as the pH was adjusted from 5 to 9, while the concentration of DOC remains almost stable. These results indicated that the concentration of hydrogen ion in the water sample had no significant effect on the removal of DOC compounds with low TiO_2 concentration.

In order to investigate pH effect in UV/TiO_2 process, the pH of water samples was readjusted to that of raw water before chlorination. It was clear that THMs concentrations were gradually decreased as the pH increased from 5 to 9 (Fig. 4(b)). The pH has a significant effect on the electrostatic charge of TiO_2 surface; this may determine the density of TiO_2H^+ groups and photogenerated holes. The surface became positively charged when pH value was lower than PZC (point of zero charge, 6.5) of titania, and it was the opposite for pH > PZC, according to the following equilibria:

$$\mathrm{pH} < \mathrm{PZC}:\ \mathrm{TiOH} + \mathrm{H}^+ \leftrightarrow \mathrm{TiOH}_2^+ \tag{3}$$

$$\mathrm{pH} > \mathrm{PZC}:\ \mathrm{TiOH} + \mathrm{OH}^- \leftrightarrow \mathrm{TiO}^- + \mathrm{H_2O} \tag{4}$$

Under alkaline conditions, the photogenerated hole (h^+) was more likely to be transferred onto the surface of organic matters and oxidize OH^- and H_2O into $OH^{\cdot}$ radical which could degrade organic substances into intermediates or even mineralize them with strong oxidation capacity [41]. As a result, the absorption of organic matter by TiO_2 as well as the photocatalytic reactivity of TiO_2 was dependent of pH [20].

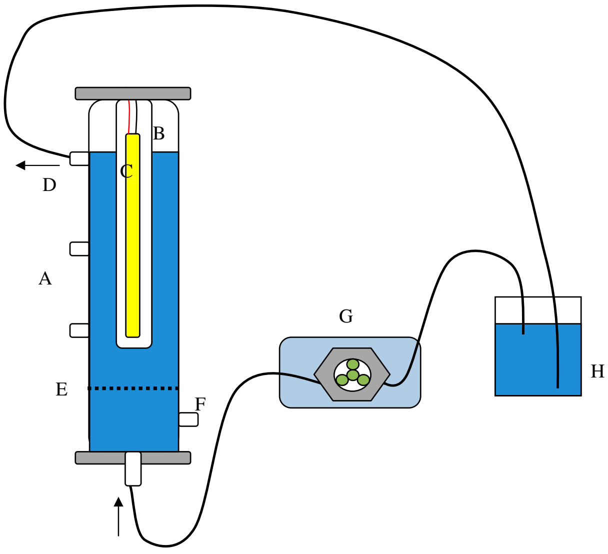

Fig. 1. Experimental setup for photocatalytic reaction. The description was as follows: (A) photocatalytic reactor; (B) quartz tube; (C) UV lamp; (D) sample port; (E) porous filter plate; (F) outlet; (G) peristaltic pump; (H) water circulation tank.

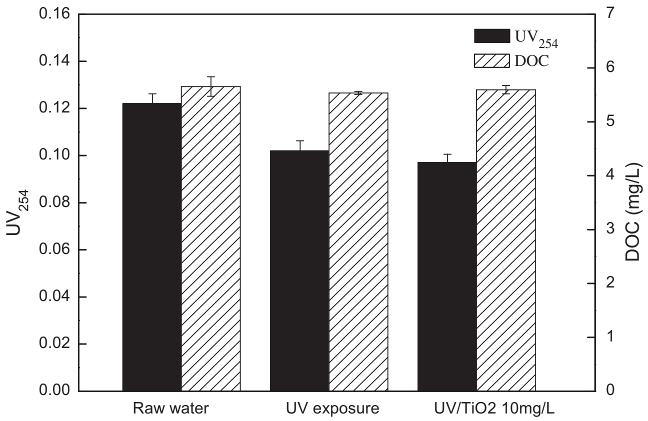

Fig. 2(a). UV_{254} and DOC concentration of raw treated water after UV and UV-TiO_2 disinfection (error bars represent of the data range of two independent samples) (reaction condition: 15-W UV lamp; exposed time = 30 min; TiO_2 concentration = 10 mg/L).

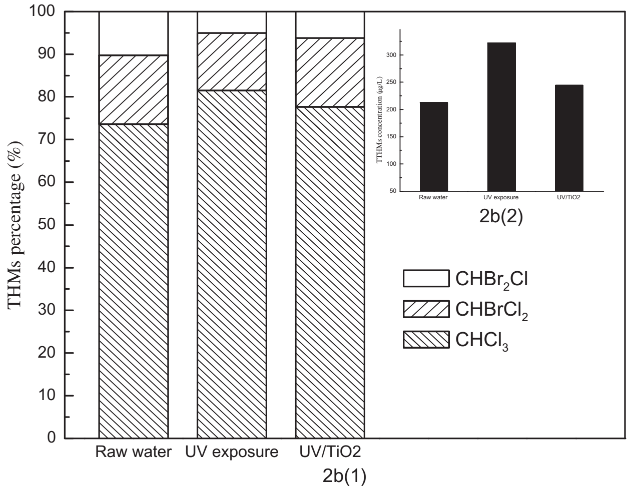

Fig. 2(b). THMs percentages and concentration of different species in treated water after UV and UV-TiO_2 disinfection (reaction condition: chlorine dosage = 20 mg/L, contact time = 72 h).

3.4. Effect of TiO_2 dose on TiO_2 photocatalysis and THMs formation

UV_{254}, DOC, and TTHMs removal were investigated under four different TiO_2 dosages, and the results were illustrated in Figs. 5(a) and 5(b) respectively. As the dosage of TiO_2 increased, UV_{254} of treated water was

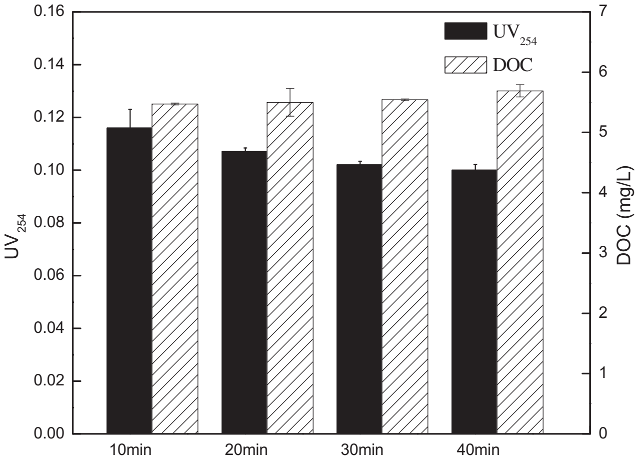

Fig. 3(a). UV_{254} and DOC concentration of treated water after UV-TiO_2 disinfection under different exposed time (error bars represent of the data range of two independent samples) (reaction condition: TiO_2 concentration = 10 mg/L).

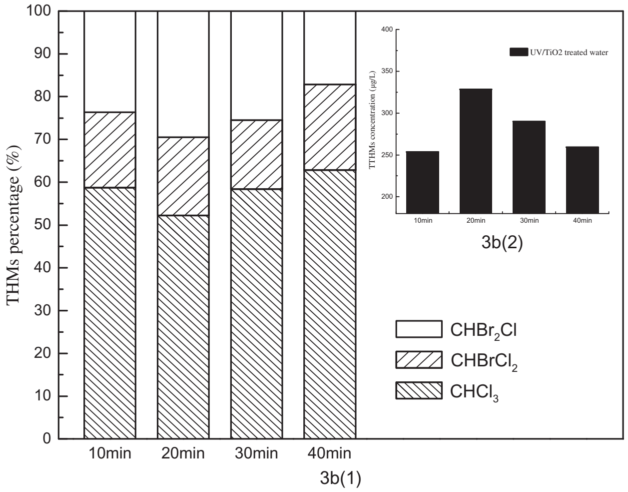

Fig. 3(b). THMs percentages and concentration of different species in treated water after UV-TiO_2 disinfection under different exposed time (reaction condition: chlorine dosage = 20 mg/L, contact time = 72 h).

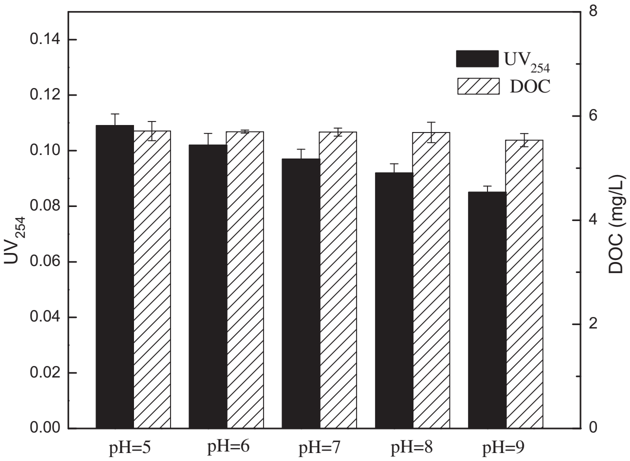

Fig. 4(a). UV_{254} and DOC concentration of treated water after UV-TiO_2 disinfection under different pH (error bars represent of the data range of two independent samples) (reaction condition: exposed time = 30 min; TiO_2 concentration = 10 mg/L).

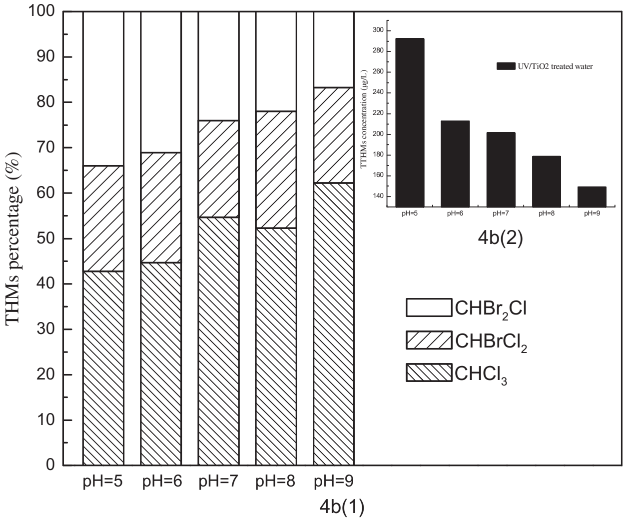

Fig. 4(b). THMs percentages and concentration of different species in treated water after UV-TiO_2 disinfection under different pH (reaction condition: chlorine dosage = 20 mg/L, contact time = 72 h).

progressively decreased. DOC also showed an apparent downtrend with the increasing TiO_2 concentration. These results indicated that the amount of TiO_2 in the water samples was essential to the degradation of NOM. The increased amount of TiO_2 provided more hydroxyl radicals and photogenerated holes which strengthened the oxidation capability of the whole system. Therefore, a large amount of aromatic compounds were degraded into intermediates, and some of the NOM was mineralized. This result was also consistent with the work of Liu using higher TiO_2 doses [29]. In contrast, TiO_2 concentration was quite low in this study, so the potential adsorption of organic onto TiO_2 surface could be ignored [21].

Fig. 5(b) presented changes of THMs yield after UV/TiO_2 treatment with different TiO_2 doses. As shown in Fig. 5(b), TTHMs were dramatically decreased from 303 to 150 μg/L when the TiO_2 dose was increased from 3 to 15 mg/L. $CHCl_3$ was the major THMs species, followed by $CHCl_2Br$ and

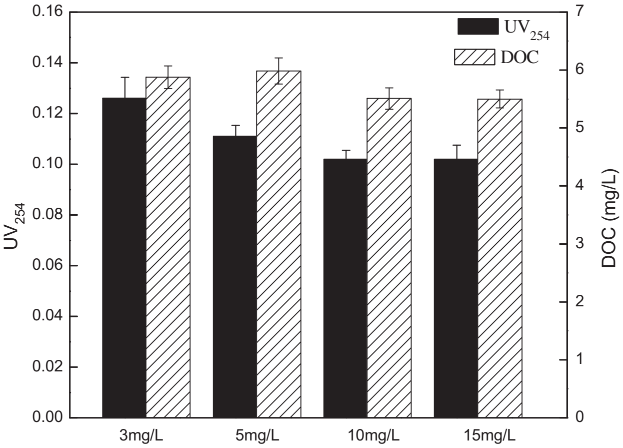

Fig. 5(a). UV_{254} and DOC concentration of treated water after UV-TiO_2 disinfection under different TiO_2 concentration (error bars represent of the data range of two independent samples) (reaction condition: exposed time = 30 min).

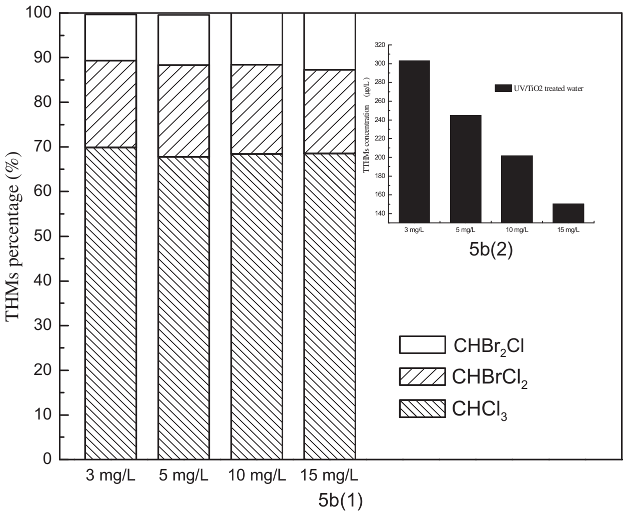

Fig. 5(b). THMs percentages and concentration of different species in treated water after UV-TiO_2 disinfection under different TiO_2 concentration (reaction condition: chlorine dosage = 20 mg/L, contact time = 72 h).

$CHClBr_2$. The concentration of $CHBr_3$ in the water samples was below the detection limit. The decrease in TTHMs concentration after photocatalytic treatment was connected with the removal of UV_{254} and DOC. Although complete mineralization could not be achieved, the photocatalytic oxidation induces chemical structure changes of THMs precursors which generate organic chemicals with less sensitive to chlorine [21]. As a result, TTHM formation was decreased with increased TiO_2 dosage.

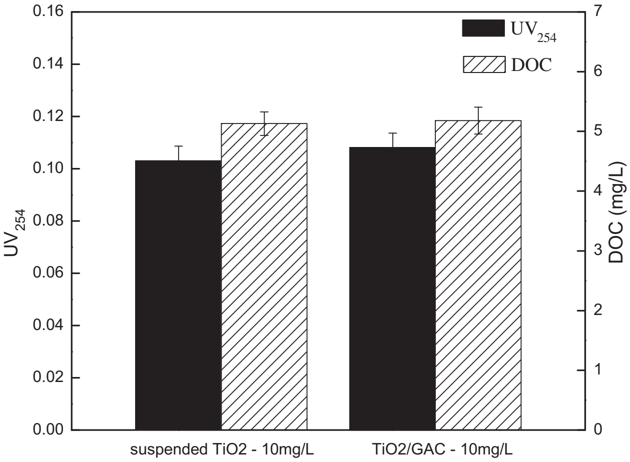

Fig. 6(a). UV_{254} and DOC concentration of treated water after UV-TiO_2 disinfection under different TiO_2 morphology (error bars represent of the data range of two independent samples) (reaction condition: exposed time = 30 min; TiO_2 concentration = 10 mg/L).

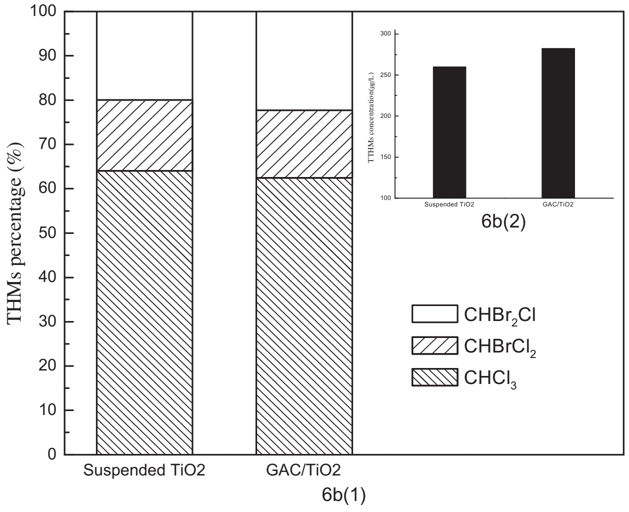

Fig. 6(b). THMs percentages and concentration of different species in treated water under different TiO_2 morphology (reaction condition: chlorine dosage = 20 mg/L, contact time = 72 h).

3.5. *Comparison of different TiO_2 forms on TiO_2 photocatalysis and THMs formation*

Fig. 6(a) showed the effects of different forms of TiO_2 in UV/TiO_2 treatments on UV_{254} and DOC. Suspension TiO_2 settlement represented slight higher removal efficiency on UV_{254} and DOC than TiO_2/GAC settlement. The same result was also found in THMs analysis shown in Fig. 6(b). These findings suggested that coated TiO_2 was a less efficient catalyst for

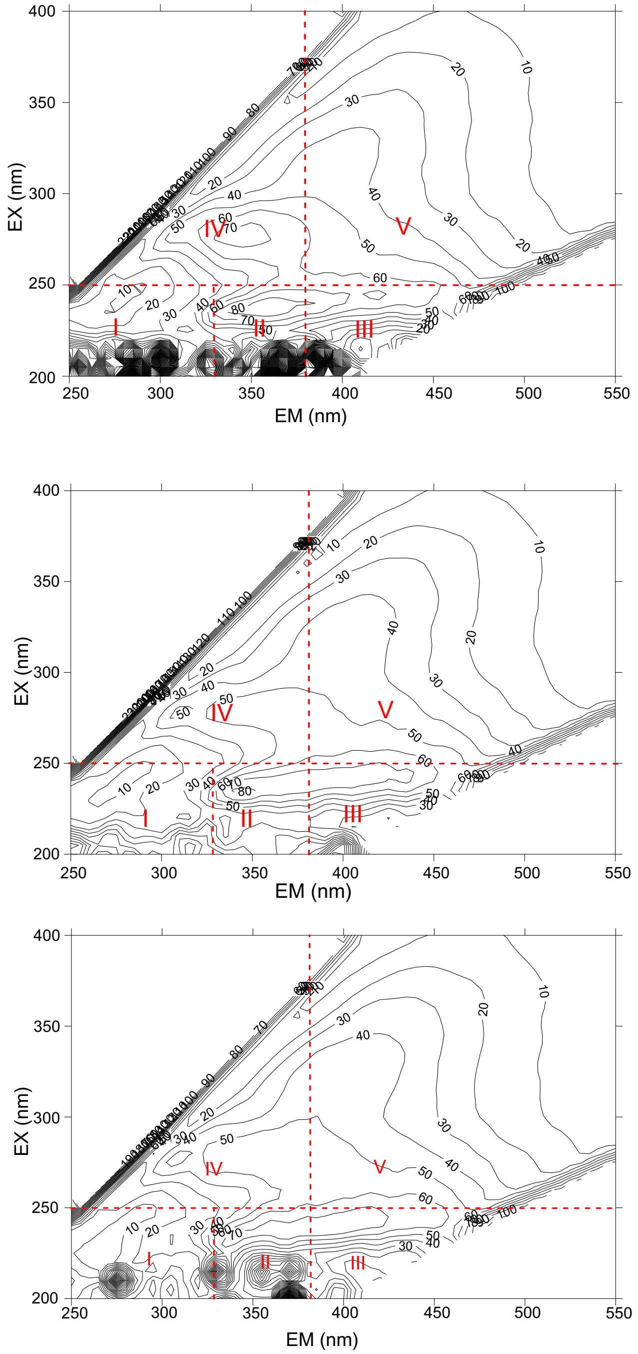

Fig. 7(a). EEM spectra of raw water, UV-treated water, and UV-TiO$_2$-treated water.

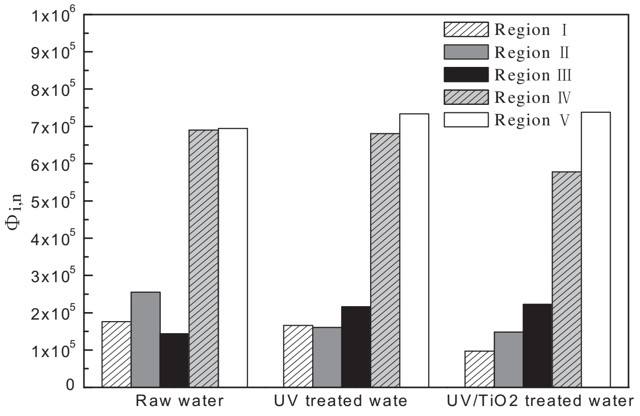

Fig. 7(b). FRI results for raw water, UV-treated water, and UV-TiO$_2$-treated water. $\Phi_{i,n}$ is the cumulative fluorescence of DOM in each region.

degradation of NOM and THMs precursors than suspended TiO$_2$. Lower removal of NOM and THMs precursors by coated TiO$_2$ was presumably associated with mass transfer limitations. Since the particles in the suspension were spread thorough out the sample, 10 mg/L of TiO$_2$ suspension had a higher surface area to contact with the sample than TiO$_2$/GAC configuration. Although the TiO$_2$/GAC complex was expanded all over the reactor using peristaltic pomp, the fluidity was still limited. The loaded TiO$_2$ had a very high surface area due to granular carbon morphology; NOMs in water samples would first transfer to the surface of TiO$_2$/GAC in order to be exposed to the oxidants. These oxidants were generally short-lived and would not immigrate too far from the surface of TiO$_2$/GAC [21]. However, combined UV and TiO$_2$/GAC treatment still has wide application prospects due to its easy separation from reaction system [42]. In this study, TiO$_2$/GAC was effectively separated from treated water by porous filter plate (Fig. 1). It is reported that TiO$_2$/GAC degradation efficiency maintains above 90% after five cycles reused [43]. The TiO$_2$/GAC blocked in particle separation device could be collected for reutilizing. Moreover, TiO$_2$/GAC complex may have a better performance when the coating condition was optimized.

3.6. *EEM spectra of DOM in water samples after UV and UV/TiO$_2$ treatment*

DOM in secondary effluent of urban wastewater was complex and may lead to production of most majority of chlorination byproduct. Therefore, it is crucial to clarify the changes of DOM characteristics in detail during UV and UV/TiO$_2$ treatment as well as investigate the influences of DOM sources and chemical compositions on THMs formation. Figs. 7(a) and 7(b) show the EEM spectra and FRI results of raw water, UV, and UV/TiO$_2$-treated water, respectively. Region V exhibited the highest Φ value, accounting for more than 35% of the total cumulative fluorescence intensities for the three DOM samples. This indicated

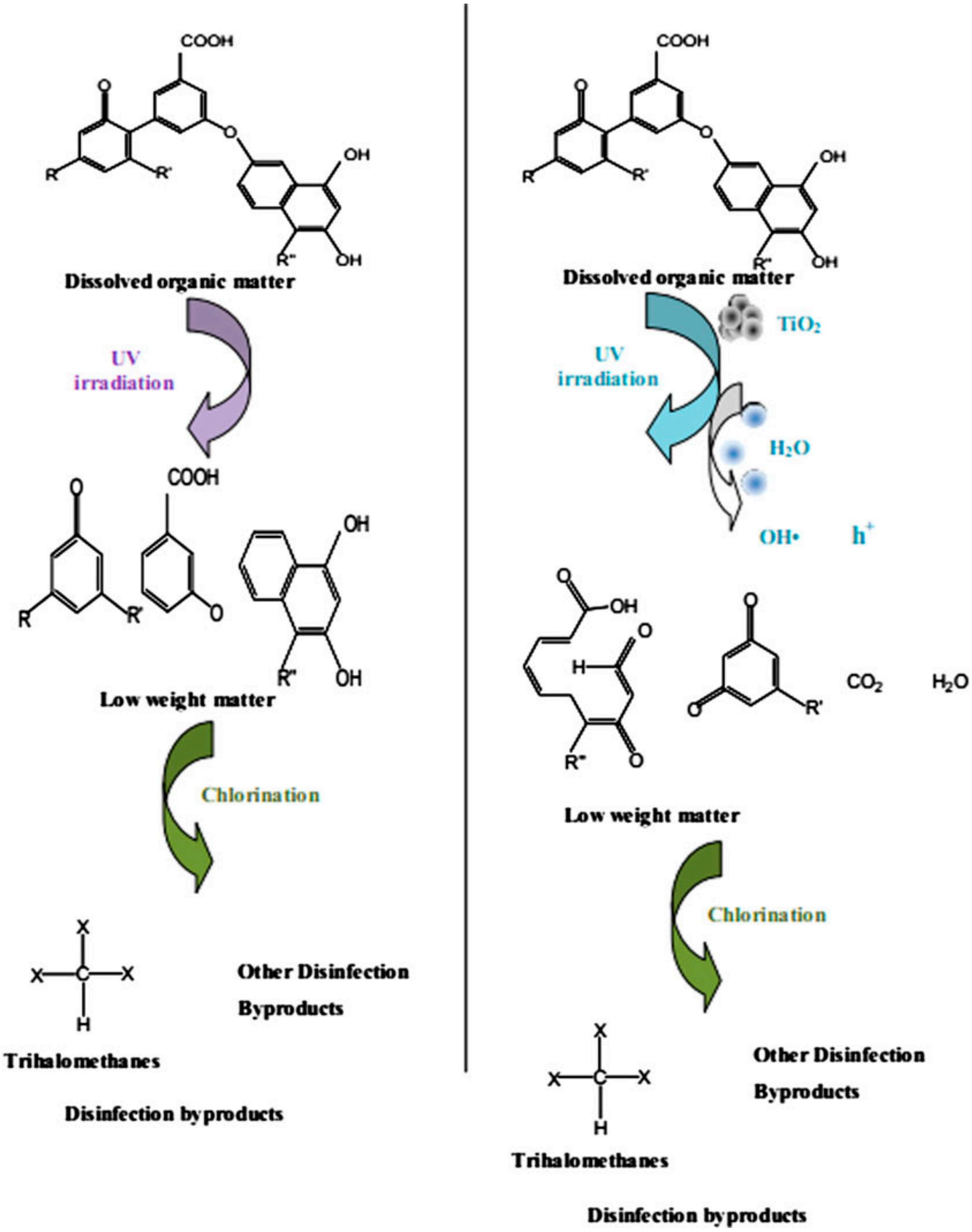

Fig. 8. Scheme for DOM degradation after UV and UV-TiO_2 treatment and reaction pathways of DBPs during chlorination [44,45].

that humic-like acids were the most abundant components in all water samples. Soluble microbial-like products was the second most abundant fluorescent substance in these three water samples, which represented over 30% of total fluorescent DOM. For raw water, the cumulative fluorescence intensities of DOM were in the order of: Region V > Region IV > Region II > Region I > Region III. After UV exposure, the FRI value (Φ) represented a decrease in Region I and Region II, while it showed a higher value in Region III and Region V. In UV/TiO_2-treated water, the FRI value of DOM was in the order of: Region V > Region IV >Region III > Region II > Region I. Compared to UV/TiO_2-treated water, raw water and UV-treated water contained much larger aromatic proteins I and aromatic proteins II. Lee et al. [23] found that simple aromatic proteins (aromatic proteins I) were important THMs precursors which exhibited the highest chlorine reactivity. However, UV-treated water and UV/TiO_2-treated water represented larger amount of humic-like acids than raw water. Humic acids have been found to exhibit higher chlorine reactivity than fulvic acids which dominate the formation of DBPs among the fluorescence organics contained in DOM; this indicated that UV exposure would increase humic-like acids and the added TiO_2 could dramatically decrease aromatic proteins. As a result, the yields of THMs increased after UV irradiation while they showed a downtrend with the TiO_2 addition. The pathways of DOM degradation after UV and UV/TiO_2 are illustrated in Fig. 8 [44,45].

4. Conclusion

In this study, UV irradiation coupled with chlorination was employed for reclaimed water disinfection. The treated water was available to reuse as nonpotable water. UV exposure could increase the yield of THMs in subsequent chlorination due to the increasing humic-like acids in water sample. The addition of TiO_2 in UV could offset the bad side effect caused by UV irradiation by dramatically decrease of aromatic proteins. Increased exposure time, pH, and TiO_2 dose could improve the removal of UV_{254} and THMs, whereas only a rise of TiO_2 concentration could lead a downtrend of DOC.

Coated TiO_2 used in this study was less effective than the suspended one. However, considering the wide application prospect due to its easy separation, the degradation pathway of DBPs precursors using optimized GAC-TiO_2 was still a promising approach which was worth a further study in the future.

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References

[1] D. Ma, B. Gao, D. Hou, Y. Wang, Q. Yue, Q. Li, Evaluation of a submerged membrane bioreactor (SMBR) coupled with chlorine disinfection for municipal wastewater treatment and reuse, Desalination 313 (2013) 134–139.

[2] A.D. Benetti, Water reuse: Issues, technologies, and applications, Engenharia Sanitaria e Ambiental 13 (2008) 247–248.

[3] C. Shang, E.R. Blatchley III, Chlorination of pure bacterial cultures in aqueous solution, Water Res. 35 (2001) 244–254.

[4] K. Davies, A. Goldberg, Oxygen radicals stimulate intracellular proteolysis and lipid peroxidation by independent mechanisms in erythrocytes, J. Biol. Chem. 262 (1987) 8220–8226.

[5] X. Wang, X. Hu, H. Wang, C. Hu, Synergistic effect of the sequential use of UV irradiation and chlorine to disinfect reclaimed water, Water Res. 46 (2012) 1225–1232.

[6] S. Fane, J. Willets, K. Abeysuriya, Evaluating reliability and life-cycle cost for decentralized wastewater within the context of asset management, 1st International Conference on Onsite Wastewater Treatment and Recycling, Australia, Feb. 11–13, 2004.

[7] M. Guo, J. Huang, H. Hu, W. Liu, Growth and repair potential of three species of bacteria in reclaimed wastewater after UV disinfection, Biomed. Environ. Sci. 24 (2011) 400–407.

[8] M. Brahmi, N.H. Belhadi, H. Hamdi, A. Hassen, Modeling of secondary treated wastewater disinfection by UV irradiation: Effects of suspended solids content, J. Environ. Sci. 22 (2010) 1218–1224.

[9] M. Guo, H. Hu, W. Liu, Preliminary investigation on safety of post-UV disinfection of wastewater: Bio-stability in laboratory-scale simulated reuse water pipelines, Desalination 239 (2009) 22–28.

[10] N.A. Ballester, J.P. Malley, Sequential disinfection of adenovirus type 2 with UV-chlorine-chloramine, J. Am. Water Works Assoc. 96 (2004) 97–103.

[11] A.B. Silva, N.M. Lima Filho, M.A.P.F. Palha, S.M. Sarmento, Kinetics of water disinfection using UV-C radiation, Fuel 110 (2013) 114–123.

[12] U. Gunten, Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine, Water Res. 37 (2003) 1469–1487.

[13] W. Liu, L.M. Cheung, X. Yang, C. Shang, THM, HAA and CNCl formation from UV irradiation and chlor(am)ination of selected organic waters, Water Res. 40 (2006) 2033–2043.

[14] A. Chin, P.R. Bérubé, Removal of disinfection by-product precursors with ozone-UV advanced oxidation process, Water Res. 39 (2005) 2136–2144.

[15] A.M. Moncayo-Lasso, A.G. Rincon, C. Pulgarin, N. Benitez, Significant decrease of THMs generated during chlorination of river water by previous photo-Fenton treatment at near neutral pH, J. Photochem. Photobiol. A 229 (2012) 46–52.

[16] H. Shemer, K.G. Linden, Degradation and by-product formation of diazinon in water during UV and UV/H_2O_2 treatment, J. Hazard. Mater. 136 (2006) 553–559.

[17] S. Malato-Rodriguez, Solar photocatalytic detoxification and disinfection of water: Recent overview, J. Solar Energy Eng. 129 (2007) 4–15.

[18] J. Lee, J. Kim, W. Choi, TiO_2 photocatalysis for the redox conversion of aquatic pollutants, Aquat. Redox Chem. 1071 (2011) 199–222.

[19] M. Bertelli, E. Selli, Reaction paths and efficiency of photocatalysis on TiO_2 and of H_2O_2 photolysis in the

degradation of 2-chlorophenol, J. Hazard. Mater. 138 (2006) 46–52.

[20] A. Rincon, Effect of pH, inorganic ions, organic matter and H_2O_2 on *E. coli* K12 photocatalytic inactivation by TiO_2: Implications in solar water disinfection, Appl. Catal. B 51 (2004) 283–302.

[21] F.C. Kent, K.R. Montreuil, R.M. Brookman, R. Sanderson, J.R. Dahn, G.A. Gagnon, Photocatalytic oxidation of DBP precursors using UV with suspended and fixed TiO_2, Water Res. 45 (2011) 6173–6180.

[22] S.D. Richardson, A.D. Thruston, T.W. Collette, K.S. Patterson, B.W. Lykins, J.C. Ireland, Identification of TiO_2/UV disinfection byproducts in drinking water, Environ. Sci. Technol. 30 (1996) 3327–3334.

[23] D.T.S. Lee, S.S.M. Chan, D.S. Sahota, A.S.K. Yip, M. Tsui, T.K.H. Chung, A prevalence study of antenatal depression among Chinese women, J. Affect Disorders 82 (2004) 93–99.

[24] Y. Liu, S. Yang, J. Hong, C. Sun, Low-temperature preparation and microwave photocatalytic activity study of TiO_2-mounted activated carbon, J. Hazard. Mater. 142 (2007) 208–215.

[25] X. Huang, M. Leal, Q. Li, Degradation of natural organic matter by TiO_2 photocatalytic oxidation and its effect on fouling of low-pressure membranes, Water Res. 42 (2008) 1142–1150.

[26] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence excitation−emission matrix regional integration to quantify spectra for dissolved organic matter, Environ. Sci. Technol. 37 (2003) 5701–5710.

[27] L.S. Cleceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association & Water Environmental Association, Washington, DC, 1998.

[28] K.K. Philippe, C. Hans, J. MacAdam, B. Jefferson, J. Hart, S.A. Parsons, Photocatalytic oxidation of natural organic matter surrogates and the impact on trihalomethane formation potential, Chemosphere 81 (2010) 1509–1516.

[29] S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas, R. Amal, TiO_2 photocatalysis of natural organic matter in surface water: Impact on trihalomethane and haloacetic acid formation potential, Environ. Sci. Technol. 42 (2008) 6218–6223.

[30] Y.X. Sun, Q.Y. Wu, H.Y. Hu, J. Tian, Effect of bromide on the formation of disinfection by-products during wastewater chlorination, Water Res. 43 (2009) 2391–2398.

[31] L. Liberti, M. Notarnicola, D. Petruzzelli, Advanced treatment for municipal wastewater reuse in agriculture. UV disinfection: Parasite removal and by-product formation, Desalination 152 (2003) 315–324.

[32] C. Nurizzo, M. Antonelli, M. Profaizer, L. Romele, By-products in surface and reclaimed water disinfected with various agents, Desalination 176 (2005) 241–253.

[33] M.L. Magnuson, C.A. Kelty, C.M. Sharpless, K.G. Linden, W. Fromme, D.H. Metz, R. Kashinkunti, Effect of UV Irradiation on organic matter extracted from treated Ohio River water studied through the use of electrospray mass spectrometry, Environ. Sci. Technol. 36 (2002) 5252–5260.

[34] N. Corin, P. Backlund, M. Kulovaara, Degradation products formed during UV-irradiation of humic waters, Chemosphere 33 (1996) 245–255.

[35] L. Muszkat, L. Feigelson, L. Bir, K.A. Muszkat, Titanium dioxide photocatalyzed oxidation of proteins in biocontaminated waters, J. Photochem. Photobiol. B 60 (2001) 32–36.

[36] Y.H. Chuang, A.Y.C. Lin, X.H. Wang, H.H. Tung, The contribution of dissolved organic nitrogen and chloramines to nitrogenous disinfection byproduct formation from natural organic matter, Water Res. 47 (2013) 1308–1316.

[37] C. Hallmich, R. Gehr, Effect of pre- and post-UV disinfection conditions on photoreactivation of fecal coliforms in wastewater effluents, Water Res. 44 (2010) 2885–2893.

[38] W. Buchanan, F. Roddick, N. Porter, Formation of hazardous by-products resulting from the irradiation of natural organic matter: Comparison between UV and VUV irradiation, Chemosphere 63 (2006) 1130–1141.

[39] R.P. Galapate, A.U. Baes, M. Okada, Transformation of dissolved organic matter during ozonation: Effects on trihalomethane formation potential, Water Res. 35 (2001) 2201–2206.

[40] F. Soltermann, M. Lee, S. Canonica, U. von Gunten, Enhanced N-nitrosamine formation in pool water by UV irradiation of chlorinated secondary amines in the presence of monochloramine, Water Res. 47 (2013) 79–90.

[41] P.V. Kamat, Photochemistry on nonreactive and reactive (semiconductor) surfaces, Chem. Rev. 93 (1993) 267–300.

[42] H. Choi, E. Stathatos, D.D. Dionysiou, Photocatalytic TiO_2 films and membranes for the development of efficient wastewater treatment and reuse systems, Desalination 202 (2007) 199–206.

[43] J.C. Sin, S.M. Lam, A. Mohamed, Optimizing photocatalytic degradation of phenol by TiO_2/GAC using response surface methodology, Korean J. Chem. Eng. 28 (2011) 84–92.

[44] X. Yang, C. Shang, W. Lee, P. Westerhoff, C. Fan, Correlations between organic matter properties and DBP formation during chloramination, Water Res. 42 (2008) 2329–2339.

[45] J. Wenk, M. Aeschbacher, E. Salhi, S. Canonica, U. von Gunten, M. Sander, Chemical oxidation of dissolved organic matter by chlorine dioxide, chlorine, and ozone: Effects on its optical and antioxidant properties, Environ. Sci. Technol. 47 (2013) 11147–11156.