Control of halophenol formation in seawater during chlorination using UV/TiO_2 pre-treatment

Ning Ding, Xiufeng Yin, Zhe Yang and Yingxue Sun

ABSTRACT

Seawater is a valuable water resource in coastal regions. However, during seawater chlorination, a group of halophenols (HPs) may be formed. These HPs have lower odor and taste detection thresholds than other disinfection by-products (DBPs), however these are usually more toxic than most of the abundantly detected DBPs. Hence, an effective approach for control of HP formation during seawater chlorination is required to minimize highly toxic HP formation. Pretreatment using TiO_2 photocatalysis was applied in this study to assess its ability for removal of HP precursors. Seawater samples with external addition of 1 mg/L phenol were spiked with TiO_2 from 0.1 to 10.0 g/L and exposed under UV light for 2 to 120 min. The UV absorbance at 254 nm and the excitation–emission matrix fluorescence of dissolved organic matter were measured for each treated sample. It was observed that the optimal treatment condition to achieve the highest UV_{254} removal was 4.0 g/L TiO_2 with UV exposure of 30 min. By pretreatment using this method and stated dose and exposure, only two types of HPs were detected during chlorination, compared with four types of HPs formed in the untreated samples. Moreover, the pretreatment greatly reduced the concentration of 2,4,6-TBP from more than 400 μg/L to less than 1 μg/L. The significance of this research study is to identify the effectiveness of UV/TiO_2 in reducing DBP formation by analyzing the mechanisms during the process, which indicates the use of UV/TiO_2 pretreatment for control of HP formation in seawater during chlorination.

Key words | chlorination, excitation emission matrix fluorescence, halophenol, seawater, UV/TiO_2

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INTRODUCTION

The use of seawater as a source of water to cope with freshwater shortages has been a common practice in many areas, especially in coastal regions. Seawater may be applied for industrial cooling and heating purposes, and/or serves as an alternative source for drinking water (Kim *et al.* 2015; Manasfi *et al.* 2019). However, one of primary issues associated with the uses of seawater has been biofouling, which may reduce heat-transfer coefficients during cooling and heating processes, or clog the reverse osmosis membranes that are commonly applied for seawater desalination (Kim *et al.* 2015; Manasfi *et al.* 2019). Chlorination is the most widely used anti-biofouling technique for seawater to prevent bacterial and biofilm growth (Khalanski & Jenner 2012; Kim *et al.* 2015). The unintended consequences during seawater chlorination are the formation of a vast array of disinfection by-products (DBPs), resulting from reactions of chlorine with organic and inorganic compounds, which are a cause for concern for the impact on the environment and human health. Being low in total organic carbon levels, it is expected that DBP formation would be lower in seawater than in municipal wastewater, however, the high levels of bromide (50,000 to 80,000 μg/L) present in seawater likely enhance the formation of brominated DBPs during chlorination, which are more cytotoxic than their chlorinated analogues (Kim *et al.* 2015). Therefore, it is critical to control DBP formation in seawater applications.

doi: 10.2166/ws.2019.173

The trihalomethanes (THMs) and haloacetic acids (HAAs) are the most abundant and frequently identified DBPs in chlorinated seawater (Kim et al. 2015). Other DBPs, though detected at lower levels, such as bromophenols, have been reported to be more toxic than the former two classes (Liu & Zhang 2014). Furthermore, the low taste and odor threshold of bromophenols (in the range of μg/L to ng/L) makes the problem more prominent in phenol- and bromide (Br^-)-containing seawater than in drinking water (Agus & Sedlak 2010). In addition to bromophenols, chloro- and chlorobromo-phenols may also be formed in chlorinated seawater (Acero et al. 2005). Few studies have investigated pretreatment technologies to reduce halophenol (HP) formation during chlorination. It has been demonstrated that pre-ozonation may effectively degrade HP precursors, while the potential for the generation of other DBPs with bromide could impede its use for seawater (Ding et al. 2018).

As an environmentally friendly advanced oxidation process, photocatalytic oxidation is based on using light of wavelength near UV radiation to photoexcite semiconductor catalysts in the presence of oxygen to attack organic contaminants in water. Among various photocatalysts, titanium dioxide (TiO_2) has been most widely used in water treatment, due to its high photocatalytic activity and low cytotoxicity (Sillanpää et al. 2018). UV/TiO_2 is able to degrade water contaminants such as bacteria (Rincón & Pulgarin 2004), taste and odor compounds (Fotiou et al. 2016), as well as natural organic matter (NOM) (Gora et al. 2018), which is a primary contributor of DBP precursors. It has been reported that reduction in the total THM formation potential and total HAA formation potential by using UV/TiO_2 could be in the range of 20% and 90%, respectively (Kent et al. 2011). So far, little information is known on the efficacy of UV/TiO_2 in control of halophenol formation during seawater chlorination. The significance of this research study is to identify the effectiveness of UV/TiO_2 in reducing DBP formation by analyzing the mechanisms during the process, which indicates the use of UV/TiO_2 pretreatment for control of HP formation in seawater during chlorination.

The objectives of this study are for (a) analysis of the changes of the characteristics of dissolved organic matter in seawater by UV/TiO_2, (b) optimization of the effectiveness of UV/TiO_2 for HP precursor degradation, and (c) identification of the species and degradation of HPs formed during seawater chlorination by UV/TiO_2 pretreatment.

MATERIALS AND METHODS

Seawater samples

The seawater samples were collected from Bohai Bay in Tianjin, China, immediately followed by filtration by glass fiber filters (0.22 μm), and were transported and stored at 4 °C before use. A final concentration of 1 mg/L phenol was added to the seawater sample for the following experiments. The characteristics of the seawater sample with phenol and the original seawater sample are shown in Table 1 and Table S1 in the Supplementary Material. The methodologies for the characterization of the seawater sample in Table 1 and the preparation of the phenol standard sample are described in Ding et al. (2018).

Characterization of the treated seawater samples

The UV absorbance at 254 nm was analyzed by a UV-2401PC UV-VIS recording spectrophotometer (Shimadzu, Japan). Characteristics of the dissolved organic matter (DOM) components in the seawater samples were identified by excitation–emission matrix (EEM) fluorescence spectroscopy using an F-7000 fluorescence spectrophotometer (Hitachi, Japan). Quantification of EEM fluorescence was conducted by the fluorescence regional integration (FRI) method described in Chen et al. (2003). The EEM was operationally divided into five regions, using consistent excitation and emission wavelength boundaries. The EEM peaks have been associated with tyrosine-like aromatic protein (region I), tryptophan-like aromatic protein (region II), fulvic acid-like (region III), soluble microbial by-product-like (region IV), and humic acid-like organic

Table 1 | Characteristics of the seawater sample with phenol

DOC (mg/L)	UV_{254} (cm^{-1})	pH	Br^- (mg/L)
3.98 ± 0.20	0.055 ± 0.003	8.29 ± 0.06	43.5 ± 0.5

compounds (region V). The FRI method was to integrate the area beneath the EEM spectra to obtain the volume (Φ_i), as shown in Equation (1); the normalized excitation–emission area volume ($\Phi_{i,n}$) was calculated by Equation (2). The total normalized excitation–emission area volume of the five regions ($\Phi_{T,n}$) and the percentage of fluorescence response ($P_{i,n}$) were calculated by Equations (3) and (4):

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

$$\Phi_{i,n} = MF_i\Phi_i \quad (2)$$

$$\Phi_{T,n} = \sum_{i=1}^{5}\Phi_{i,n} \quad (3)$$

$$P_{i,n} = \Phi_{i,n}/\Phi_{T,n} \times 100\% \quad (4)$$

where λ_{ex} is the excitation wavelength (nm), λ_{em} is the emission wavelength (nm), I ($\lambda_{ex}\lambda_{em}$) is the fluorescence intensity at each excitation–emission wavelength pair (au), and MF_i is the multiple factor applied to the secondary or tertiary responses at longer wavelengths.

UV/TiO_2 treatment experiment

The UV/TiO_2 treatment experiment was carried out in a collimated beam reaction apparatus equipped with a 500 W mercury lamp. The lamp emitted UV light at nearly 254 nm and was mounted horizontally above a 250 mm long $\times$70 mm i.d. stainless steel collimating tube in the collimated beam apparatus. The photo fluence was measured with a UV fluence meter with a detection range of 0.1–199.9 $\times$ 10^3 μW/cm^2 (UV-A, Photoelectric Instrument Factory of Beijing Normal University, China). The reaction samples were placed on an adjusted platform mounted over a stirrer beneath the open end of the tube. The average irradiation intensity at the reaction platform was 1.47 mW/cm^2, which was measured at the pure water condition without any suspended solids. A different concentration of nanoscale TiO_2 (99.8%, Huaweiruike, China), of 0.1, 0.3, 0.5, 0.7, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 g/L, was added into each reaction sample, respectively, and stirred uniformly in the dark at 700 rpm for 30 min, immediately followed by UV exposure. For each UV exposure, a 100 mL seawater sample with TiO_2 suspension was exposed to UV for up to 120 min. The stirring speed was 700 rpm. Samples were withdrawn at 2, 4, 6, 8, 10, 15, 20, 25, 30, 45, 60, 75, 90, 105, and 120 min, and immediately filtered by glass fiber filters (0.22 μm) for UV_{254} analysis and EEM identification. Quality assurance and quality control (QA/QC) is presented in the Supplementary Material.

Chlorination

Raw and irradiated seawater samples with phenol were chlorinated by 2.5 mg Cl_2/L free chlorine up to 30 min. Samples were withdrawn at 2, 4, 6, 8, 10, 15, 20, 25, and 30 min for HP analysis. Detailed procedures are described in Ding *et al.* (2018).

Identification of HPs and characterization of the seawater samples

The HPs in the seawater samples were subjected to solid phase extraction and derivatization with a silylation reagent (BSTFA + TMCS, 99:1, Supelco, USA), followed by analysis by gas chromatography–mass spectrometry (GC/MS) (DB-5 ms, 30 m $\times$ 0.25 mm $\times$ 0.25 μm; GCMS-QP2010 Plus, Shimadzu, Japan). Detailed procedures were described in Ding *et al.* (2018). A total of 11 species of HPs were analyzed: 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,5-dichlorophenol (2,5-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2-bromophenol (2-BP), 4-bromophenol (4-BP), 2,4-dibromophenol (2,4-DBP), 2,6-dibromophenol (2,6-DBP), and 2,4,6-tribromophenol (2,4,6-TBP).

RESULTS AND DISCUSSION

The UV_{254} of seawater samples treated by UV/TiO_2 is presented in Figure 1 (tabular data shown in Table S2, Supplementary Material). It is shown that as UV exposure time extended, UV_{254} of seawater samples without the addition of TiO_2 slightly increased without great variation. For those samples treated by UV/TiO_2, UV_{254} rapidly increased until UV exposure of up to 20 min, and then it gradually decreased as UV exposure time extended to

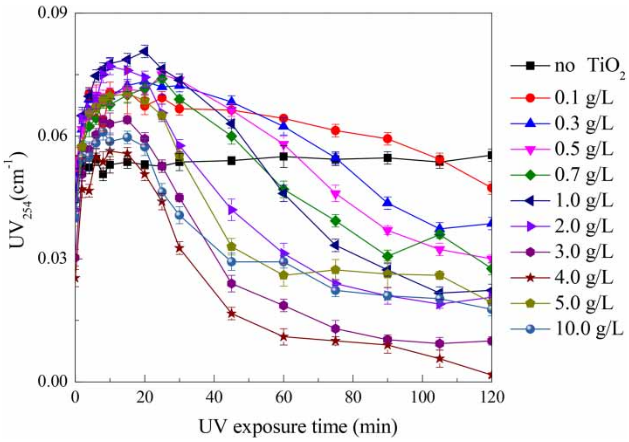

Figure 1 | UV_{254} of seawater samples treated by UV/TiO_2.

120 min. UV_{254} is an indicator of typical DOM with more than three conjugated double bonds (Noethe *et al.* 2009). Under lower UV doses (UV exposure less than 20 min), the free radicals excited by photocatalysis may not completely oxidize NOM, but may cause a shifting in the organics towards smaller and less aromatic moieties (Mayer *et al.* 2014), while by extending UV exposure time, the mineralization of organic matter can be readily achieved with oxidants (Liu *et al.* 2008; Mayer *et al.* 2014). It is observed that the optimal TiO_2 for removal of UV_{254} was 4.0 g/L (Figure 1). As TiO_2 dose increased up to the optimum of 4.0 g/L, the number of active sites on the photocatalysts increased, which enhanced the generation of hydroxyl and superoxide radicals (Akpan & Hameed 2009). However, once the concentration of the photocatalyst increased beyond the optimal value, the increased turbidity caused by excess photocatalysts limited the illumination, thus the photocatalytic degradation efficiency reduced accordingly (Lathasree *et al.* 2004; Sun *et al.* 2008). In addition, the high concentration beyond the optimum might have resulted in agglomeration of the photocatalyst, which inhibited the active sites for photon absorption and led to a lower photocatalytic activity (Huang *et al.* 2008).

By plotting EEM fluorescence spectra (Figure S1, Supplementary Material), it is shown that the fluorescence intensity of regions I and VI are the highest among the five regions, hence tyrosine-like aromatic protein and soluble microbial by-product-like organic compounds were the primary components in DOM. The volumes beneath EEM of regions I and IV of the seawater samples treated with different doses of TiO_2 and UV are presented in Figure 2. The major components of DOM degraded as UV doses increased, even without the addition of TiO_2. The addition of TiO_2 increased the normalized excitation–emission area volume ($\Phi_{i,n}$) of EEM in the first place, while by UV irradiation, it drastically decreased to the level below that of the raw samples. It is noted that the application of TiO_2 greatly enhanced the effectiveness of UV exposure. By increasing TiO_2 dose from 0.5 to 1.0 g/L, the degradation of soluble microbial by-product-like organic compounds and tyrosine-like aromatic protein gradually increased. However, further increasing TiO_2 doses up to 10.0 g/L only slightly raised the efficacy of degradation. On

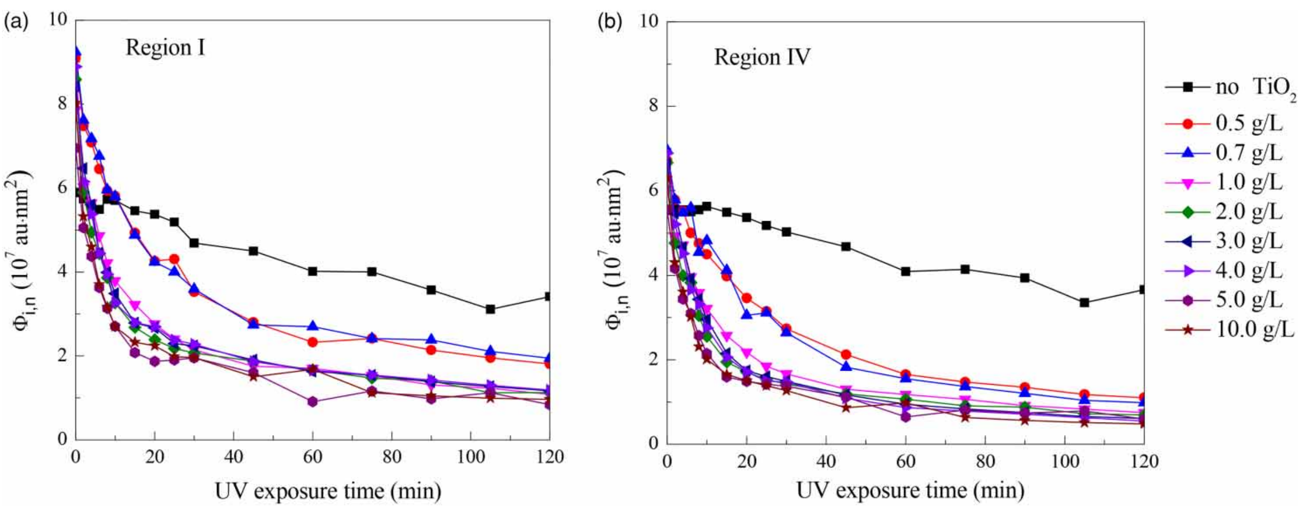

Figure 2 | Normalized excitation–emission area volume ($\Phi_{i,n}$) of (a) region I and (b) region IV of UV/TiO_2 treated seawater samples.

the other hand, with TiO_2 doses higher than 1.0 g/L, $\Phi_{i,n}$ rapidly decreased with UV exposure extended to 30 min, followed by entering a lag phase after that. In consideration of the removal efficacy of UV_{254} (shown in Figure 1, tabular data shown in Table S2) and the major components of DOM (shown in Figure 2, tabular data shown in Tables S3 and S4), the optimal and economic UV/TiO_2 treatment condition of 4.0 g/L TiO_2 with UV exposure of 30 min was selected for the chlorination experiment.

The changes of the percentage of fluorescence response ($P_{i,n}$) of DOM by the UV/TiO_2 treatment are shown in Figure 3. By treatment with 4.0 g/L TiO_2 under UV for 30 min, the primary components of tyrosine-like aromatic protein and soluble microbial by-product-like organic compounds were greatly reduced, thus $P_{i,n}$ of regions I and IV decreased from 37.2% and 33.4% to 18.5% and 14.5%, respectively. UV/TiO_2 treatment was less efficient for degradation of DOM in regions II, III, and V, which were of much smaller amounts than the components in regions I and IV. This was in agreement with the findings of the raw seawater samples pretreated by ozonation in our previous study (Ding et al. 2018). UV/TiO_2 treatment in this condition achieved a reduction of EEM intensity higher than that with ozonation at 5 mg O_3/L but lower than that at 10 mg O_3/L.

The effect of treatment by 4.0 g/L TiO_2 under UV exposure for 30 min is shown in Figure 4. During chlorination, four types of HPs including 4-BP, 2,4,6-TCP,

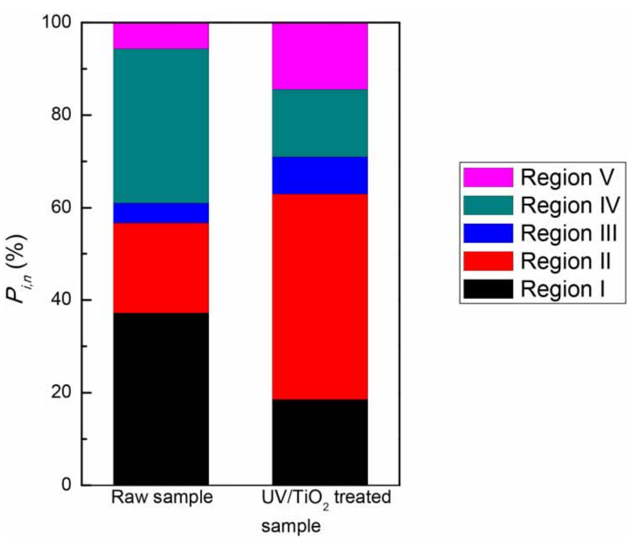

Figure 3 | Changes of $P_{i,n}$ of the raw seawater sample by UV/TiO_2 treatment.

2,4-DBP, and 2,4,6-TBP were formed in the raw seawater sample. The concentrations of 2,4,6-TCP and 2,4-DBP were constantly below 5 μg/L. The concentration of 4-BP was rapidly increased to 13.9 μg/L in the first two minutes of chlorination, and decreased to below 5 μg/L within 10 min. The concentration of 2,4,6-TBP was very much higher than the other HPs, which reached 687.4 μg/L at 4-min chlorination, and gradually decreased and fluctuated at nearly 400 μg/L at 30 min. By treatment of UV/TiO_2, only two types of HPs, 2,4-DBP and 2,4,6-TBP, were formed. UV/TiO_2 treatment did not change much the concentration of 2,4-DBP formed during chlorination, while it greatly decreased the concentration of 2,4,6-TBP, which was reduced from nearly 400 to less than 1 μg/L. The chlorine consumption of seawater samples was also reduced after UV/TiO_2 treatment (Figure S2, Supplementary Material).

It is noted that the optimum dose of the catalyst TiO_2 varied in regard to the target contaminant and the aqueous matrix. For example, the degradation of the dye Fast Green continuously increased as TiO_2 increased from 0.5 to 4.0 g/L, while the degradation of Acid Blue reached the optimum at TiO_2 of 2.0 g/L (Saquib et al. 2008). In this study, the optimal dose of TiO_2 (0.5–10.0 g/L) for HP degradation was 4.0 g/L. However, when considering industrial application, the cost of catalysts must be taken into account for a tradeoff.

In this study, the concentration of 2,4-DBP and 2,4,6-TBP remained constantly below 5 μg/L, indicating that no new HPs formed during chlorination. At neutral or higher pHs, hydroxyl radicals (·OH) are considered the predominant species during UV/TiO_2 treatment. In alkaline solution, hydroxyl ions facilitate the generation of ·OH on the surface of TiO_2 (Tunesi & Anderson 1991). The most probable pathways of the reactions are as follows (Zhang et al. 2014): (1) when irradiated by UV light (with photons of greater energy than the bandwidth energy), an electron/hole (e^-/h^+) pair is formed in the TiO_2 particle (Equation (5)) (De Heredia et al. 2001; Linsebigler et al. 1995); (2) the holes (h^+) in the valence band produce hydroxyl radicals (·OH) by oxidizing water or hydroxide ions (Equations (6) and (7)) (De Heredia et al. 2001); (3) the electrons (e^+) excited to the conduction band reduce dissolved oxygen to superoxide radicals (O_2^-·) (Equation (8)) (De Heredia et al. 2001); (4) O_2^-· and its protonated form produce hydrogen peroxide (H_2O_2) and a peroxide anion. By photocatalytic

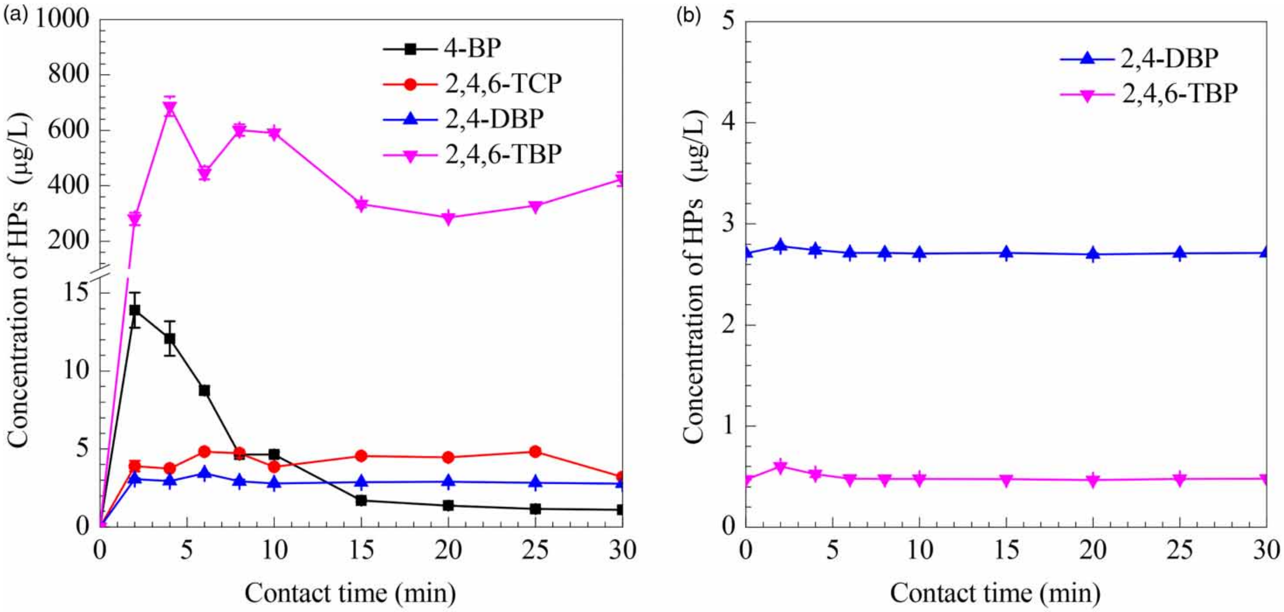

Figure 4 | Formation of HPs in the (a) raw seawater sample and (b) UV/TiO_2 treated seawater sample during chlorination.

reduction of H_2O_2 by e^-, next ·OH is produced (Equations (9) and (10)) (Hashimoto *et al.* 2005).

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (5)$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \quad (6)$$

$$OH^- + h^+ \rightarrow \cdot OH \quad (7)$$

$$O_2 + e^- \rightarrow O_2^{-\cdot} \quad (8)$$

$$2O_2^{-\cdot} + 2H^+ \leftrightarrow 2HO_2\cdot \rightarrow H_2O_2 + O_2 \quad (9)$$

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \quad (10)$$

It is shown that the pretreatment with 4.0 g/L TiO_2 under UV exposure for 30 min was able to effectively control the formation of HPs during chlorination. In our previous study, the seawater sample was pretreated with 5 mg O_3/L, and the types of HPs formed during chlorination were reduced to 2,4,6-TBP, 2,4-DBP, and 4-BP (Ding *et al.* 2018). Among the formed HPs, the concentration of 2,4,6-TBP was the highest, which reached 7.5 μg/L at 10-min chlorination and decreased to around 1.5 μg/L at 30 min. One major concern associated with ozone pretreatment is the formation of bromate (OBr^-), a probable human carcinogen, in the presence of high Br^-. Molecular ozone was found to directly oxidize Br^- into HOBr, while the indirect oxidization pathway of ·OH generated during ozonation has also been reported to oxidize Br^- into HOBr through the intermediate Br· (von Gunten 2003). The reactions involved in the presence of Br^- and ·OH are in Equations (11)–(13) (von Gunten & Hoigne 1994):

$$Br^- + \cdot OH \leftrightarrow BrOH^- \quad (11)$$

$$BrOH^- \rightarrow Br \cdot + OH^- \quad (12)$$

$$Br \cdot + Br^- \rightarrow Br_2^- \quad (13)$$

It is suggested that HOBr and OBr^- must be present in order for bromate to form further. In the absence of the above two compounds, however, the formation of $BrOH^-$ is reversible, and no bromate has been detected as a result of TiO_2 photocatalysis (Brookman *et al.* 2011).

CONCLUSION

In this study, UV/TiO_2 pre-treatment has been assessed to control the formation of halophenol in seawater during chlorination. TiO_2 dose and UV exposure time both affected the removal of UV_{254} and DOM, and the optimal condition was determined to be 4.0 g/L TiO_2 with UV exposure of 30 min. The primary components of tyrosine-like aromatic protein and soluble microbial by-product-like organic compounds were greatly degraded under this condition. By UV/TiO_2 pretreatment, 4-BP and 2,4,6-TCP disappeared, and 2,4,6-TBP was significantly reduced from more than 400 to lower than 1 μg/L during chlorination. It is suggested that UV/TiO_2 may serve as a potential pretreatment approach for control of halophenol formation in seawater during chlorination.

ACKNOWLEDGEMENTS

This study was funded by the China Postdoctoral Science Foundation (2019M650493) and Annual Beijing Scientific Research Plan Project (KM201810011011).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/ws.2019.173.

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First received 12 June 2019; accepted in revised form 8 November 2019. Available online 26 November 2019