Effects of Bromide on Inactivation Efficacy and Disinfection Byproduct Formation in Photocatalytic Inactivation

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Abstract

The high effectiveness of TiO₂-UVA system in bacterial disinfection has gained attention to use this technology in water treatment on different source waters, including desalinated sea water and grey water. However, source waters containing a significant level of bromide could have different chemical pathways during TiO₂-UVA disinfection process because reactive bromine species could be formed. To illustrate the water safety from the Br-TiO₂-UVA system, this study investigated bacterial inactivation efficiency and disinfection byproduct (DBP) formation under different pH, TiO₂ dosages and bromide concentrations in a laboratory setting. At a high bromide concentration (65 mg/L, equivalent to the concentration of natural sea water), the bacterial inactivation rate increased 2 times at pH 5 and more than 5 times at pH 8. However, a significant increase of brominated DBPs, which were considered more carcinogenic and toxic than chlorinated DBPs, was observed. The bacterial inactivation pattern was shifted from the “shoulder-log” to the “log-tail” under different bromide concentrations, suggesting the existence of bromide altered the bacterial inactivation mechanisms. We also observed that the inactivation kinetics of Br-TiO₂-UVA system was greatly influenced by water pH. Our laboratory experiments demonstrated that bromide could improve the performance of photocatalytic inactivation, but it also could reduce the water safety by generating a higher level of brominated-DBPs in treated water. Water engineers should pay attention to the brominated DBP formation when applying TiO₂-UVA photocatalysis on source waters with a significant level of bromide.

Keywords: Bromoform, *E. coli* inactivation, TiO₂-UVA, Trihalomethane

1. Introduction

The need of clean drinking water is increasing in the 21st century. There are 1.2 billion people lack access to safe and clean drinking water and 2.6 billion have drinking water with little or no sanitation [1]. Thousands of children are died annually from diseases transmitted through unsafe water or human excreta [1-2]. Therefore improving the technology for drinking water sanitation is one of the least expensive and most effective means to improve public health and save lives [2]. On the other hands, though disinfection process can inactivate pathogenic microbes in the water, various disinfection byproducts (DBP) are usually produced in the processes. Different bacterial cellular components, such as nucleic acid, amino acid and extracellular polymeric substances, are proved to be DBP precursors [3-6]. These DBPs are toxic and carcinogenic which increase the risk of health in drinking water [7-9]. In order to balance the risk of pathogen bacterial and DBPs, achieving high disinfection efficiency with low DBPs formation become a major target in the improvement of water disinfection technology.

Photocatalytic inactivation has been extensively studied for water disinfection. Photocatalytic inactivation not only effectively inactivates different microorganisms [10-12], but also produces less DBPs when compared with chlorination [13]. Therefore, it is believed to be a good alternative disinfection process. Recently, there are studies showing that presence of bromide in the water can effectively enhance the disinfection efficiency of photocatalytic inactivation, due to the formation of the powerful reactive bromine species [14]. On the other hands, bromide is an inorganic DBP precursor and its existence in water usually increases the quantity of DBP formation in disinfection process. In the study of DBP formation of chlorination, a higher DBP formation is usually observed in the presence of bromide due to the higher reactivity of HOBr

and OBr^- [15]. Moreover, the presence of bromide increase the formation of brominated DBP (Br-DBP) [15-16], which are more toxic and carcinogenic in nature compared to traditional carbeneous-DBP (C-DBP) [15,17]. Bromide is commonly present in many aqueous systems, in the range from several mg/L in surface water [18-21] to over 60 mg/L in sea water [15]. Formation of DBP from disinfection of desalinated water also received increasing concern. As the concentrations of bromide and iodide in desalinated water are high, the formation of more toxic Br-DBP and I-DBP poses a risk on environment and human health [22]. Thus, understanding the effects of bromide on the inactivation efficiency and DBP formation of photocatalytic inactivation is important for evaluating the performance and safety of photocatalytic disinfection for seawater or wastewater with high bromide concentration.

However, there is no study to investigate the effect of bromide on the inactivation efficiency and the formation of DBPs of photocatalytic inactivation simultaneously. This study aims to investigate the balance of the bacterial inactivation efficiency and DBP formation of Br- TiO_2 -UVA photocatalytic inactivation. The bacterial inactivation efficiency, as well as the DBP formation of TiO_2 -UVA system under different pH, TiO_2 dosage and bromide concentration, were investigated.

2. Materials and methods

2.1 Bacterial inactivation

Escherichia coli K12 (ATCC, USA) were cultured in nutrient broth (BioLife, Italy) at 37 °C in incubator for 16 h to reach the stationary stage (10^9 colony forming unit (cfu)/mL). The cultures were then aseptically centrifuged and washed three times with phosphate buffer solution (PBS,

pH 7.4). Finally, the cell concentrations were adjusted to 1.5×10^7 cfu/mL in each reaction. To prevent contamination, all Milli-Q water (Millipore, USA), PBS solution, and pipette tips were autoclaved (121 °C for 20 min) before use.

The photocatalytic inactivation procedures followed the method reported by Zhang et al. [23]. Briefly, TiO₂/UVA photocatalytic inactivation was conducted in air-tight glass flasks with 100 mL mixture of PBS and bacterial cells. UVA lamp (Cole-Parmer, USA) with intensity of 0.22 mW/cm² was used as the lighting source. Samples were collected at different time intervals (0, 5, 20, 40, 60 and 80 min). The inactivation efficiency was evaluated by monitoring the bacteria survival using viable plate count method [23] while the DBP formation was evaluated using U.S. EPA Method 551.1 mentioned in the next section. The effect of pH (5 and 8), TiO₂ dosage (100 and 250 mg/L TiO₂, P-25, Degussa Corporation, Germany) and bromide concentration (0, 20 and 65 mg/L) on the disinfection efficiency and DBP formation was investigated.

2.2 Inactivation kinetic

To compare the rate of inactivation of *E. coli*, the inactivation kinetic was calculated according the should-log-tail model proposed by Geeraerd et al. [24]. The inactivation kinetic of the parental strains and mutants were fitted into the shoulder-linear-tail (Equation 1) with the software GInaFit [25].

$$\log(N) = \log \left[\left(10^{\log(N_0)} - 10^{\log(N_{res})} \right) \times e^{-K_{max}t} \times \frac{e^{(K_{max}S_1)}}{1 + (e^{K_{max}S_1} - 1) \times e^{(-K_{max}t)}} + 10^{\log(N_{res})} \right] \quad (1)$$

where

115 $K_{\max}$ = specific inactivation rate [min^{-1}]

116 S_l = shoulder length [min]

117 N_{res} = residue population density [cfu/mL]

118 N_0 = initial population density [cfu/mL]

119 t = reaction time [min]

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121 2.3 DBP analytical method

122 The DBPs analyzed including four THMs (chloroform (CHCl_3), bromodichloromethane
123 (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3), four HANs
124 (trichloroacetonitrile (Cl_3CCN), dichloroacetonitrile (Cl_2CHCN), bromochloroacetonitrile
125 (BrClCHCN) and dibromoacetonitrile (Br_2CHCN), dichloropropanone ($\text{Cl}_2\text{CHCO}(\text{CH}_3)$) and
126 chloral hydrate ($\text{Cl}_3\text{CCH}(\text{OH})_2$). All DBP standards were purchased from Sigma Aldrich (USA)
127 and prepared before experiments for calibration. All samples were treated with methyl-tertiary-
128 butyl-ether (MTBE) (Fluka, Switzerland) and sodium sulfate (Na_2SO_4) for liquid/liquid
129 extraction of DBPs from aqueous solution according to U.S. EPA Method 551.1 [26] (detection
130 limit = 1 ng/L). Samples were kept in refrigerator at 4 °C and analyzed within 10 days. Gas
131 chromatography and electron capture detection (GC-ECD) was used to quantify the DBP
132 concentrations. GC column (A - 0.25 mm ID x 30 m fused silica capillary) was used and the
133 temperature program was slightly modified as follows: held at 30°C for 7 min then increased to
134 100°C at 20°C/min and held for 3min, and then increased to 260°C at 30°C/min and held for 2
135 min. The injector and detector temperature were set at 250°C.

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The bromine substitution factor (BSF) was calculated for representing the yield of brominated species in THM formation [27]. BSF is equal to 0% if pure chloroform (CHCl_3) is formed and is equal to 100% if pure bromoform (CHBr_3) is produced.

$$\text{BSF} = \frac{\sum_{n=0}^3 n[\text{CHCl}_{(3-n)}\text{Br}_n]}{3 \sum_{n=0}^3 \text{CHCl}_{(3-n)}\text{Br}_n} \times 100\% \quad (2)$$

3. Results and discussion

3.1 Bromide enhances on photocatalytic bacterial inactivation but deteriorates DBP formation

The results of bacterial inactivation under two pH and two TiO_2 dosages were summarized in Fig. 1. As shown, the cell density decreased remarkably with increasing bromide concentration in all testing conditions, proving the presence of bromide effectively enhanced the bacterial inactivation in TiO_2 -UVA system. Notably, the bacterial inactivation rates at pH 5 with 250 mg/L of TiO_2 were the highest among other tested conditions, suggesting a slightly acidic condition with a higher TiO_2 dosage favored the bacterial inactivation in TiO_2 -UVA system.

For a better comparison of the bromide effect on the bacterial inactivation, the reaction kinetic of bacterial inactivation under different treatment conditions was fitted into the kinetic model proposed by Geeraerd et al. [24] and their kinetic constants of the inactivation were listed in Table 1. $K_{\max}$ is the maximum reaction rate of the bacterial inactivation and S_i , termed as houlder length, represents time required for the accumulation of ROS before the damage of bacterial cells can be observed. Noticeably, UVA intensity of 0.22 mW/cm^2 did not cause significant inactivation of *E. coli* within 80 min according to our previous study[28]. In general, $K_{\max}$ increased with bromine concentration. Considering the treatment at pH 5 with 250 mg/L of TiO_2

as an example (Fig 1b & Table 1). The $K_{\max}$ increased from 0.22 min^{-1} at 0 mg/L of bromide to 0.58 and 0.66 min^{-1} at 20 and 65 mg/L of bromide, respectively. Beside an increase of $K_{\max}$, shortening of S_1 was also observed when the bromide level increased at high TiO_2 dosage and slightly alkaline condition (pH 8). The S_1 was decreased from 53.4 min at 0 mg/L of bromide to 20.95 and 0 min at 20 and 65 mg/L of bromide, respectively, when 250 mg/L of TiO_2 were applied.

Beside bromide concentration, water pH is an important factor affecting the bacterial inactivation in TiO_2 -UVA system. In general, a faster reaction rate ($K_{\max}$) with a shorter shoulder length (S_1) was observed in slightly acidic conditions (pH 5) than that in slightly alkaline condition (pH 8), indicating that the inactivation was faster at low pH. Moreover, the enhancement of bacterial inactivation by bromide was also more remarkable at pH 8. No obvious bacterial inactivation was observed with no bromide presence and a remarkable inactivation was achieved when the bromide concentration increased. For example, with TiO_2 of 100 mg/L, the $K_{\max}$ increased from 0.01 to 0.71 min^{-1} when the bromide concentration increased. While with TiO_2 of 250 mg/L, the S_1 decreased from 53.4 to 0 min when the bromide concentration increased. The enhancement was not so obvious at pH 5 as significant bacterial inactivation was still observed when no bromide was presence in the system.

Fig. 1. Inactivation of *E. coli* K-12 in TiO₂/UVA system under different pH, bromide concentrations and TiO₂ dosages

180 Table 1. The reaction constant of the bacterial inactivation of TiO₂/UVA system, under different pH, bromide concentration and TiO₂
181 dosages

	pH = 5						pH = 8					
TiO ₂ (mg/L)	100			250			100			250		
[Br ⁻] (mg/L)	0	20	65	0	20	65	0	20	65	0	20	65
S _l (min)	32.9	0	0	0	0	0	7.1	28.6	20.5	53.4	21.0	0
K _{max} (min ⁻¹)	0.34	0.22	0.60	0.22	0.58	0.66	0.01	0.09	0.71	0.13	0.53	0.64
N _{res} (cfu/mL)	0	0	0.46	0	0.15	0.54	0	0	0.51	0	0.57	0.10

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183 S_l = shoulder length

184 K_{max} = specific inactivation rate

185 N_{res} = residue population density

186

The results of DBP formation in our Br-TiO₂-UVA systems were listed in Fig. 2. The DBP formation increased when the bromide concentration increased. No DBPs was observed when no bromide was added. In the presence of 20 mg/L of bromide with a high dosage of TiO₂ (250 mg/L) and slightly alkaline (pH 8) condition, formation of CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃ and Cl₃CCH(OH)₂ were detected. The effect of bromide on DBP formation was more remarkable when the bromide level was increased to 65 mg/L. Besides the aforementioned DBPs, Br₂CHCN (4.91±0.8 µg/L) was also observed at 250 mg/L of TiO₂ at pH 8, which was not observed in our other testing conditions. Among different DBPs, formation of CHBr₃ was the highest, which ranged from 1.84 to 8.96 µg/L. The bromine substitution factor (BSF) of the THMs formed at pH 5 was 60.3 and 64.7% in 100 and 250 mg/L of TiO₂, respectively. While the BSF of THMs formed at pH 8 was 64.7 and 77.3% in 100 and 250 mg/L of TiO₂, respectively. Noticeably, The UV dosage used in this study was 1056 mJ/cm² which might split chemical bonds or change the characteristics of functional groups of organic matter [29]. However, the UV dosage of each treatment was the same, thus the effect of UVA irradiation on the DBP should be the same for all the treatment.

Fig. 2. DBP formation from *E.coli* K-12 in TiO₂/UVA inactivation under different conditions. No DBPs were observed when no bromide was added. Cl₃CCN, Cl₂CHCN, BrClCHCN and Cl₂CHCO(CH₃) were below detection limit in all treatments. BSF values in each figure shows the bromine substitution factor of THMs only.

3.2 Bromide altered photocatalytic bacterial inactivation mechanisms

Our experiments demonstrated that an addition of bromide into water could enhance bacterial inactivation in TiO₂-UVA system and the inactivation kinetic pattern shifted from “shoulder-log” to “log-tail”. This shift was more obvious in a water solution at pH 8 with 250 mg/L of TiO₂. In

general, a “shoulder-log” inactivation pattern is observed with mild disinfectants, such as H_2O_2 [30] and a “log-tail” inactivation pattern is observed with stronger disinfectants, such as $\bullet OH$ produced by Fenton reaction [31]. The shoulder in the “shoulder-log” inactivation pattern is attributed to the time requirement for the diffusion or accumulate of the disinfectants (i.e. H_2O_2 needs to diffuse across the cell membrane and produce $\bullet OH$ to attack bacterial DNA through Fenton reaction [30]). While the tail in “log-tail is attributed to the quenching of ROS by the internal organic matter leakage in the latter stage of the disinfection process. The change of inactivation pattern suggests that stronger bromine reactive species are involved when the system changed from TiO_2 -UVA to Br - TiO_2 -UVA. In fact, a variety of bromine reactive species such as bromine radicals ($\bullet Br$), hypobromous acid ($HOBr$), and dibromide radical ($\bullet Br_2^-$) can be formed in advanced oxidation processes when bromide is existed in source waters [21,32].

Li et al. [33] reported that these bromine species are generally more effective in inactivating bacteria. Therefore, the addition of bromide results in the enhancement of bacterial inactivation of TiO_2 /UVA system, in terms of a decrease in S_l and an increase of K_{max} .

On the other hands, these reactive bromine species also react with organic matter in source water and increase DBP formation. Since PBS also contains chloride, at low bromide level,

Chlorinated DBP (Cl-DBP) was still the major DBP species. Formation of different bromine-related ions, such as HOBr and hypobromite ion (BrO^-), are important intermediate in TiO_2 -UVA system. These ions and radicals, compared to ROS and h^+ , not only have a higher activity to react with the cellular components and biomolecule that increase the DBP formation, but also increase the bromination. Although reactive chlorine species were also be formed in the reaction (PBS also contains chloride), the formation of bromide radical is more favorable than that of chloride radical [34-35]. Therefore, the majority of the DBP shifted from Cl-DBP to Br-DBP when bromide concentration increased. As seen in Figure 2, the concentration of CHBr_3 was the highest in the DBP formation study under the presence of 65 mg/L of bromide and the BSF of THMs increase with increasing bromide concentration. The formation of brominated species further confirms that reactive bromine species existed in Br- TiO_2 -UVA system.

3.3 Water pH determines reactive bromine species distribution and bacterial inactivation mechanisms

Water pH can influence the rate of bacterial inactivation and yield of DBP formation in Br- TiO_2 -UV because the speciation of reactive bromine species changes with water pH. Bromide can be converted to different bromine species through photocatalysis as described in equation (3)-(6). However, the dominant species depend on water pH. Taking Br_2 , HOBr, and BrO^- as an example. Br_2 is the dominant aqueous bromine species at $\text{pH} < 5.0$. On the other hands, HOBr at pH between 5.0 and 8.7 and OBr^- at $\text{pH} > 8.7$ are the dominant in water (Eq 7-9) [36] and the reactivity and reaction kinetics of different bromine species are different [37]

In addition to the bromine chemistry, water pH affects the electrical charges in the surfaces of TiO_2 particles and bacterial cells. Bacterial cell surface is usually negatively charged, whereas TiO_2 particle is at the point of zero charge (named isoelectric point) at pH ranging from 6.2 to 7.5 [38-39]. Hence the surfaces of TiO_2 particles become electronegative and repulse bacterial cells when water pH is higher than 7.5 [40]. In acidic water environment, there could be an attraction between positive-charged TiO_2 particles and negative-charged bacterial cells [41]. Hence the photogenerated hole (h^+) can directly oxidize the bacterial cells. In this case, the reaction kinetic patterns in most cases are log or log-tail (without the present of shoulder length) and bacterial inactivation is effective even without the presence of bromide (Figs. 1a and 1b). The formation of bromine related radicals would only assist the bacterial inactivation as both h^+ and bromine related radicals involved in the inactivation. In contrast, the direct oxidization by h^+ is difficult at pH 8 because of the repulsion between the TiO_2 particles and bacterial cells with same charge. The bacterial inactivation relies on other ROS such as hydroxyl radical ($\bullet\text{OH}$) and H_2O_2 when no bromide is presence in the solution. This is supported by the long shoulder length (S_1) and low reaction rate (K_{max}) at pH 8. Therefore, the bacterial inactivation would be mainly relied on the bromine related radicals, which are powerful and long lasting [33]. Thus the improvement of the presence of bromide in bacterial inactivation was more remarkable at pH 8.

Similarly, the effect of bromide on the increase of DBP formation was more remarkable at pH 8. It is also related to the inactivation mechanisms as mentioned. Since at slightly alkaline pH,

contact between the TiO_2 particles and bacterial cells is poor, the inactivation would mainly rely on the bromine related radicals. As the DBP formation, especially the brominated-DBP, are higher from the inactivation by reactive bromine species compared to the h^+ . Therefore, the quantity of DBPs and the BSF of THMs are both higher at pH 8 when bromide is present.

Moreover, the reactivity of reactive bromine species towards organic compound is higher than that of reactive chlorine species [15,21]. Shan et al. [42] also reported that the effect of bromide on the chlorination of amino acids and amino sugars. Results indicated that addition of bromide in solution would increase the THMs formation, as well as the BSF of THMs (i.e. brominated species). These results comply with the results of present study and suggested that reactive bromine species were formed in the TiO_2 /UVA system in the presence of bromine, leading to the increase of DBP formation and BSF of THMs.

3.3 Environmental Implication

The salinity of water could have great influent on the inactivation efficiency of photocatalysis [43], because of the presence of different ions in the water. Effects of different anions in water have been well investigated and most of them would decrease the photocatalytic inactivation efficiency. For example, the present of SO_4^{2-} and $\text{NH}_4^+/\text{NH}_3$ could consume the reactive species (usually h^+ or $\bullet\text{OH}$) and form a weaker oxidative radical, such as $\bullet\text{SO}_4^-$ [44-45]. In contrast, bromide is one of the few anions that can enhance the photocatalytic bacterial inactivation [34]. The results of this study revealed that the presence of bromide enhanced the photocatalytic bacterial inactivation due to the formation of active bromide species. However, the DBP formation, especially brominated DBP, also increased with the present of bromide in water.

Although the presence of bromide in water increased both the inactivation efficiency and DBP formation, but the increase of inactivation efficiency was more remarkable. An addition of 20 mg/L of bromide significantly improved the inactivation efficiency in all our tested conditions; whereas the formation of DBPs was only observed at pH 8 with 250 mg/L of TiO_2 (Fig. 2d). In typical source water including desalinized waters, the concentration of bromide should be less than 10 mg/L [15,18,19]. According to the results of this study, DBP formation in TiO_2 /UVA system in this concentration of bromide should be negligible. Therefore, the bromide in surface water should enhance the bacterial inactivation efficiency of TiO_2 /UVA system with no observable increase in DBP formation. However, the bromide level in sea water is around 65 mg/L [20-21] and maybe even higher than 100 mg/L in some wastewater effluent [15]. In this case, the formation of DBPs should not be ignored.

Bromide is generally more reactive in water disinfection processes. Similar to the results of this photocatalytic disinfection study, an increase of bromide concentration in water chlorination increases the disinfection efficiency and concentration of Br-DBP formation [46]. However, the DBP formation in Br- TiO_2 -UVA system is still relatively lower than that in chlorination. In our previous study, the BSF of THMs in the chlorination of *P. aureginosa* in the presence of 2 mg/L of bromide ranged from 62-95% [16], which is higher than the highest BSF (60.3-77.3%) of THMs with the presence of 65 mg/L of bromide in this study. Therefore, disinfection with TiO_2 /UVA system under high bromide concentration still renders the merit of lower DBP formation compared with chlorination. Notably, the reaction time for effective disinfection by chlorination is still much shorter (usually in 10 min) than that of photocatalysis (usually 30-120

min) [47]. Therefore, in the presence of small amount of bromide (i.e. < 20 mg/L), photocatalysis can be used as a pretreatment of water to inactivate a portion of bacteria (say 90-99%) and oxidize organic matter in water first, then couple with chlorination to disinfect the residual bacteria as may be a potential method to achieve high disinfection efficiency with low DBP formation.

4. Conclusion

This laboratory study showed that an increase of bromide concentration in water could enhance bacterial inactivation efficiency, but it can also increase DBP formation in treated water. The increase of inactivation efficiency and DBP formation in Br-TiO₂-UVA system should be attributed for the formation of reactive bromide species, such as HOBr and •Br₂⁻. Water pH also has a great influence on bacterial inactivation mechanism and DBP formation in Br-TiO₂-UVA system. Slightly alkaline conditions decreased the bacterial inactivation and increase the Br-DBP formation. The results indicate a great influence of bromide on the performance and safety of photocatalytic disinfection of waters with high level of bromide, such as desalinized or natural sea waters. Therefore, the concentration of bromide should be considered for application of photocatalytic treatment of water with high salinity in order to balance the disinfection efficiency and DBP formation.

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Effects of Bromide on Inactivation Efficacy and Disinfection

Byproduct Formation in Photocatalytic Inactivation

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Graphical Abstract