Photolysis of aqueous free chlorine species (HOCl and OCl⁻) with 254 nm ultraviolet light[1]

Yangang Feng, Daniel W. Smith, and James R. Bolton

Abstract: The quantum yields of the UV photolysis of free chlorine (OCl⁻ and HOCl) at 254 nm were measured in a series of batch reactor experiments from pH 5 to 10 and at various concentrations. When the concentration of free chlorine is low (3.5 mg Cl/L) to moderate (70 mg Cl/L), the quantum yields of HOCl and OCl⁻ are 1.0 ± 0.1 and 0.9 ± 0.1, respectively. When the concentration increases to higher levels (>70 mg Cl/L), the quantum yield of HOCl photolysis increases significantly, whereas the quantum yield of OCl⁻ photolysis is essentially independent of concentration. In addition, based on the experimental results obtained in this research, a mathematic model was developed that can be used for the prediction of the quantum yield for the UV photolysis of free chlorine at 254 nm. The quantum yields predicted by this model agree very well with the measured data. Also, the dependence of free chlorine decomposition on the fluence (UV dose) and the effect of water quality on the quantum yield of free chlorine species were investigated in this research.

Key words: ultraviolet irradiation, free chlorine, fluence, UV dose, quantum yield, disinfection.

Résumé : Les rendements quantiques de la photolyse UV à 254 nm du chlore libre (OCl⁻ et HOCl) ont été mesurés dans une série d'expériences en réacteur discontinu à des pH de 5 à 10 et à diverses concentrations. Lorsque la concentration en chlore libre est de faible (3,5 mg Cl/L) à modérée (70 mg Cl/L), les rendements quantiques du HOCl et du OCl⁻ sont de 1,0 ± 0,1 et 0,9 ± 0,1 respectivement. Lorsque la concentration augmente à des niveaux plus élevés (>70 mg Cl/L), le rendement quantique de la photolyse du HOCl augmentait de manière significative, alors que le rendement quantique de la photolyse du OCl⁻ est essentiellement indépendante de la concentration. De plus, en se basant sur les résultats expérimentaux obtenus au cours de cette recherche, un modèle mathématique a été mis au point qui peut être utilisé pour prédire le rendement quantique de la photolyse UV du chlore libre à 254 nm. Les rendements quantiques prédits par ce modèle concordent très bien avec les données mesurées. La dépendance de la décomposition du chlore libre sur la fluence (dose UV) et l'effet de la qualité de l'eau sur le rendement quantique des espèces de chlore libre ont également été examinés au cours de cette recherche.

Mots-clés : rayonnement ultraviolet, chlore libre, fluence, dose UV, rendement quantique, désinfection.

[Traduit par la Rédaction]

Introduction

In many ultraviolet (UV) disinfection installations, free chlorine is present in the water as it passes through the UV reactors. A good example is the E.L. Smith Water Treatment Plant of EPCOR Water Services in Edmonton, Canada, which has one of the largest UV disinfection systems in the world. Here the UV equipment was installed after the chlorine microorganism reduction (MOR) unit (EPCOR 2004). A major advantage of this combined process is that the UV light can inactivate proto-zoa (e.g., *Cryptosporidium* spp., and *Giardia* spp.), which are difficult to treat by chlorination (Bolton et al. 1998; Bukhari et al. 1999; Clancy et al. 2000). From another point of view, the interactions between free chlorine and UV light could have some negative effects on the disinfection ability of this kind of process. Örmeci et al. (2005) found that the UV fluence is influenced slightly by free or combined chlorine, which can increase the UV absorbance of the drinking water. However, the free chlorine itself can be affected significantly by UV light. For example, in the daily operation of outdoor swimming pools, one usually finds that the free chlorine level shows a marked decrease on sunny days, arising from photolysis by the UV portion of sunlight. In an experiment in which UV disinfection was employed in water chlorinated upstream of the UV disinfection unit, Zheng et al. (1999) reported that the higher the fluence (UV dose) applied the greater the chlorine dose that was required to keep a fixed chlorine concentration in the effluent water. At the highest fluence (UV dose) of 4825 mJ/cm² employed, the chlorine demand was about 5 times that obtained without UV applied. In addition, according to the authors' private communication with staff of EPCOR in Edmonton, Canada, the concentration of free chlorine residual shows a distinct decrease as the water passes through the UV reactor in the E.L. Smith Water Treatment Plant cited above.

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Written discussion of this article is welcomed and will be received by the Editor until 30 September 2007.

[1] This article is one of a selection of papers published in this special issue on application of ultraviolet light to air, water, and wastewater treatment.

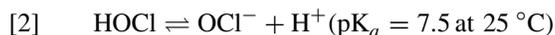[2] Corresponding author (e-mail: jb3@ualberta.ca).

Fig. 1. Dependence of the ratio $HOCl/OCl^-$ on pH ($pK_a = 7.5$).
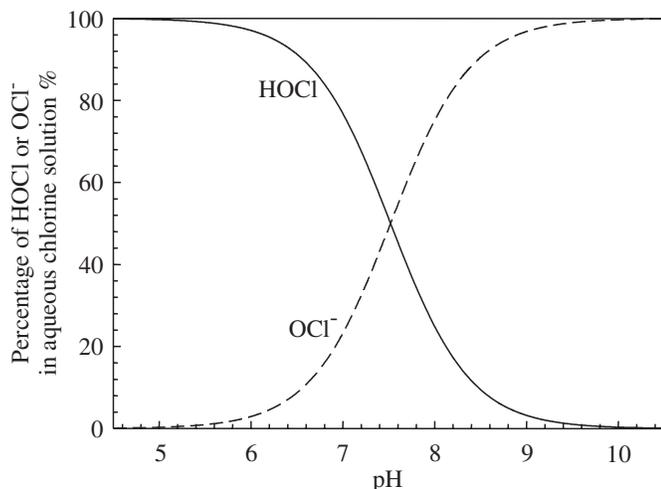
When Cl_2 is added to water, it reacts according to

[1] $Cl_2 + H_2O \rightarrow HOCl + HCl$

HOCl is a weak acid such that the relative concentrations of the acid (HOCl) and its conjugate base (OCl^-) are strongly dependent on pH and follow the equilibrium

[2] $HOCl \rightleftharpoons OCl^- + H^+$ ($pK_a = 7.5$ at 25 °C)

The lower the pH, the higher the percentage of HOCl; at higher pH, OCl^- will be the predominant species. According to the equilibrium of reaction 2,[3] more than 99% of the free chlorine is HOCl at pH 5 and similarly more than 99% is OCl^- at pH 10. Figure 1 shows this relation graphically.

There have been some earlier studies concerning the reactions occurring in the UV photolysis of aqueous free chlorine. Primarily hydroxyl radicals (·OH) and chlorine radicals (·Cl) are generated in the photodecomposition of free chlorine in water (Nowell and Hoigné 1992a). Because of the presence of some organic matter in drinking water, two chain-reactions have been proposed for the decomposition of HOCl by Oliver and Carey (1977):

·OH radical chain

[3a] $\cdot OH + RH \rightarrow \cdot R + H_2O$

[3b] $\cdot R + HOCl \rightarrow RCl + \cdot OH$

·Cl radical chain

[4a] $\cdot Cl + RH \rightarrow \cdot R + HCl$

[4b] $\cdot R + HOCl \rightarrow ROH + \cdot Cl$

Buxton and Subhani (1972a) carried out a systematic investigation of the photodecomposition mechanism of hypochlorite ions (OCl^-) in aqueous solution. They found that the quantum yield for OCl^- decomposition is about 0.85 at 254 nm.

[3] Morris (1966), Snoeyink and Jenkins (1980), and Sawyer et al. (1994).

Nowell and Hoigné (1992a) studied the free chlorine exposed to sunlight or UV light at 254 nm and found that the production ratio of ·OH generated by OCl^- (pH > 8) is only about 0.1 and HOCl (pH 5) yielded 0.7 ·OH in sunlight and 0.9 ·OH with 254 nm UV light. However, the molar absorption coefficients of HOCl and OCl^- at 254 nm reported by Nowell and Hoigné (1992b) are much higher than those obtained by other researchers. Table 1 summarizes published values of the molar absorption coefficients at about 25 °C.

Since in practice the pH is such that both HOCl and OCl^- are present in most water or wastewater treatment, the overall quantum yield of free chlorine decomposed is more important than the individual quantum yields of HOCl and OCl^- reported as a unique species. In addition, the concentration of free chlorine may have an influence on the quantum yield because of possible chain reactions. Therefore, the main objective of this research was to investigate the effects of pH and concentration of free chlorine in solution on the overall photolysis quantum yield at 254 nm. Based on the experimental results, a model was derived for predicting the overall quantum yield of free chlorine, which can be applied to practical operations.

Experimental

Materials and methods

All chemicals used in this research were analytical reagent grade and deionized water (chlorine demand free) was used for all analytic determinations. Fresh sodium hypochlorite solution (5.65 ~ 6%, Fisher Scientific Co., Canada) was diluted to produce the samples of free chlorine in all experiments. Other compounds used in this research were stock reagent grade chemicals. A quasi collimated beam UV apparatus (Model PSI-1-120, Calgon Carbon Corporation, USA) and a 10 W low-pressure UV lamp (Ster-L-Ray Germicidal Lamp, model G12T6L 15114, Atlantic Ultraviolet Corporation, USA) were used to generate a nearly parallel beam of UV light at 254 nm. The UV irradiance at the center of the UV beam on the surface of the free chlorine sample was measured by a radiometer (Model IL 1400A with an SED240 Detector, International Light Inc.), which was calibrated at 254 nm. An Ultraspec 2000 UV-Visible spectrophotometer (Pharmacia Biotech, Fisher Scientific Co., Canada) and either a 10.0 or a 50.0 mm path length quartz cell (Fisher Scientific Co., Canada) were used to determine the UV absorbance of samples. In addition, some glassware (chlorine demand free) and other routine equipments, such as a pH meter, electronic balance, and magnetic stirrer, were also used in this research.

UV exposure and irradiance measurements

Two aliquots of free chlorine samples were used in each run: one was used for exposure to UV light, and the other was used as a dark control sample. The former sample was placed under the open end of the plastic collimating tube of the UV collimated beam apparatus in the center of the beam, and the latter sample was placed in the dark on a bench that was far away from the UV apparatus. The surface of the solution to be exposed was about 300 mm from the UV lamp. The UV exposure time of the

Table 1. Comparison of reported molar absorption coefficients of HOCl and OCl$^-$.

ε_{235}/M^{-1} cm^{-1}	ε_{292}/M^{-1} cm^{-1}	ε_{254}/M^{-1} cm^{-1}		
HOCl	OCl$^-$	OCl$^-$	HOCl	Reference
—	368	155	121	Nowell and Hoigné (1992*b*)
100	350	58	62	Morris (1966)
105	—	60	—	Thomsen et al. (2001)
—	362	—	—	Chen (1967)
101±2	365±8	66±1	59±1	This work

Note: These data were determined at approximately 25 °C.

free chlorine solution was controlled by means of a pneumatic shutter located at the top of the collimating tube beneath the UV lamp, and was activated using a stopwatch. During the exposure period, a 3 mm × 12 mm Teflon™-coated stir bar was added into each of these two samples to provide sufficient stirring. At the beginning and end of the UV exposure, the concentration of free chlorine in each sample was measured in order to determine the amount of free chlorine decomposed due to UV light exposure. The incident irradiance was measured by positioning the radiometer vertically, such that the reference calibration marker on the radiometer detector head was placed at the same level as the top surface of the sample solution. During these experiments, two similar (internal diameter 31.2 mm) Pyrex® beakers were used as the photolysis reactor and the control reactor. In addition, the beaker exposed to UV light was covered with an opaque cap, containing a 14.2 mm diameter hole in the center of the cover to let UV light into the sample in the beaker. This was done to avoid any interaction of the UV beam with the sides of the beaker. To allow for the same conditions as the UV irradiated sample, a similar cap was also used for the dark control sample. About 25 mL of the free chlorine sample was added into the beaker for each run. Figure 2 is a schematic diagram of the UV exposure test apparatus.

Quantum yield

The quantum yield, , is defined as the number of moles of product formed or reactant removed per einstein[4] of photons absorbed. Therefore, the quantum yield of free chlorine decomposed can be determined from

[5] $\quad \Phi = \dfrac{\text{moles of free chlorine decomposed}}{\text{einsteins absorbed at 254 nm}}$

where "free chlorine" includes OCl$^-$ and (or) HOCl present in the samples. In the pH range of 5 to 10 and in the absence of free ammonia and amines, free chlorine exists primarily as an equilibrium mixture of OCl$^-$ and HOCl. When the concentration of free chlorine was lower than 50 mg Cl/L it was measured by the DPD method in this research (APHA et al. 1995). Otherwise, the concentration was determined by the UV absorbance of samples at an appropriate wavelength divided by the molar absorption coefficient of the free chlorine at this wavelength.

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[4] One einstein is a mole (6.023 × 10^{23}) of photons.

Fig. 2. Schematic of the collimated beam apparatus.
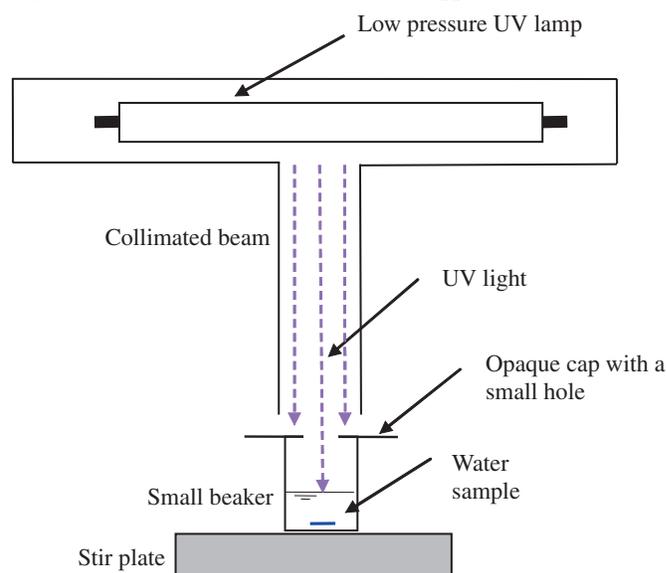
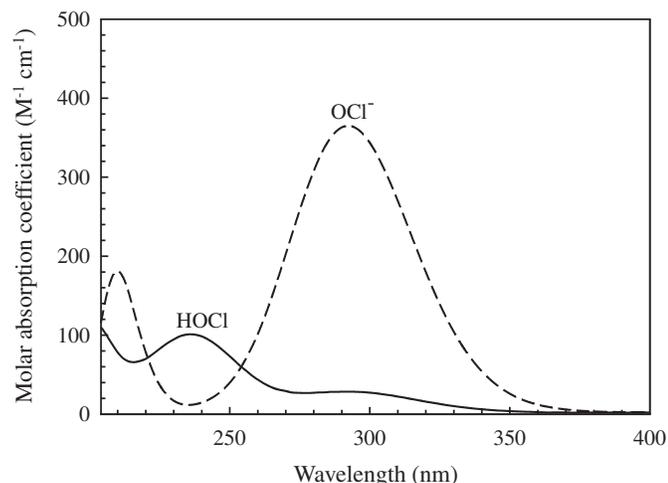Then, the amount of free chlorine decomposed can be calculated according to

[6] moles of free chlorine decomposed

$$= (C_{bi} V_{bi} - C_{ai} V_{ai}) - (C_{bc} V_{bc} - C_{ac} V_{ac}) \frac{V_{mi}}{V_{mc}}$$

where, C is the concentration of free chlorine samples in M; V is the volume of samples in L; the subscripts of "i" and "c" are the "irradiated sample by UV light" and "dark control sample"; the subscripts of "b" and "a" are the "before" and "after" exposed to UV light; and "m" means mean. The "einsteins absorbed at 254 nm" can be determined from

[7] einsteins absorbed at 254 nm

$$= \frac{E \times \text{PF} \times A \times t \times (1 - R) \times (1 - 10^{-A_{254}})}{U_\lambda}$$

where, E is the irradiance (W/cm^2) measured at the center of sample position; PF is Petri Factor defined as the average irradiance over the surface of sample exposed to UV light divided by the irradiance at the center; A is the area of sample surface directly exposed to UV light (i.e., the cross-sectional area of the hole on the opaque cap covered on the sample beaker, cm^2); t is

Fig. 3. Absorption spectra of HOCl and OCl⁻. The absorbance of HOCl and OCl⁻ was measured, respectively, at pH 5 and pH 10 (temperature 21 ± 2 °C).

Fig. 4. Quantum yield of HOCl at pH 5 (temperature 21 ± 2 °C): (*a*) Concentration < 71 mg Cl/L, and (*b*) Concentration >71 mg Cl/L.

the exposure time (s); R is the reflection coefficient (0.025) at the sample surface; A_{254} is the mean absorbance of the sample at 254 nm during the exposure time; and U_λ is the energy of one einstein of photons at 254 nm (471527.6 J/einstein).

Fluence (UV dose)

The fluence (UV dose) F was determined according to the protocols specified by Bolton and Linden (2003). Specifically, this involved converting the incident fluence rate (irradiance) E_o, as determined using the radiometer, to the average fluence rate E_{avg} utilizing the various correction factors specified in that protocol.

Results and discussion

Absorption spectra and molar absorption coefficients of HOCl and OCl⁻

The absorption spectra and molar absorption coefficients of free chlorine are very important to this research. The reason is that the components of free chlorine mainly depend on pH. According to the equilibrium of reaction 2, for free chorine samples at pH 5 the dominant species is HOCl, whereas at pH 10, the dominant species is OCl⁻. Therefore, the amount of free chlorine decomposed by UV light at different pH could be different due to the different free chlorine species and their different absorption spectra. The absorption spectra of HOCl and OCl⁻ are shown in Fig. 3.

The absorption spectra show that there is an absorption peak at about 236 nm for HOCl; whereas for OCl⁻, the peak is at about 292 nm. Using more than 15 concentrations over the range of 0 to 1000 mg Cl/L, the molar absorption coefficient obtained by regression at 236 nm for HOCl is 101 ± 2 M⁻¹ cm⁻¹. In the same manner, the molar absorption coefficient at 292 nm for OCl⁻ was determined to be 365 ± 8 M⁻¹ cm⁻¹. When the concentration of free chlorine was more than 50 mg Cl/L, it was measured in this research by the UV absorbance of samples at 236 or 292 nm divided by the molar absorption coefficient at
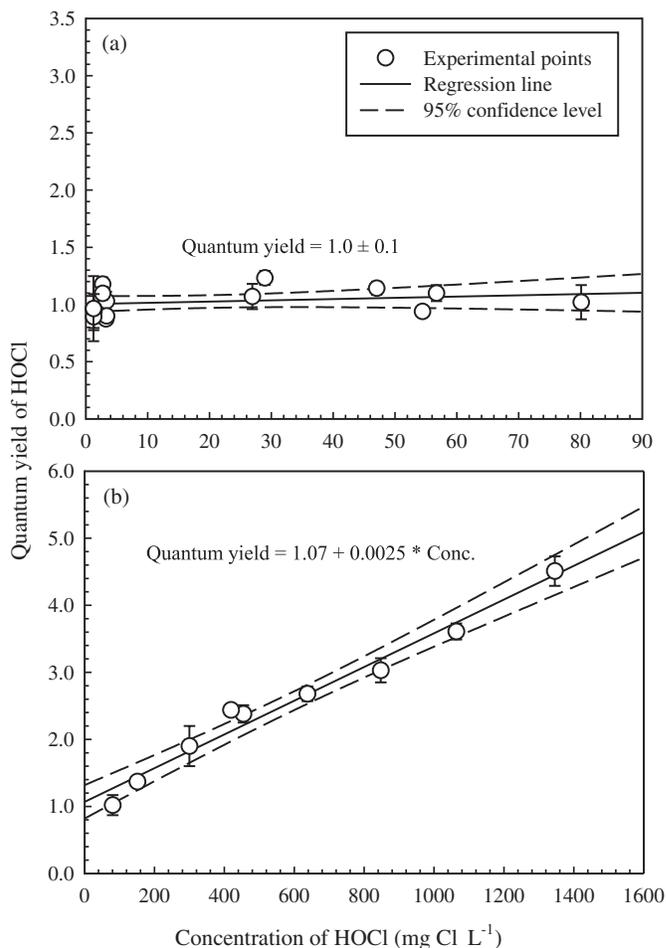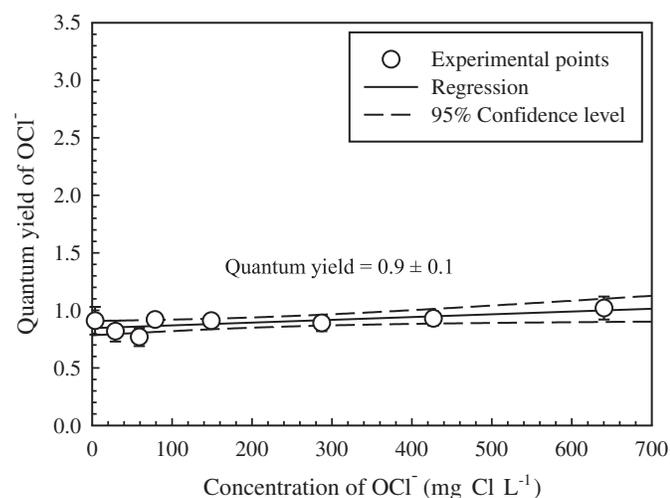
the corresponding wavelength. In addition, the molar absorption coefficients of HOCl and OCl⁻ at 254 nm were also determined to be 59 ± 1 and 66 ± 1 M⁻¹ cm⁻¹, respectively. These values were used for the calculation of fluence absorbed by free chlorine samples. Compared with the values listed in Table 1, the results obtained in this research are very consistent with data reported by Morris (1966), Chen (1967), and Thomsen et al. (2001).

Quantum yields of free chlorine

The quantum yields of free chlorine (HOCl and OCl⁻) were determined from Figs. 4(*a*)–4(*b*) and Fig. 5. The quantum yield of HOCl is essentially constant at 1.0 ± 0.1 as long as the concentration is less than 71 mg Cl/L; however, for concentrations from 71 to 1350 mg Cl/L, the quantum yield increases linearly with a slope of 0.0025 (mg Cl/L)⁻¹, such that at 1350 mg Cl/L, the quantum yield is 4.5 ± 0.2. In contrast, the quantum yield of OCl⁻ is virtually independent of concentration at 0.9 ± 0.1 when the concentration ranges from 3.5 to 640 mg Cl/L.

As reported by other researchers (Oliver and Carey 1977; Buxton and Subhani 1972*a*), the concentration dependence of the photolysis of HOCl can be explained by a chain reaction

Fig. 5. Quantum yield of OCl$^-$ at pH 10 (temperature 21 ± 2 °C).
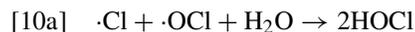

initiated by the reactions

[8a]	$HOCl + h\nu(UV\ photons) \rightarrow \cdot OH + \cdot Cl$

[8b]	$\cdot OH + HOCl \rightarrow H_2O + \cdot OCl$

where the $\cdot Cl$ and (or) $\cdot OCl$ species may participate in further reactions that deplete the HOCl.[5]

For example, the $\cdot Cl$ atom may react with HOCl by

[9]	$\cdot Cl + HOCl \rightarrow HCl + \cdot OCl$

Chain termination may involve the reactions

[10a]	$\cdot Cl + \cdot OCl + H_2O \rightarrow 2HOCl$

[10b]	$2\ \cdot OCl + H_2O \rightarrow HCl + HClO_3$

The experimental results of this research indicate that the above reactions have a greater effect on the quantum yield of HOCl at higher concentrations than at lower concentration. At pH 10, $\cdot OH$ radicals can be generated by the reactions

[11a]	$OCl^- + h\nu(UV\ photons) \rightarrow \cdot O^- + \cdot Cl$

[11b]	$\cdot O^- + H_2O \rightarrow \cdot OH + OH^-$

The $\cdot OH$ radical reacts with OCl$^-$ by electron transfer with a rate constant of $8.8 \times 10^9\ M^{-1}\ s^{-1}$ (Buxton and Subhani 1972b) to generate $\cdot OCl$. However, at pH 10, it appears that $\cdot Cl$ and (or) $\cdot OCl$ species do not initiate any chain reactions, since the quantum yield is independent of concentration at this pH.

A model for the prediction of the quantum yield of free chlorine decomposed by UV light at 254 nm

According to the above discussion, free chlorine exists primarily as an equilibrium mixture of hypochlorous acid (HOCl) and its conjugate base (OCl$^-$) with a pK$_a$ of 7.5. Based on

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[5]No rate constant is available for reaction 8(b); however, it is likely that this reaction proceeds with a rate constant near diffusion controlled ($\sim 10^{10}\ M^{-1}\ s^{-1}$).

the equilibrium of reaction 2, the fraction of HOCl existing in free chlorine samples can be expressed as a function of pH as follows:

[12]	$f = \dfrac{[HOCl]}{[OCl^-] + [HOCl]} = \dfrac{1}{1 + 10^{pH - pK_a}}$

where, f is the fraction of HOCl present in free chlorine samples.

From the absorption spectra of HOCl and OCl$^-$ (Fig. 3), the molar absorption coefficient of HOCl at 254 nm is different from that of OCl$^-$. In addition, the quantum yields of HOCl and OCl$^-$ and their tendency to change along with their concentrations are different from each other. Assuming that the photolysis of HOCl and OCl$^-$ are two independent processes and that the interactions between these two processes are negligible, the overall quantum yield of free chlorine (HOCl and OCl$^-$) decomposed by UV irradiation at 254 nm at a given pH value may be estimated by the following equation:

[13]	$\Phi_{overall} = \dfrac{f\varepsilon_{HOCl}}{f\varepsilon_{HOCl} + (1 - f)\varepsilon_{OCl^-}}\Phi_{HOCl}$

$\qquad\qquad + \dfrac{(1 - f)\varepsilon_{OCl^-}}{f\varepsilon_{HOCl} + (1 - f)\varepsilon_{OCl^-}}\Phi_{OCl^-}$

where ε_{HOCl}, is the molar absorption coefficient of HOCl at 254 nm; ε_{OCl^-} is the molar absorption coefficient of OCl$^-$ at 254 nm; f is the fraction of HOCl present in free chlorine samples; Φ_{HOCl} is the quantum yield of HOCl; Φ_{OCl^-} is the quantum yield of OCl$^-$; $\Phi_{overall}$ is the overall quantum yield of aqueous chlorine at a given pH condition.

In the above equation, it needs to be emphasized that the quantum yield of HOCl is not a constant. As discussed in the above section, it is about 1.0 ± 0.1 when the concentration is less than 71 mg Cl/L. Otherwise, it will be a function of its concentration as shown in Fig. 4(*b*). Therefore, when eq. [13] is used for the prediction of quantum yield of free chlorine decomposed, the quantum yield of HOCl corresponding to its concentration should be employed. In addition, the parameters (molar absorption coefficient, quantum yield, etc.) were determined at 254 nm, so this model should only be used for the condition of low pressure UV lamps.

Validation of the quantum yield model

As discussed in the above section, the model (eq. [13]) was developed based on the assumption of no interactions between the photolysis processes of HOCl and OCl$^-$. Because only a unique component, HOCl or OCl$^-$, is present in free chlorine samples at pH 5 or 10, the assumption of the model is met under these critical conditions and, obviously, the model can work very well for the quantum yield prediction. However, at intermediate pH values, free chlorine samples always consist of both HOCl and OCl$^-$. Therefore, several experiments were performed in order to examine if the model can be applied at different pH values. Figures 6(*a*)–6(*d*) show that the quantum yields predicted by the model at various pH values are consistent with those measured by the experiments. These figures also indicate that the assumptions of the model are essentially

Fig. 6. Comparison of experimental results and data calculated by the model at various concentrations: (*a*) 71 mg Cl/L; (*b*) 140 mg Cl/L; (*c*) 284 mg Cl/L; and (*d*) 670 mg Cl/L (temperature 21 ± 2 °C).
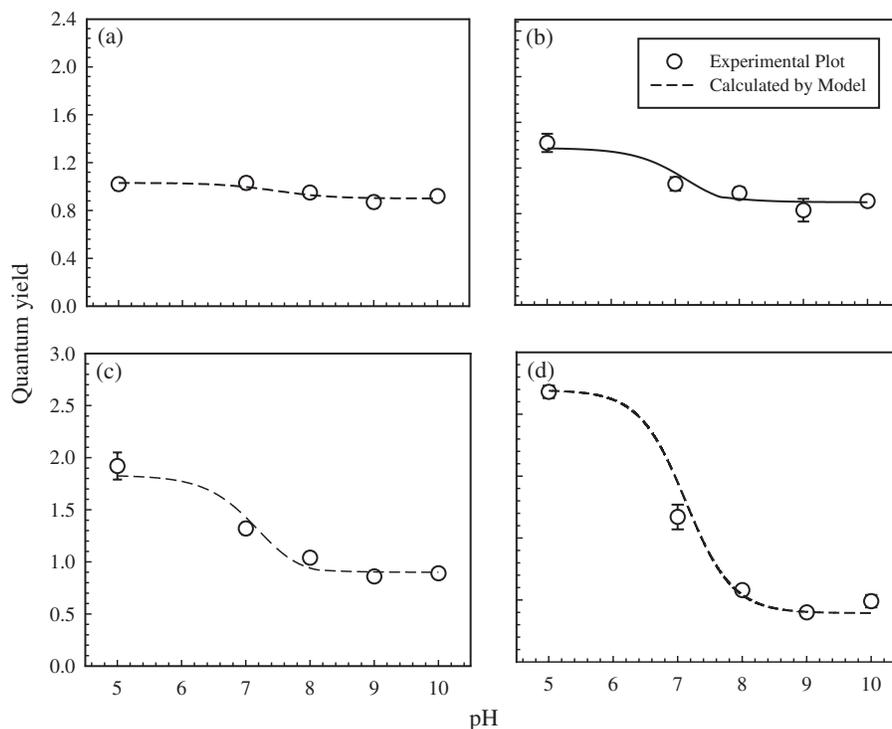

correct. Hence, this model should be appropriate to estimate the overall photolysis quantum yield of free chlorine under various pH conditions.

Effect of water quality on the quantum yield

It should be stressed that the quantum yields discussed in the above paragraphs were determined in DI water. Actually, the drinking water quality varies greatly from place to place and because the strong oxidant, hydroxyl radical (·OH), is produced in the photolysis of free chlorine, the materials dissolved in drinking water may have an important effect on the quantum yield. In this research, methanol, simple organic compound to model dissolved organic matter, was added to DI water. The quantum yields of free chlorine were then studied as a function of the concentration of methanol. Figure 7 shows that the amount of free chlorine (HOCl) decomposed depends linearly on the concentration of methanol at pH 5, such that the quantum yield is over 50 for a methanol concentration of 120 mM. Clearly at pH 5, the product of the oxidation of methanol by ·OH (the ·CH$_2$OH radical) initiates a chain reaction involving HOCl to cause the increase in the quantum yield. By contrast, the quantum yields of OCl$^-$ obtained at pH 10 are always around 1.2 ± 0.2 when the methanol concentration increases from 20 to 50 mM. Compared with the quantum yield (0.9 ± 0.1) obtained in DI water at pH 10, these results indicate that methanol has little impact on the decomposition of OCl$^-$. In practice, the quantum yield of free chlorine could be affected by dissolved organic matter in the drinking water and more chlorine could be decomposed at low pH rather than at high pH.

Fig. 7. Dependence of quantum yield of free chlorine (HOCl) on the concentration of methanol at pH 5 (temperature 21 ± 2 °C).
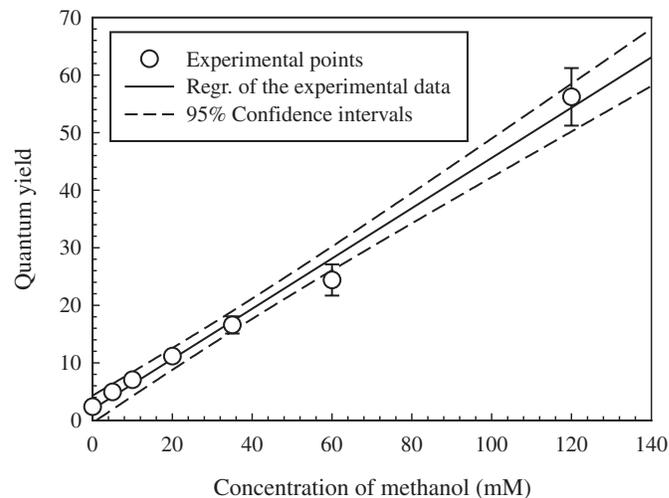
Dependence of free chlorine decomposition on the fluence

When the concentration of free chlorine is not very high (<70 mg Cl/L), the quantum yield of free chlorine can be assumed to be independent of the concentration of free chlorine. Therefore, the rate of free chlorine destruction follows a first order kinetics and usually can be expressed as

[14a] $\quad \ln \dfrac{[C]_\mathrm{o}}{[C]_t} = k_1' t$

where $[C]_o$ and $[C]_t$ are the free chlorine concentration before and after exposure to UV light for a time of t min; k is the first-order constant in units of min^{-1}. Because the time-based first-order rate constant (k) can be affected by the experimental conditions (e.g., irradiance, absorbance, path length, etc.) and is difficult to reproduce, eq. [14a] can be modified to

$$[14b] \quad \ln \frac{[C]_o}{[C]_F} = k_1' F$$

where $[C]_o$ and $[C]_F$ are the chlorine species concentration before and after being exposed to the UV fluence of F; k_1' is the fluence-based first-order rate constant (Bolton and Stefan 2003). Here k_1' only depends on the quantum yield and molar absorption coefficient of the UV light absorber (see eq. [15]). So, theoretically k_1' is a constant for a certain UV light absorber and can be easily reproduced.

$$[15] \quad k_1' = \frac{\Phi \varepsilon \ln(10)}{10 U_\lambda}$$

where ε is the molar absorption coefficient (M^{-1} cm^{-1}) of the UV light absorber and other terms are defined as above. According to eq. [14b], one can plot the logarithm (base e) of the free chlorine reduction vs. fluence absorbed to get the fluence-based first-order constant k'. Then, the quantum yield can be calculated by eq. [15].

As an example, Figures 8(a) and 8(b) show that the logarithmic (base e) reduction of free chlorine increases linearly with fluence and the fluence-based first-order rate constant k' is 2.9×10^5 m^2 J^{-1} in both cases, when the concentration of free chlorine is about 20 mg Cl/L. Based on the fluence-based rate constant, the quantum yields estimated according to eq. [15] were about 1.0. This result is very close to the value obtained by the method given in the above section on "quantum yield". Figures 8a and 8b also indicate that only a slight amount ($\sim$1%) of free chlorine was decomposed when the concentration of free chlorine was about 20 mg Cl/L, and the UV fluence was 400 J/m^2, a fluence that is often specified in UV disinfection regulations. Because DI water was used in the research, it is possible that a larger fraction of free chlorine could be destroyed in drinking water as discussed in the above section. Generally, the destruction of free chlorine depends not only on the fluence, but also on the concentration of free chlorine, water quality, and the pH. Data on this destruction are presented in Table 2.

Conclusions

The molar absorption coefficients of HOCl and OCl$^-$ at 254 nm obtained in this research are 59 ± 1 and 66 ± 1 M^{-1}cm^{-1}, respectively. These results are very consistent with other reported results (Morris 1966; Chen 1967; and Thomsen et al. 2001). In DI water, the concentration of free chlorine and pH are important factors affecting the photolysis of free chlorine samples. At low concentrations ($<$71 mg Cl/L), the quantum yields of HOCl and OCl$^-$ are approximately constant at 1.0 ± 0.1 and 0.9 ± 0.1, respectively, as obtained in this research. However, at higher concentrations ($>$71 mg Cl/L) the

Fig. 8. Logarithmic (base e) reduction of free chlorine as a function of UV fluence (UV dose): (a) 71 mg Cl/L free chlorine at pH 5; (b) 71 mg Cl/L free chlorine at pH 10.
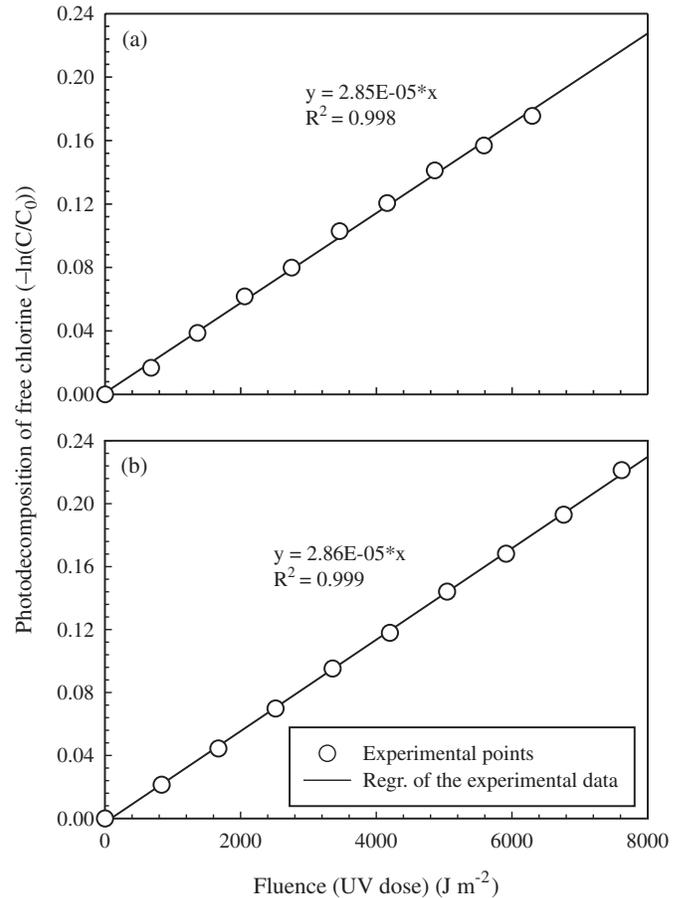
Table 2. Percent of free chlorine destructed at the fluence of 400 J m^{-2}.

Characteristics of water sample	Percent of chlorine species reduced
71 mg Cl/L free chlorine in DI water at pH 5	1.1%
71 mg Cl/L free chlorine in DI water at pH 10	1.1%
213 mg Cl/L free chlorine in DI water at pH 5	2.8%
213 mg Cl/L free chlorine in DI water at pH 10	1.2%
213 mg Cl/L free chlorine and 1.6 g/L methanol in DI water at pH 10	1.3%
213 mg Cl/L free chlorine and 1.1 g/L methanol in DI water at pH 5	18%
213 mg Cl/L free chlorine and 0.7 g/L 1,4-dioxane in DI water at pH 5	11%

quantum yield of HOCl increases linearly with the concentration at a rate of 0.0025 (mg Cl/L)$^{-1}$. Compared with HOCl, it was found that the concentration has an insignificant effect on the quantum yield of OCl$^-$ over the investigated concentration range of 3.5 to 640 mg Cl/L in this research. A model (eq. [13])

was established for the prediction of overall quantum yield of free chlorine decomposed by UV irradiation at 254 nm in DI water. Compared with the experimental results measured at various pH values, the predictions calculated by this model agree quite well with the measured quantum yields. In addition, the effect of water quality is very significant on the quantum yield of HOCl, but not on the quantum yield of OCl^-. The addition of methanol at pH 5 can cause a large increase in the quantum yield of HOCl; whereas, at pH 10, the effect of methanol addition was minimal. The decomposition of free chlorine depends on the pH, concentration of free chlorine, fluence, and water quality. At fluence of 400 J/m^2, the decomposition of free chlorine is very slight ($\sim$1%) in DI water when the concentration of free chlorine is not very high ($\sim$20 mg Cl/L).

Acknowledgements

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