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2015

Xiao, Y., Zhang, L., Yue, J., Webster, R. D., & Lim, T.-T. (2015). Kinetic modeling and energy efficiency of UV/H₂O₂ treatment of iodinated trihalomethanes. *Water Research*, 75, 259-269.

<https://hdl.handle.net/10356/106198>

<https://doi.org/10.1016/j.watres.2015.02.044>

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Kinetic Modeling and Energy Efficiency of UV/H₂O₂ Treatment of Iodinated Trihalomethanes

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Abstract

Photodegradation of I-THMs including CHCl₂I and CHI₃ by the UV/H₂O₂ system was investigated in this study. CHCl₂I and CHI₃ react rapidly with hydroxyl radical ([•]OH) produced by the UV/H₂O₂ system, with second-order rate constants of 8.0 × 10⁹ and 8.9 × 10⁹ M⁻¹ s⁻¹, respectively. A fraction of CHCl₂I could be completely mineralized within 15 min and the remaining fraction was mainly converted to formic acid (HCO₂H). Cl⁻ and I⁻ were identified as the predominant end-products. No ClO₃⁻ was observed during the photodegradation process, while IO₃⁻ was detected but at less than 2% of the total liberated iodine species at the end of the reaction. The effects of pH, H₂O₂ dose, and matrix species such as humic acid (HA), HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻ on the photodegradation kinetics was evaluated. The steady-state kinetic model has been proven to successfully predict the destruction of CHCl₂I and CHI₃ by UV/H₂O₂ in different water matrices. On this basis, the kinetic model combined with electrical energy per order (EE/O) concept was applied to

evaluate the efficiency of the photodegradation process and to optimize the H_2O_2 dose for different scenarios. The optimal H_2O_2 doses in deionized (DI) water, model natural water, and surface water are estimated at 5, 12, and 16 mg L^{-1} , respectively, which correspond to the lowest total energy consumption ($\text{EE}/\text{O}_{\text{total}}$) of 0.2, 0.31, and 0.45 $\text{kWhm}^{-3}\text{order}^{-1}$.

Keywords: Iodinated disinfection by-product, indirect photolysis, matrix species, scavenging effect, steady-state kinetic model, electrical energy per order

1. Introduction

Iodinated trihalomethanes (I-THMs) can be formed as disinfection by-products via the reaction of the disinfectant such as chloramines with natural organic matter, when iodide is present in the source water (Bichsel and Von Gunten, 2000). I-THMs have been detected in the water samples from both water and wastewater treatment plants worldwide (Cancho et al., 2000; Krasner et al., 2006; Allard et al., 2012; Farré et al., 2012). For example, in an U.S. Nationwide Occurrence Study, the concentrations of I-THMs were reported at $\mu\text{g/L}$ level for total 12 drinking water treatment plants surveyed and could be as high as 15 $\mu\text{g/L}$ at one water plant that used chloramines as the primary disinfectant. The total I-THMs were 81% of the total 4 regulated THMs in one sample collected from this plant (Krasner et al., 2006). Early concerns about I-THMs were due to their pharmaceutical or medicinal odors and taste. The odor threshold concentration of CHI_3 was reported at 0.02 $\mu\text{g/L}$, which is much lower than those of CHBr_3 and CHCl_3 (100 and 300 $\mu\text{g/L}$, respectively) (Cancho et al., 2000). In recent decades, I-THMs have been found to be more cytotoxic and/or genotoxic than their chlorinated and brominated analogues (Plewa et al., 2004; Richardson et al., 2008). For example, one previous study demonstrated that CHI_3 was 60 times and 146 times more cytotoxic than CHBr_3 and CHCl_3 , respectively (Richardson et al., 2008). Thus, the formation of I-THMs has caused more concerns (Richardson et al., 2008; Pressman et al., 2010).

With the recent introduction of the standard solutions of I-THMs to the market, more research efforts have been directed toward increasing the understanding of the formation, analysis, occurrences, and toxicities of I-THMs (Krasner et al., 2006; Richardson et al., 2008; Pressman et al., 2010; Jones et al., 2011; Allard et al., 2012; Ye et al., 2014). However, to date, only a few studies have been performed to investigate the fate of I-THMs in water and wastewater treatment processes (Cancho et al., 2000; Allard et al., 2012; Farré et al., 2012). These previous studies showed that the conventional treatment processes such as sedimentation, filtration, and ozonation as well as advanced membrane technology like reverse osmosis could not remove I-THMs effectively (Cancho et al., 2000; Allard et al., 2012; Farré et al., 2012). In this context, direct photolysis of I-THMs (CHCl_2I , CHClBrI , CHClI_2 , CHBr_2I , CHBrI_2 , and CHI_3) by UV254 was investigated in our previous study (Xiao et al., 2014), as energy of UV254 photon (472 kJ/mol) is sufficiently high to photo-cleavage the carbon-halogen bonds (209, 280, and 397 kJ/mol for C-I, C-Br, and C-Cl, respectively) (Weast et al., 1986; Jones and Carpenter, 2005). I-THMs underwent a considerable photodegradation process through cleavage of the carbon-halogen bond. However, the removal efficiency of direct photolysis of I-THMs was very low at a common UV dose of 140 mJ cm^{-2} applied for disinfection. For example, the removal percentage of the comparatively photo-recalcitrant CHCl_2I and photo-labile CHI_3 was less than 5% and 24%, respectively (Xiao et al., 2014). It suggested that a higher dose than the usual dose for disinfection or alternative advanced oxidation processes (AOPs) is required to significantly remove I-THMs.

In recent decades, various AOPs that produce highly reactive and non-selective oxidative species such as $\cdot\text{OH}$ have been developed and applied to destroy recalcitrant organic pollutants in a variety of applications including drinking water treatment and groundwater remediation etc. (Sharpless and Linden, 2003; Rosenfeldt et al., 2005; Pereira et al., 2007;

Baeza and Knappe, 2011). UV/H₂O₂ is one of the most widely used AOPs for water and wastewater treatment. With addition of H₂O₂, the overall micropollutants photodegradation involve both UV direct photolysis and ·OH-assisted indirect photolysis (Sharpless and Linden, 2003; Pereira et al., 2007). However, in the UV/H₂O₂ system, matrix species in water may significantly affect the removal of target pollutants as they can act as competitive UV absorber and/or ·OH scavenger (Rosenfeldt and Linden, 2007). In this context, the steady-state kinetic models have been developed to model the impact of matrix species on the photodegradation kinetics (Glaze et al., 1995; Crittenden et al., 1999; Rosenfeldt and Linden, 2004; Yao et al., 2013).

In this study, photodegradation of I-THMs by UV/H₂O₂ was investigated for its process kinetics, degradation products and energy efficiency. CHCl₂I and CHI₃ commonly detected in drinking water were selected as the target compounds. CHCl₂I is the most recalcitrant to UV254 direct photolysis (Xiao et al., 2014), while CHI₃ is the most cytotoxic among the I-THMs (Richardson et al., 2008). The impact of some operational variables such as pH, H₂O₂ dose, and matrix species such as humic acid (HA), HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻ on the photodegradation kinetics were evaluated. The parameters including pseudo-first-order rate constants, second-order rate constants of ·OH reacting with I-THMs, UV absorbance of water matrix were determined to characterize the photodegradation process. A steady-state kinetic model was established to predict the destruction of I-THMs in different water matrices. Furthermore, in order to provide the requisite data for process scale-up, economic analysis, and energetic comparison with other treatment technologies such as ozonation and other AOPs, electrical energy per order (EE/O) was used to evaluate the efficiency of the UV/H₂O₂ process and to determine the optimal H₂O₂ dose. Finally, the end-products of I-THMs degradation by the UV/H₂O₂ process were identified.

2. Materials and Methods

2.1 Reagents and sample preparation

Reaction solution for both UV direct photolysis and UV/H₂O₂ advanced oxidation were prepared using deionized (DI) water (Millipore, USA). Dichloroiodomethane (CHCl₂I, 95+%) was purchased from Cansyn Chemical Corp (Canada). Iodoform (CHI₃, 99%) and *p*-xylene were purchased from Sigma-Aldrich (Singapore). H₂O₂ (35% w/w aqueous solution) was purchased from Alfa Aesar (Singapore).

2.2 Chemical analysis

Both CHCl₂I and CHI₃ were analysed by automatic purge-and-trap (P&T) extraction (Tekmar, Atomx) coupled with GC (Agilent, 6890A)/MS (Agilent, 5973C) at ng L⁻¹ level in water. More details about analytical method of I-THMs were described in our previous study (Xiao et al., 2014). Total organic carbon (TOC) was analyzed by a TOC analyzer (Shimadzu, TOC-V_{CSH}). UV254 absorbance of water samples were measured by a UV/vis spectrophotometer (Shimadzu, UV-2550). I⁻ and IO₃⁻ were detected by an ion chromatography (IC) coupled with ICP-MS (Agilent, G3151A). ClO₃⁻ and HCO₂⁻ were analyzed by IC coupled with thermal conductivity detector (Dionex, ICS-3000). The concentration of H₂O₂ was measured by a WTW Photolab S12. More details about the detection limits of all of the target analytes were listed in Table S1 (supporting information).

2.3 UV Photoreactor and photodegradation experiment

Photodegradation experiments were conducted in a 740 mL cylindrical glass reactor at room temperature. A 5-W LP mercury vapor lamp (Philips) with emission peak at 254 nm was placed coaxially with the reactor in a quartz sleeve. A small stir bar was placed at the bottom of the reactor to ensure completely mixed batch conditions. Using H₂O₂ as an

actinometer (Beltrán et al., 1995), the average photonic intensity per volume (I_0) and effective optical path length (b) of the photoreactor were determined as $3.19 \times 10^{-6} \text{ E L}^{-1}\text{s}^{-1}$ and 2.6 cm, respectively .

As a base-line study, UV direct photolysis of reaction solution containing individual I-THMs including CHCl_2I and CHI_3 in DI water was evaluated at different UV doses to determine the photodegradation rate constant. Aliquots were sampled at predetermined time intervals and analyzed immediately by P&T-GC/MS. The UV/ H_2O_2 advanced oxidation experiments were conducted using different water matrices with addition of H_2O_2 doses and pH adjustment before exposure to UV irradiation. The water matrices used in this study included DI water, model natural water, and surface water. The typical doses of H_2O_2 used were 2, 6, and 15 mg L^{-1} or otherwise indicated. The initial pH of the reaction solution was adjusted to 7 (3 or 11) by 0.1 mol L^{-1} H_2SO_4 and NaOH solution. The initial concentration of the individual I-THM (CHI_3 or CHCl_2I) in the UV/ H_2O_2 process was 0.5 $\mu\text{mol L}^{-1}$ or otherwise indicated. A competition kinetic approach was used to determine the second-order rate constants of I-THMs reacting with $\cdot\text{OH}$ using *p*-xylene as the reference compound. The initial concentrations of the individual I-THM (CHI_3 or CHCl_2I), *p*-xylene, and H_2O_2 in DI water were 0.5 $\mu\text{mol L}^{-1}$, 0.5 $\mu\text{mol L}^{-1}$, and 58.8 $\mu\text{mol L}^{-1}$, respectively.

3. Results and Discussion

3.1 UV direct photolysis

In order to characterize the photodegradation process, the parameters such as molar absorption coefficient (ϵ_λ), quantum yield (Φ_λ), and photodegradation rate constant of I-THMs were determined and listed in Table 1. The molar absorption coefficients (ϵ_λ) of I-THMs at UV254 were measured in the range of 167 to 1131 $\text{M}^{-1} \text{ cm}^{-1}$. This indicates that direct photolysis of I-THMs is viable due to their evident UV absorbance. Direct photolysis

of I-THMs followed first-order kinetics with rate constants in the range of 0.1 to 0.6 min⁻¹ (Table 1). The degradation rate constant of CHCl₂I was determined at 0.093 min⁻¹, which is the lowest among the 6 I-THMs. It suggests that CHCl₂I is the most recalcitrant to UV254 among the 6 I-THMs.

Based on the Beer-Lambert Law and the definition of quantum yield, the overall photodegradation rate of target compound could be described as follows (Beltrán et al., 1995; Fang et al., 2013).

$$-\frac{dC}{dt} = \Phi_{\lambda} I_o (1 - e^{-2.303\epsilon_{\lambda} bC}) \quad (1)$$

where C is the concentration of target compound in mol L⁻¹; dC/dt is the photodegradation rate of target compound in mol L⁻¹ s⁻¹; Φ_{λ} is the quantum yield at the wavelength in question in mol E⁻¹; I_o is the average photonic intensity per volume of the lamp used in E L⁻¹ s⁻¹; ϵ_{λ} is the molar absorption coefficient at the wavelength in question in M⁻¹ cm⁻¹; and b is the optical path length in cm.

When the UV absorbance of the reaction solution is low (i.e., 2.303 $\epsilon_{\lambda} bC$ < 0.02), 1 - e^{-2.303 $\epsilon_{\lambda} bC$} in Equation (1) could be simplified as 2.303 $\epsilon_{\lambda} bC$ (Equation 2) through Taylor expansion.

$$-\frac{dC}{dt} = 2.303\Phi_{\lambda} I_o \epsilon_{\lambda} bC \quad (2)$$

As the direct photolysis of I-THM follows first-order kinetics, its quantum yield can be determined according to Equation (3) (Beltrán et al., 1995; Fang et al., 2013):

$$\Phi_{\lambda} = \frac{k}{2.303I_o \epsilon_{\lambda} b} \quad (3)$$

where k is the first-order rate constant in min⁻¹. The average photonic intensity per volume and optical path length of the photoreactor were determined using H₂O₂ as an actinometer.

Subsequently, substituting the obtained k and ϵ_λ values into Equation (3), the quantum yield of I-THMs were determined from 0.38 to 0.52 (Table 1).

To assess the viability of UV254 irradiation to photodegrade I-THMs in real water treatment processes, the removal efficiency of I-THMs was determined at a dose of 140 mJ cm⁻², which is typically applied for disinfection (Baeza and Knappe, 2011). Less than 5% of comparatively photo-recalcitrant CHCl₂I could be removed at this UV dose, while the removal percentage of the photo-labile species such as CHI₃ was still less than 24%. It suggested that AOPs such as UV/H₂O₂ can be considered to provide engineering solution for significant removal of I-THMs.

3.2 UV/H₂O₂ AOP

Photodegradation of individual CHCl₂I and CHI₃ by UV/H₂O₂ was investigated in the following study. Both CHCl₂I and CHI₃ photodegradation in the UV/H₂O₂ system also followed the pseudo-first-order kinetics (Fig. 1). The degradation rate increased dramatically in the UV/H₂O₂ system due to generation of $\cdot$ OH, as compared to direct photolysis. Without UV irradiation, there was no reduction of CHCl₂I and CHI₃ concentration in the presence of 6 mg L⁻¹ H₂O₂ over 60 min in a control experiment (Fig. 1). Apparently, CHCl₂I and CHI₃ can be removed effectively by UV/H₂O₂, due to a combined effect of $\cdot$ OH-assisted indirect photolysis and direct photolysis, rather than direct oxidation by H₂O₂.

The indirect photolysis can be affected by many factors including pH, H₂O₂ dose, matrix species in water (Crittenden et al., 2012) etc. Therefore, these factors were further investigated in order to holistically evaluate the efficiency of I-THMs photodegradation under different conditions.

3.2.1 Effect of pH

The effect of pH on CHCl_2I and CHI_3 photodegradation was studied by conducting experiment at pH 3, 7 and 11. The degradation rate at pH 3 was slightly higher than that at pH 7, possibly due to a higher redox potential of $\cdot\text{OH}/\text{H}_2\text{O}$ at pH 3. For example, according to Equation (4) (derived from Nernst equation), the redox potential of $\cdot\text{OH}/\text{H}_2\text{O}$ at pH 3, 7, and 11 are 2.62, 2.39, and 2.15 V, respectively (for $E_{\cdot\text{OH}/\text{H}_2\text{O}}^\circ = 2.80 \text{ V}$).

$$E_{\cdot\text{OH}} = E_{\cdot\text{OH}/\text{H}_2\text{O}}^\circ - 0.059\text{pH} \quad (4)$$

On the other hand, the degradation rate at pH 11 decreased dramatically, as compared to that at pH 7 (Fig. 2). The major cause for this reduction should be $\cdot\text{OH}$ scavenging by hydroperoxide anion (HO_2^-). As $\text{p}K_a$ is 11.75 for $\text{H}_2\text{O}_2/\text{HO}_2^-$, an alkaline condition is favorable for the generation of HO_2^- in the UV/ H_2O_2 system. Although HO_2^- can promote the formation of $\cdot\text{OH}$, it can also act as a strong $\cdot\text{OH}$ scavenger and react with $\cdot\text{OH}$ approximately 280 times faster than H_2O_2 (Table 2, reaction 3). Furthermore, the redox potential of $\cdot\text{OH}/\text{H}_2\text{O}$ decreases under an alkaline condition. Considering that most treatment processes are operated at circumneutral condition, the reaction solution would be adjusted to pH 7 in the following experiments.

3.2.2 Effect of initial dose of H_2O_2

The degradation rate of I-THMs including CHCl_2I and CHI_3 were also affected by the concentration of H_2O_2 in the UV/ H_2O_2 system. At a low concentration of H_2O_2 , the degradation rate of CHCl_2I was limited (Fig. 3), as only a small amount of $\cdot\text{OH}$ was generated. Nevertheless, the degradation rate of CHI_3 was still relatively high even at a low concentration of H_2O_2 due to its effective direct photolysis. With the increasing of H_2O_2 dose, the amount of $\cdot\text{OH}$ increased correspondingly, which led to enhanced degradation rate of CHCl_2I and CHI_3 . However, the degradation rate decreased slightly in the presence of excess

of H₂O₂ which could act as a ·OH scavenger and produce the less reactive HO₂· radical (Table 2, reaction 2) . Additionally, H₂O₂ at a high concentration can act as a competitive UV absorber (screening effect) which reduces the direct photolysis of target pollutants (Wu et al., 2007).

3.2.3 Effect of matrix species

Further investigation was conducted to evaluate the impact of matrix species on the photodegradation rates. HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻, and HA were selected as matrix species in this study as they are commonly found in natural water systems as well as wastewater.

As pK_{a1} = 6.3 and pK_{a2} = 10.3 for H₂CO₃ / HCO₃⁻ / CO₃²⁻ system (Snoeyink and Jenkins, 1980), the predominant species at pH 7 is HCO₃⁻. ·OH can react with HCO₃⁻ to produce less reactive species, CO₃⁻ (Table 2, reaction 6). Thus, the presence of HCO₃⁻ had a negative effect on the photodegradation rates of CHCl₂I due to its strong scavenging effect (Fig. 4a).

The redox potentials of SO₄⁻ / SO₄²⁻ and NO₃[·] / NO₃⁻ are almost similar to that of ·OH/H₂O at pH 7 (Table 3). Thus, both SO₄²⁻ and NO₃⁻ react slowly with ·OH and thus their scavenging effect can be neglected. In the presence of SO₄²⁻ from 1 to 4 mmol L⁻¹, the degradation rates of CHCl₂I remained constant (Fig.4a). However, in the presence of NO₃⁻, a slight increment of the degradation rate was observed. One possible reason for this improvement is that additional ·OH can be produced at a low quantum yield via direct photolysis of NO₃⁻ (Equation 5) (Keen et al., 2012).

The redox potential of $\text{Cl}^\cdot/\text{Cl}^-$ is also similar to that of $\cdot\text{OH}/\text{H}_2\text{O}$ at pH 7 (Table 3). It suggests that the scavenging effect of Cl^- is limited. However, some previous studies reported that Cl^- could react with $\cdot\text{OH}$ to produce $\text{ClHO}^\cdot$, which could protonate to produce $\text{HClHO}^\cdot$ under the acidic condition (Liao et al., 2001; Deng et al., 2013; Yang et al., 2014). Subsequently, $\text{HClHO}^\cdot$ would be further converted to less reactive chlorine species such as $\text{Cl}^\cdot$. In contrast, there was a backward reaction ($\text{ClHO}^\cdot \rightarrow \cdot\text{OH} + \text{Cl}^-$) at $\text{pH} > 7.2$ (Liao et al., 2001; Deng et al., 2013; Yang et al., 2014). It indicates that the scavenging effectiveness of Cl^- is offset by the release of $\cdot\text{OH}$ from the transient intermediate ($\text{ClHO}^\cdot$) under the basic condition (Deng et al., 2013). The above phenomenon explains the observation that the photodegradation rates of CHCl_2I at pH 7 was not affected by Cl^- concentration. To check the reactivity of $\text{Cl}^\cdot$ with I-THMs, photodegradation of CHCl_2I by UV/ H_2O_2 in the presence of 4 mmol L^{-1} Cl^- at pH 3 was conducted. According to the above explanation, $\text{Cl}^\cdot$ could be generated under an acidic condition. The degradation rate of CHCl_2I decreased obviously in the presence of 4 mmol L^{-1} Cl^- at pH 3, as compared to that obtained without Cl^- at pH 3 (Fig.4b). It suggests that $\text{Cl}^\cdot$ reacts slowly with CHCl_2I , as compared to $\cdot\text{OH}$. Based on the above results, both H_2SO_4 and NaOH solutions (0.1 mol L^{-1}) were selected to adjust the pH of reaction solution in this study.

HA had a negative effect on the photodegradation rates. On the one hand, the filtering of UV light by HA reduced the fraction of UV light absorbed by CHCl_2I and H_2O_2 , which led to reduced rate of direct photolysis. On the other hand, HA could act as a strong scavenger of $\cdot\text{OH}$ (Crittenden et al., 1999). These two effects resulted in a significant inhibition of the photodegradation of CHCl_2I in the presence of HA (Fig. 4a).

3.2.4 Mathematical modeling of UV/ H_2O_2 process

The parameters such as quantum yield, molar absorption coefficient, second-order rate constant, UV absorbance of the reaction solution, average photonic intensity per volume (I_0) and optical path length (b) of the photoreactor etc. were incorporated into a mathematical model to predict the impact of the matrix species on CHCl_2I and CHI_3 photodegradation in different types of water.

In the UV/ H_2O_2 system, the overall degradation involves both direct photolysis and $\cdot\text{OH}$ -assisted indirect photolysis (Rosenfeldt and Linden, 2004; Pereira et al., 2007).

$$-\frac{dC}{dt} = k_d + k_i \quad (6)$$

where k_d is the pseudo-first-order rate constant of direct photolysis in s^{-1} ; k_i is the pseudo-first-order rate constant of $\cdot\text{OH}$ -assisted indirect photolysis in s^{-1} .

With the obtained Φ_λ , ϵ_λ of target compound as well as I_0 and b of the photoreactor, direct photolysis rate of target compound in a water matrix comprising various UV absorbers can be described by Equations (7) and (8) (Crittenden et al., 2012).

$$-\frac{dC}{dt} = \Phi_\lambda I_0 f(1 - e^{-2.303\epsilon_\lambda bC}) = \Phi_\lambda I_0 \frac{\epsilon_\lambda b(1 - e^{-2.303A})}{A} C \quad (7)$$

$$k_d = \Phi_\lambda I_0 \frac{\epsilon_\lambda b(1 - e^{-2.303A})}{A} \quad (8)$$

where f is the fraction of light absorbed by target compound; and A is the total UV absorbance of the reaction solution ($A = \sum_{i=1}^n \epsilon_{\lambda,i} bC_i$). Equation (8) can be simplified to Equation (3) when UV absorbance of the reaction solution is low (i.e., $2.303\epsilon_\lambda bC < 0.02$) (Beltrán et al., 1995).

The indirect photolysis rate (k_i) can be expressed as a function of the second-order rate constant of target compound reacting with $\cdot\text{OH}$ and the steady-state concentration of $\cdot\text{OH}$ (Rosenfeldt and Linden, 2004; Pereira et al., 2007).

$$k_i = k_{\cdot\text{OH}, \text{I-THM}} C_{\cdot\text{OH}} \quad (9)$$

The experiments of competition kinetics were conducted to determine the second-order rate constant of $\cdot\text{OH}$ reacting with CHCl_2I and CHI_3 . *p*-xylene ($k_{\cdot\text{OH}} = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7) was chosen as the reference compound because it essentially does not undergo direct photolysis (Buxton et al., 1988), and it is easy to be analyzed together with target I-THMs by P&T-GC/MS. As described above, CHCl_2I and CHI_3 underwent considerable direct photolysis. Hence, such effect should be taken into consideration in determining the second-order rate constant in the UV/ H_2O_2 system. The degradation rates of I-THMs and *p*-xylene could be expressed by Equations (10) and (11), respectively.

$$k_{\text{obs, I-THM}} = k_{\cdot\text{OH, I-THM}} C_{\cdot\text{OH}} + k_d \quad (10)$$

$$k_{\text{obs, } p\text{-xylene}} = k_{\cdot\text{OH, } p\text{-xylene}} C_{\cdot\text{OH}} \quad (11)$$

where $k_{\text{obs, I-THM}}$ and $k_{\text{obs, } p\text{-xylene}}$ are the observed pseudo-first-order rate constants of I-THM and *p*-xylene in s^{-1} , respectively; $C_{\cdot\text{OH}}$ is the steady-state concentration of $\cdot\text{OH}$ in mol L^{-1} ; and k_d is the direct photolysis rate constant of I-THMs in s^{-1} . Substituting Equation (11) into (10), $k_{\cdot\text{OH, I-THM}}$ can be calculated as follows:

$$k_{\cdot\text{OH, I-THM}} = \frac{k_{\text{obs, I-THM}} - k_d}{k_{\text{obs, } p\text{-xylene}}} k_{\cdot\text{OH, } p\text{-xylene}} \quad (12)$$

The derived second-order rate constants of $\cdot\text{OH}$ reacting CHCl_2I and CHI_3 are 8.0×10^9 and $8.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Table 2). Considering that the typical second-order rate constants of organic compounds with $\cdot\text{OH}$ vary from 10^6 to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Schwarzenbach et al., 1993), I-THMs appear to be the fast-reacting compounds with $\cdot\text{OH}$.

The steady-state concentration of $\cdot\text{OH}$ can be estimated by a simplified pseudo-steady-state method whereby the concentration of $\cdot\text{OH}$ is assumed constant (at the respective initial concentration) over the reaction period. It can be calculated as the ratio of the formation of $\cdot\text{OH}$ to the consumption of $\cdot\text{OH}$ according to Equation (13) (Rosenfeldt and Linden, 2004).

$$C_{\cdot\text{OH}} = \frac{\Phi_{\cdot\text{OH}} I_0 f_{\text{H}_2\text{O}_2} (1 - e^{-2.303A})}{\sum k_{\cdot\text{OH},S} C_S} \quad (13)$$

where $\Phi_{\cdot\text{OH}}$ is the quantum yield of the production of $\cdot\text{OH}$ by photolysis of H_2O_2 (assumed to be 1.0 mol E^{-1}) (Rosenfeldt and Linden, 2007); $k_{\cdot\text{OH},S}$ is the second-order rate constant of scavenger reacting with $\cdot\text{OH}$ in $\text{M}^{-1} \text{s}^{-1}$ (Table 2); C_S is the concentration of scavenger in mol L^{-1} and all of the components are assumed at their constant concentrations over the reaction period; other terms are as defined previously.

The predicted kinetics is compared with the experimental results for different water types in the present study. Firstly, the comparison was conducted using model natural water (MNW). As the exact composition in MNW is known, this allows accurate prediction of the steady-state concentration of $\cdot\text{OH}$ as a function of water quality. In this study, HA (DOC, 1 mg L^{-1}) and HCO_3^- (2 mmol L^{-1}) were spiked into DI water to prepare MNW as these two species had a significant effect on the photodegradation kinetics of CHCl_2I in the UV/ H_2O_2 system. The calculated total scavenging factor ($\sum k_{\cdot\text{OH},S} C_S$) and the fraction of UV light absorbed by H_2O_2 are listed in Table 4. With the obtained parameters such as Φ , ε , I_0 , b , a , $f_{\text{H}_2\text{O}_2}$, and $\sum k_{\cdot\text{OH},S} C_S$, direct photolysis rate constant (k_d) and $\cdot\text{OH}$ -assisted indirect photolysis rate constant (k_i) could be determined according to Equations (8) and (9), respectively. As shown in Table 4, for CHCl_2I , indirect photolysis played a dominant role in its degradation and its rate increased significantly with increasing H_2O_2 concentration. For CHI_3 , both direct and indirect photolysis were important in its degradation at a low concentration of H_2O_2 (i.e., 2 mg L^{-1}), while its indirect photolysis becomes increasingly dominant with increasing H_2O_2 concentration. Because of the relatively high UV absorption capability of I-THMs and weak C-I bond (especially for CHI_3), it is essential to delineate the roles of indirect photolysis and direct photolysis in the UV-AOP process. Through the kinetic model, the respective contributions from the direct photolysis and indirect photolysis in degradation of I-THMs

under different reaction conditions were determined. Therefore, the model study could help to gain insights into the UV-AOP process and delineate the respective reaction kinetics for CHCl_2I & CHI_3 .

In general, there is a good agreement between the predicted (k_p) and experimentally measured rate constants (k_m) for both CHCl_2I and CHI_3 (Fig. 5a). These results again indicate that NOM, alkalinity, and H_2O_2 are the major scavengers of $\cdot\text{OH}$.

NOM could be degraded as the UV254 doses increases, the composition of DOC will change correspondingly. However, the steady-state concentration of $\cdot\text{OH}$ is estimated based on the initial concentration of all components and is assumed to remain virtually constant over the reaction period. In fact, the concentration of $\cdot\text{OH}$ increases as the contribution of the dominant scavenger such as NOM is reduced. This is one possible reason why the k_p values are slightly smaller than the k_m values. Additionally, measurement uncertainty such as the second-order rate constants for I-THMs and pseudo-first-order rate constants could also contribute to the difference between the predicted and the experimentally measured values. Even with these uncertainties, the differences between the values of k_p and k_m are less than 20%.

To further examine how accurate this established kinetic model is in predicting the destruction of I-THMs in a natural water system, photodegradation of CHCl_2I and CHI_3 by UV/ H_2O_2 in surface water (SW) that was used as the source water in a waterworks in Singapore was conducted. Samples were filtered through 0.45 μm filter to remove particles, and water quality parameters of the filtrate such as pH, TOC, alkalinity, and UV254 absorbance are shown in Table 4. The degradation rates of both CHCl_2I and CHI_3 in SW decreased significantly due to a stronger combined negative effect of the aqueous matrix species as compared to that of MNW. A good correlation between k_p and k_m is also obtained for the case of reaction in SW (Fig. 5b). Generally, the kinetic model based on the pseudo-

steady-state concentration of $\cdot\text{OH}$ is applicable to predict the destruction of I-THMs in different water matrices by the UV/H₂O₂ system.

3.2.5 Photodegradation end-product identification

Both CHCl₂I and TOC decreased concomitantly as the UV dose increased (Fig. 6). CHCl₂I was completely degraded by UV/H₂O₂ within 15 min with a corresponding TOC removal of 53%. Meanwhile, formic acid (HCO₂H) was formed concomitantly with TOC reduction and accounted for 37% of initial TOC at 15-min reaction. There were still some unidentified organic species in the reaction solution, which accounted for ~10 % of initial TOC. Cl⁻ and I⁻ were also identified as the end-products and their amounts continued to increase with the reaction time. There is a good mass balance (i.e., 95% recovery) between the produced halides and the introduced halogens in CHCl₂I. No ClO₃⁻ was observed over the reaction period, while trace level of IO₃⁻ was detected and its amount was less than 2% of the total liberated iodine species at the end of the reaction. These results suggested that there is no concern about the generation of by-products such as ClO₃⁻ and IO₃⁻ when I-THMs are treated by UV/H₂O₂ as compared to ozonation. Additionally, both formaldehyde and oxalic acid were not detectable during the photodegradation process.

3.2.6 An economic analysis using EE/O concept

The kinetic model coupled with Electrical Energy per Order (EE/O) concept is applied to evaluate the efficiency of the UV/H₂O₂ process and to determine the optimal H₂O₂ dose at a given condition. The EE/O (kWhm⁻³order⁻¹) is defined as the electrical energy (kWh) required to degrade the contaminants by one order magnitude in m³ of contaminated water (Bolton and Cater, 1994). The figures-of-merit provide the requisite reference for scale-up, economic analysis, and energy comparison with other treatment technologies such as

ozonation etc. The electrical energy of UV lamp (EE/O_{UV}) and H_2O_2 consumption (H_2O_2/O) can be calculated according to Equations (14) and (15), respectively. As the energy consumption for production of H_2O_2 is $10.81 \times 10^{-6} \text{ kWhm}^{-3}$ (Rosenfeldt et al., 2006), H_2O_2/O can be expressed in terms of equivalent electric energy consumption ($EE/O_{H_2O_2}$), which has the same energy unit ($\text{kWhm}^{-3}\text{order}^{-1}$) as EE/O_{UV} (Equation 16). Thus, the total energy consumption (EE/O_{total}) for the UV/ H_2O_2 process can be calculated using Equation (17).

$$EE / O_{UV} = \frac{P \cdot t \cdot 1000}{V \cdot \log(\frac{C_i}{C_f})} = \frac{38.4 \cdot P}{V \cdot k} (\text{kWhm}^{-3}\text{order}^{-1}) \quad (14)$$

$$H_2O_2 / O = \frac{C_{H_2O_2}}{\log(\frac{C_i}{C_f})} (\text{mgL}^{-1}\text{order}^{-1}) \quad (15)$$

$$EE / O_{H_2O_2} = 10.81 \times 10^{-3} \times H_2O_2 / O (\text{kWhm}^{-3}\text{order}^{-1})$$

(16)

$$EE / O_{total} = EE / O_{UV} + EE / O_{H_2O_2} (\text{kWhm}^{-3}\text{order}^{-1}) \quad (17)$$

where P is lamp power output in kW; t is the irradiation time in h; V is the reactor volume in L; k is the predicted first-order rate constant (k_p) in min^{-1} ; C_i is the initial concentration of target compound in mg L^{-1} ; C_f is the final concentration of target compound in mg L^{-1} ; $C_{H_2O_2}$ is the concentration of H_2O_2 in the reaction solution in mg L^{-1} .

In this study, EE/O_{UV} , $EE/O_{H_2O_2}$, and EE/O_{total} are evaluated based on 90% of target $CHCl_2I$ removal. As shown in the Fig.7a, the required UV lamp energy (EE/O_{UV}) decreased by increasing H_2O_2 dose. At a low dose of H_2O_2 (i.e., less than 10 mg L^{-1}), EE/O_{UV} is the major contributor to EE/O_{total} , as indicated by $(EE/O_{H_2O_2})/(EE/O_{UV}) < 1$ (Fig.7b). In contrast, at a high dose of H_2O_2 , the required UV energy is very limited and $EE/O_{H_2O_2}$ is the main component of EE/O_{total} . At a specific percentage of $CHCl_2I$ removal, the lowest EE/O_{total} in different water matrices follows the order: $DI < MNW < SW$ (Fig.7b), and correspond to 0.2,

0.31, and 0.45 kWhm⁻³order⁻¹, respectively. They are 8-15 times lower than the corresponding EE/O_{total} by UV direct photolysis (Table 5). The optimal H₂O₂ doses in DI, MNW, and SW for their lowest EE/O_{total} are estimated at 5, 12, and 16 mg L⁻¹, respectively, which correspond to the H₂O₂ : CHCl₂I molar ratio of 294, 705, and 941. The ratios of EE/O_{H₂O₂} versus EE/O_{UV} in DI, MNW, and SW at their respective optimal H₂O₂ doses are 0.38, 0.70, and 0.55, respectively. These results further demonstrate the effect of different water matrices on the process efficiency. It is worth to mention that energy consumption is mainly due to consumption of H₂O₂ and there is no significant difference in energy consumption for different water matrices at a high dose of H₂O₂ (Fig.7b). For example, at 120 mg L⁻¹ of H₂O₂, the EE/O_{H₂O₂} : EE/O_{UV} ratios for DI, MNW, and SW are 19, 17, and 15, respectively, while EE/O_{total} in these 3 water matrices are almost the same which is ~1.3 kWhm⁻³order⁻¹.

4. Conclusion

Photodegradation of I-THMs including CHCl₂I and CHI₃ by UV/H₂O₂ was investigated in this study. Both CHCl₂I and CHI₃ underwent a fast photodegradation process in the UV/H₂O₂ system, due to synergistic effect of ·OH-assisted indirect photolysis and direct photolysis. A fraction of CHCl₂I can be completely mineralized within 15 min and the remaining fraction was mainly converted to HCO₂H. Cl⁻ and I⁻ were identified as the predominant end-products. Some common matrix species including HA, HCO₃⁻, NO₃⁻, SO₄²⁻ and Cl⁻ were added to study the interferences, which are negative in the case of HA and HCO₃⁻, and positive for NO₃⁻. Both SO₄²⁻ and Cl⁻ had no significant effect on the photodegradation rate under the reaction conditions. A steady-state kinetic model was established to successfully predict the destruction of I-THMs by the UV/H₂O₂ process in different water matrices. The optimal H₂O₂ doses in DI, MNW, and SW are estimated at 5, 12,

and 16 mg L⁻¹, respectively, which correspond to the lowest EE/O_{total} of 0.2, 0.31, and 0.45 kWhm⁻³order⁻¹. The EE/O_{H₂O₂} : EE/O_{UV} ratios for DI, MNW, and SW at their respective optimal H₂O₂ doses are 0.38, 0.70, and 0.55, respectively. These results indicate the high efficiency of the UV/H₂O₂ system for degrading I-THMs.

Appendix A. Supplementary material

More details about the detection limits of all of the target analytes, determination of the average photonic intensity per volume (I₀) and optical path length (b) of the photoreactor used in the present study.

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Table 1. Molar absorption coefficient (ϵ), first-order rate constant (k), quantum yield (Φ), and removal efficiency describing direct photolysis of I-THMs in DI water.

Species	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	k (min^{-1})	Φ^1	%removal (140 mJ cm^{-2})
CHCl_2I	167	0.093(± 0.009)	0.47(± 0.04)	4.65(± 0.45)
CHClBrI	423	0.26 (± 0.02)	0.52(± 0.04)	12.65(± 0.97)
CHClI_2	604	0.36 (± 0.02)	0.50(± 0.03)	16.89(± 1.08)
CHBr_2I	1131	0.58 (± 0.07)	0.43(± 0.05)	25.80(± 2.66)
CHBrI_2	1068	0.52 (± 0.04)	0.41(± 0.04)	23.57(± 1.81)
CHI_3	1118	0.51(± 0.04)	0.38(± 0.03)	23.18(± 1.66)

1. H_2O_2 used as an actinometer.

Table 2. Relevant chemical reactions in the UV/ H_2O_2 system.

Item	Reactions	Rate constant ($\text{M}^{-1} \text{s}^{-1}$)	Reference
1	$\cdot\text{OH} + \text{NOM} \rightarrow \text{product}$	$2.5 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$ as organic carbon	(Larson and Zepp, 1988)
2	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2\cdot$	2.7×10^7	(Buxton et al., 1988)
3	$\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{HO}^- + \text{HO}_2^-$	7.5×10^9	(Buxton et al., 1988)
4	$\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	6.6×10^9	(Sehested et al., 1968)
5	$\cdot\text{OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{\cdot-} + \text{HO}^-$	3.9×10^8	(Buxton et al., 1988)
6	$\cdot\text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O}$	8.5×10^6	(Buxton et al., 1988)
7	$\cdot\text{OH} + \text{CHCl}_2\text{I} \rightarrow \text{product}$	8.0×10^9	This study
8	$\cdot\text{OH} + \text{CHI}_3 \rightarrow \text{product}$	8.9×10^9	This study

Table 3. Relevant redox potentials of some radicals.

Couple	E/V	Remark	Reference
$\cdot\text{OH} / \text{H}_2\text{O}$	2.62	pH = 3	Nernst equation
	2.39	pH = 7	
	2.15	pH = 11	
$\text{CO}_3^{\cdot-} / \text{CO}_3^{2-}$	1.50	–	(Oppenlander, 2003)
$\text{CO}_3^{\cdot-} / \text{HCO}_3^-$	1.78	pH = 7	(Medinas et al., 2007)
$\text{SO}_4^{\cdot-} / \text{SO}_4^{2-}$	2.43	–	(Oppenlander, 2003)
$\text{Cl}^{\cdot} / \text{Cl}^-$	2.41	–	(Huie et al., 1991)
$\text{NO}_3^{\cdot} / \text{NO}_3^-$	2.30-2.60	–	(Oppenlander, 2003)

Table 4. The parameters used for establishing kinetic model as well as the predicted (k_p) and experimentally measured rate constants (k_m).

Water matrix	Species	H ₂ O ₂ (mg L ⁻¹)	pH	TOC (mg L ⁻¹)	Total alkalinity (as CaCO ₃ , mg L ⁻¹)	a (254 nm) ² (cm ⁻¹)	f _{H₂O₂} x 100	$\Sigma k_{OH,S}C_S$ x10 ⁻⁴ (s ⁻¹)	$k_p = k_i + k_d$ (min ⁻¹)	k_m (min ⁻¹)
MNW ¹	CHCl ₂ I	2	7	1	200	0.0556	3.59	4.70	0.42=0.34+0.076	0.46
MNW	CHCl ₂ I	6	7	1	200	0.0610	8.19	5.07	0.88=0.80+0.075	0.92
MNW	CHCl ₂ I	15	7	1	200	0.0697	19.3	5.79	1.63=1.56+0.072	1.84
MNW	CHI ₃	2	7	1	200	0.0543	3.68	4.80	0.77=0.36+0.41	0.82
MNW	CHI ₃	6	7	1	200	0.0588	8.50	5.12	1.25=0.84+0.41	1.42
MNW	CHI ₃	15	7	1	200	0.0661	20.4	5.84	2.34=1.94+0.40	2.28
SW ³	CHCl ₂ I	2	7	3.9	8.70	0.0924	2.16	10.3	0.20=0.13+0.069	0.24
SW	CHCl ₂ I	6	7	3.9	8.70	0.0955	5.24	10.6	0.40=0.33+0.068	0.50
SW	CHCl ₂ I	15	7	3.9	8.70	0.1013	13.3	11.3	0.87=0.80+0.067	0.98
SW	CHI ₃	2	7	3.9	8.70	0.0964	2.10	10.4	0.52=0.15+0.37	0.65
SW	CHI ₃	6	7	3.9	8.70	0.0989	5.10	10.7	0.73=0.36+0.37	0.85
SW	CHI ₃	15	7	3.9	8.70	0.1047	12.9	11.4	1.25=0.89+0.36	1.35

1. MNW: model natural water;
2. a = absorptivity ($\epsilon_{\lambda}C$, cm⁻¹);
3. SW: surface water (Cl⁻: 24.5 mg L⁻¹, SO₄²⁻: 6.78 mg L⁻¹, NO₃⁻ as N: 0.68 mg L⁻¹).

Table 5. Comparison of energy efficiency of UV and UV/H₂O₂ removal of CHCl₂I in different water matrices.

Water matrix	UV Photolysis	UV/H ₂ O ₂			
	EE/O _{total} (kWhm ⁻³ order ⁻¹)	Lowest EE/O _{total} (kWhm ⁻³ order ⁻¹)	Optimal H ₂ O ₂ dose (mg L ⁻¹)	Molar ratio (H ₂ O ₂ : CHCl ₂ I) ¹	(EE/O _{H₂O₂})/ (EE/O _{UV})
DI	2.95	0.20	5	294	0.38
MNW	3.56	0.31	12	705	0.70
SW	3.92	0.45	16	941	0.55

1. CHCl₂I: 0.5 μmol L⁻¹.

Figure 1. Linear plot for degradation of CHCl_2I (a) and CHI_3 (b) under different treatment conditions (I-THMs: 0.5 $\mu\text{mol L}^{-1}$).

Figure 2. Effect of pH on the photodegradation kinetics of CHCl₂I and CHI₃ in DI water (I-THMs: 0.5 $\mu\text{mol L}^{-1}$; H₂O₂: 2.0 mg L⁻¹). Error bars denote standard deviations obtained from at least duplicate datasets.

Figure 3. Effect of initial dose of H₂O₂ on the photodegradation kinetics of CHCl₂I and CHI₃ in DI water (I-THMs: 0.5 $\mu\text{mol L}^{-1}$; pH 7).

Figure 4(a). Effect of matrix species including HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , and HA on the photodegradation kinetics in DI water at pH 7; **4(b).** Effect of Cl^- on the photodegradation kinetics in DI water at pH 3 and 7 (CHCl_2I : $0.5 \mu\text{mol L}^{-1}$; H_2O_2 : 2 mg L^{-1}).

Figure 5. Comparison of experimentally measured (k_m) with the predicted pseudo-first-order rate constants (k_p) for $CHCl_2I$ and CHI_3 in model natural water (a) and surface water (b) (I-THMs: 0.5 $\mu\text{mol L}^{-1}$; pH 7).

Figure 6. Time course of CHCl_2I reduction, TOC reduction, halide formation, and formic acid (HCO_2H) formation during photodegradation of CHCl_2I by the $\text{UV}/\text{H}_2\text{O}_2$ treatment. (CHCl_2I : 28 mg L^{-1} ; H_2O_2 : 45 mg L^{-1})

Figure 7(a). Plot of EE/O_{UV} , $EE/O_{H_2O_2}$, EE/O_{total} , and $(EE/O_{H_2O_2})/(EE/O_{UV})$ versus H_2O_2 dose in DI water; **7(b).** Plot of EE/O_{total} and $(EE/O_{H_2O_2})/(EE/O_{UV})$ versus H_2O_2 dose in DI water, model natural water (MNW), and surface water (SW) ($CHCl_2I$: 0.5 μ mol L⁻¹; pH 7).