

TCAA degradation in ultraviolet (UV) irradiation/hydrogen peroxide (H₂O₂)/micro-aeration (MCA) combination process

N. Y. Gao, W. H. Chu, Y. Deng and B. Xu

ABSTRACT

The photochemical degradation of trichloroacetic acid (TCAA) employing ultraviolet (UV) irradiation/hydrogen peroxide (H₂O₂)/micro-aeration (MCA) combination process was investigated by varying operational parameters. Relatively slow TCAA degradation was observed during direct UV radiation and H₂O₂ oxidation, while TCAA cannot be removed by MCA alone. UV/H₂O₂/MCA combination process proved to be more effective than UV/H₂O₂. With the initial concentration of 55.7 µg l⁻¹, more than 93.4% of TCAA can be removed within 180 min under UV radiation intensity of 1,048.7 µW cm⁻², H₂O₂ dosage of 30 mg l⁻¹ and MCA flow rate of 25 l min⁻¹ in neutral conditions. Removal rate of TCAA was sensitive to UV radiation intensity, H₂O₂ dose and solution pH, but appeared to be slightly influenced by initial TCAA concentration. There was a higher correlation between pseudo-first rate constant *k* and UV intensity and H₂O₂ dosage, implying that higher removal capacity can be achieved by improvement of both factors. The newly found trichloroacetamide (TCACAm), the potential TCAA, was more frangible than TCAA, indicating that TCAA hardly regenerates by hydrolysis of TCACAm. Finally, a preliminary cost analysis revealed that the UV/H₂O₂/MCA process was more cost-effective than the UV/H₂O₂ process in removal of TCAA from drinking water.

Key words | advanced oxidation processes, cost analysis, disinfection by-products, micro-aeration, trichloroacetamide, trichloroacetic acid

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ABBREVIATIONS

AOPs	advanced oxidation processes
DBPs	disinfection by-products
ETAC	ethyl acetate
H ₂ O ₂	hydrogen peroxide
HAAs	haloacetic acids
HAcAms	haloacetamides
LLE	liquid-liquid extraction
MCA	micro-aeration
MCL	maximum contaminant level
MTBE	methyl-tert-butyl-ether
TCAA	trichloroacetic acid

TCACAm	trichloroacetamide
THMs	trihalomethanes
UV	ultraviolet

INTRODUCTION

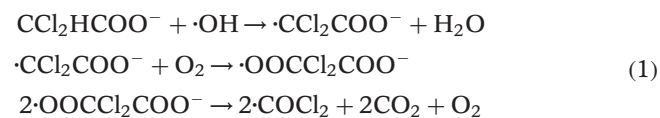
Water disinfection is one of the most important public health advances of the last century. Owing to their capacity for disinfection (microorganisms) and oxidation (e.g. taste and odour control, elimination of micro-pollutants, etc.), chemical oxidants (i.e. chlorine, chloramines, chlorine dioxide, ozone, etc.) are commonly used in water treatment

processes (Richardson *et al.* 2007). However, addition of chemical disinfectants to drinking water produces a wide range of unwanted organic disinfection by-products (DBPs) (Reckhow *et al.* 2001), especially trihalomethanes (THMs) and haloacetic acids (HAAs) (Krasner *et al.* 1989; Cowman & Singer 1996). THMs are the group of chlorinated DBPs most documented over the past 20 years. In most industrialized countries, standards for THMs have been established within drinking water regulations (Richardson 2003). Their occurrence, formation and degradation are relatively well understood (Chow *et al.* 2005; Liu *et al.* 2008).

Most recently, efforts have been made to better document the degradation of haloacetic acids (HAAs), the second most important group of chlorinated DBPs, which are probably associated with higher cancer risk and genotoxicity than THMs (Plewa *et al.* 2002). The US EPA regulated a maximum contaminant level (MCL) of $60 \mu\text{g l}^{-1}$ for the sum of five haloacetic acids, including monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA). Among these HAAs, DCAA and TCAA occur in higher concentrations in drinking water.

There are three main methods to control the concentration of DBPs (e.g. HAAs): (1) removal of precursors prior to disinfection; (2) use of alternative disinfectants (e.g. ozone) which create fewer DBPs; and (3) removal of DBPs after their formation (Singer & Reckhow 1999). Many waterworks have focused on the removal of precursors such as natural organic matter (NOM) to control DBPs. However, because of limits on operating cost, precursors (e.g. NOM) are difficult to remove effectively by improving and strengthening conventional processes prior to disinfection. Although ozone, chlorine dioxide and ultraviolet (UV) irradiation create fewer DBPs such as THMs and HAAs, among the currently available disinfectants, chlorine is still globally the most frequently used in drinking water disinfection because of its residual disinfecting capacity. In other words, in order to prevent bacteria, viruses and other harmful microorganisms from reproducing, the addition of chlorine is still necessary after alternative disinfectants (e.g. ozone), which may create more DBPs. Therefore, the study on removal of DBPs after their formation, the third method to control DBPs, is essential and significant.

The advanced oxidation process (AOP) employing UV irradiation and hydrogen peroxide (H_2O_2) is very effective in the degradation of organic compounds (Aceituno *et al.* 2002; Andreozzi *et al.* 2004). The photolysis of hydrogen peroxide generates a mass of hydroxyl radical under UV irradiation, which can oxidize a broad range of organic pollutants quickly and non-selectively (Elovitz *et al.* 2008; Kim *et al.* 2008; Zalazar *et al.* 2008). Recently the authors published the photooxidation results of herbicide employing the UV and H_2O_2 process and found that the UV/ H_2O_2 process has a lower cost for removing herbicide than UV irradiation alone under the same degradation effect conditions (Gao *et al.* 2009). In our previous study, phthalate esters (PAEs) can be completely degraded in a few hours by UV/ H_2O_2 , but are difficult to mineralize effectively because of the formation of degradation products (Xu *et al.* 2007). However, some studies have found that smaller molecular weight organics (e.g. DCAA) can be mineralized quickly and completely employing the UV/ H_2O_2 process (Zalazar *et al.* 2007, 2008). Zalazar *et al.* (2007) found that oxygen has a catalytic and promotion action on the degradation of DCAA. The catalytic reaction process can be expressed as the following Equation (1).



This finding revealed that molecular oxygen (O_2) plays a significant role in enhancement of oxidation in AOPs, which motivates us to add micro-aeration (MCA) to the UV/ H_2O_2 process. Therefore, the UV/ H_2O_2 /MCA process was developed based on the UV/ H_2O_2 process. MCA not only plays an important part in mixing and catalysis but also increases the productive rate of hydroxyl radical. As shown in Equation (2), oxygen introduced by MCA may produce ozone under UV radiation with the wavelength of 185 nm (Shirayama *et al.* 2001), and ozone can produce hydroxyl radical under UV radiation with the wavelength of 254 nm (Oh *et al.* 2005):



There have some investigations on DCAA removal by the photooxidation process (Zalazar *et al.* 2007, 2008), and we also investigated DCAA degradation with

UV/H₂O₂/MCA (Chu *et al.* 2009). However, there is a gap in studies on the control of HAAs; few reports on TCAA removal by photooxidation process could be found, especially the UV/H₂O₂/MCA combination process. The genotoxicity of TCAA is higher than that of DCAA. Unlike DCAA, TCAA has given generally negative results for gene mutation in bacteria and mammalian cells and for DNA damage *in vitro*, even when tested in closed systems. (Richardson *et al.* 2007). The purpose of the present study is to investigate the removal potential and photooxidation performance of TCAA based on the UV/H₂O₂/MCA combination process and to provide more grounds for the control of DBPs by the photooxidation process.

MATERIALS AND METHODS

Materials

All chemicals were at least analytical grade except as noted. HAAs mixture standard and 1, 2-dibromopropane internal standard were purchased from Sigma-Aldrich. Trichloroacetamide (TCaAm, 99%) was purchased from German Alfa Aesar. Extractant methyl-tert-butyl-ether (MTBE, chromatographic purity) and ethyl acetate (ETAC) were obtained from Fisher Scientific. H₂O₂ (30%, w/w) was obtained from Sinopharm Chemical Reagent Co. Ltd, China. Ultrapure water (18 MΩ cm) used to prepare the experimental solution was produced by a Milli-Q Academic water purification system. AR grade NaOH and HCl were used to adjust the pH value. Buffer solutions at pH 6, 7, 8 and 10 were prepared from phosphate salts (sodium dihydrogen phosphate, NaH₂PO₄ (0.3 M) and sodium monohydrogen phosphate, Na₂HPO₄ (0.2 M)) and buffer solution at pH 4 was prepared from acetate salts (acetic acid, HAC (0.2 M), sodium acetate, NaAC (0.2 M)) obtained from Merck.

Analytical methods

All the reactions were carried out at room controlled temperature. Prior to analysis, samples for TCAA analysis were extracted using MTBE. A surrogate standard (100 ppm 1, 2-dibromopropane in MTBE) was added to each sample to monitor method performance. After sample extraction,

TCAA analyses were carried out on a gas chromatograph (Shimadzu-QP2010) with an electron capture detector (ECD), based on the USEPA method 552.2 (USEPA 1995). UV light intensity was measured with a UV light intensity meter (SpotCure model SP365, EIT Inc, Virginia). The pH of water was measured by using an electron pH meter (Corning 320, Hanning Instruments). The column used was a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness; J&W Scientific). The corresponding method detection limits (MDL), rejectable quality level (RQL) and relative standard deviations (RSD) for TCAA were 0.05, 0.15 μg l⁻¹ and 5.13%, respectively.

TCaAm analyses consisted of liquid-liquid extraction (LLE) and determination on a GC/MS (Shimadzu-QP2010S). ETAC was used for extractant; samples with 20 ml were extracted with 1 ml organic phase in the presence of 4 g of NaCl on a IKA Lab Dancer shaker (Staufen, Germany). The final extract was analysed by gas chromatography-electron impact-mass spectrometry under select ion measurement mode (GC-EI-MS-SIM). The detailed determination conditions of GC-EI-MS-SIM were described previously (Chu & Gao 2009).

Photoreactor

The irradiation set-up was a stainless steel completely mixed batch reactor (CMBR) with an irradiated solution volume of 5 l, as shown in Figure 1. The UV lamp (emitting

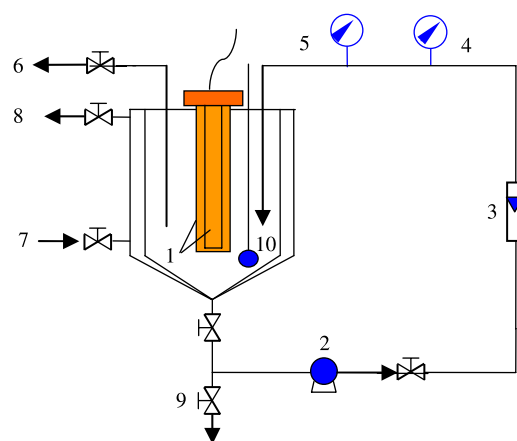


Figure 1 | The Schematic diagram of experimental apparatus: (1) quartz socket tube and UV lamps; (2) circular pump; (3) flowmeter; (4) pressure meter; (5) thermometer; (6) sample connection; (7) cooling water inlet; (8) cooling water outlet; (9) atmospheric valve; (10) aerator.

Table 1 | The intensity of UV radiation

		Number of UV lamp				
		1	2	3	4	5
Intensity ($\mu\text{W cm}^{-2}$)	254 nm	183.6	411.5	640.2	843.9	1,048.7
	185 nm	47.5	107.6	157.3	216.3	261.6

wavelength = 185 and 254 nm, 30 W, Fuzhou Longxin Electronics Co., Ltd, China) with quartz sleeves was fixed in circularity in the reactor. The UV light intensity, controlled by turning on or off the lamps, was monitored by a light intensity meter (Table 1). Air flow rate of MCA equipment (HAILEA AOC-108, 10 W) was a constant value (251 min^{-1}) which had been validated by gas flow indicator (Rixin SBL). As the air flow rate of MCA equipment was very low, we ignored the effect of bubbles on UV radiation and H_2O_2 concentration. Water temperature was controlled by circulating cooling water and a thermometer.

RESULTS AND DISCUSSION

TCAA degradation by direct UV photolysis, H_2O_2 oxidation alone, MCA alone and combination process

To investigate the direct photolysis of TCAA by UV irradiation, five sets of experiments were conducted with varying UV radiation intensities at an initial TCAA concentration of $56 \mu\text{g l}^{-1}$. TCAA concentrations decomposed slowly with direct UV radiation under all conditions studied (data not shown). After 180 min reaction, only

9.7%, 15.2%, 17.3%, 24.3% (shown in Figure 2) and 33.5% of the TCAA were degraded in the solutions corresponding to the UV radiation intensities of 183.6, 411.5, 640.2, 843.9 and $1,048.7 \mu\text{W cm}^{-2}$, respectively. These results indicate that TCAA is resistant to direct UV photolysis and more recalcitrant with respect to UV-photolysis than DCAA (Chu *et al.* 2009). Experiments were also carried out to examine the TCAA degradation by H_2O_2 oxidation only and MCA only, but the TCAA concentration decreased very slowly over 180 min, which implied that TCAA was very difficult to degrade by the above-mentioned separate process.

As shown in Figure 2, the removal effects of TCAA employing UV/ H_2O_2 and UV/ H_2O_2 /MCA processes were both better than separate processes. Experimental data from UV/ H_2O_2 and UV/ H_2O_2 /MCA were both fitted to pseudo-first order kinetics and the apparent reaction rate constant k was $0.0056 < 0.0082$, respectively, which is lower than for DCAA (Chu *et al.* 2009). In experimental water solution, dissolved oxygen quickly increased during MCA and further formed ozone in UV irradiation (Shirayama *et al.* 2001). The ozone formed can have an important synergetic effect with H_2O_2 to produce more hydroxyl radical (Oh *et al.* 2005; Kim *et al.* 2008). Therefore, the removal performance of TCAA in different processes follows the order: UV/ H_2O_2 /MCA > UV/ H_2O_2 > UV alone > H_2O_2 alone > MCA.

Effect of UV radiation intensity

As seen in Figure 3, the degradation effect of TCAA by UV/ H_2O_2 /MCA was investigated at five radiation levels: 183.6,

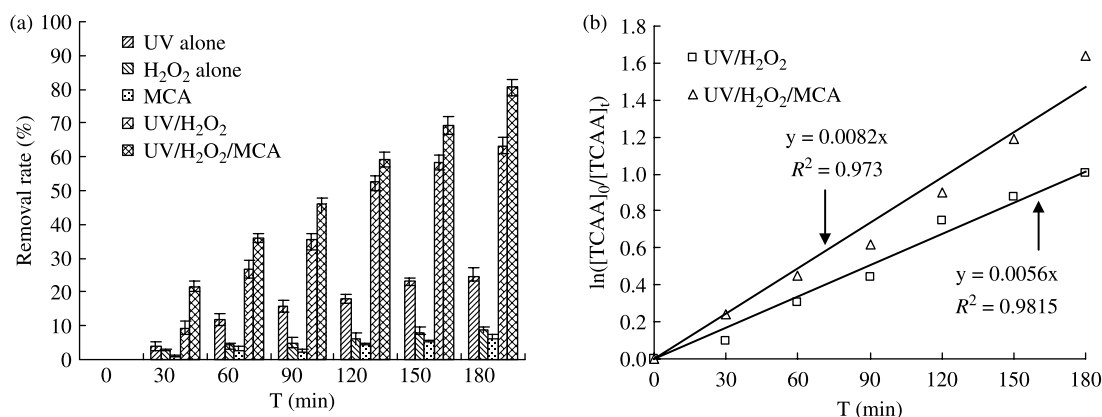


Figure 2 | TCAA degradation in UV/ H_2O_2 and UV/ H_2O_2 /MCA processes. (Conditions: reaction time = 180 min, initial TCAA = $55.7 \pm 0.3 \mu\text{g l}^{-1}$, pH = 7, H_2O_2 dosage = 30 mg l^{-1} , UV radiation intensity = $843.9 \mu\text{W cm}^{-2}$ for wavelength = 254 nm and UV radiation intensity = $261.6 \mu\text{W cm}^{-2}$ for wavelength = 185 nm).

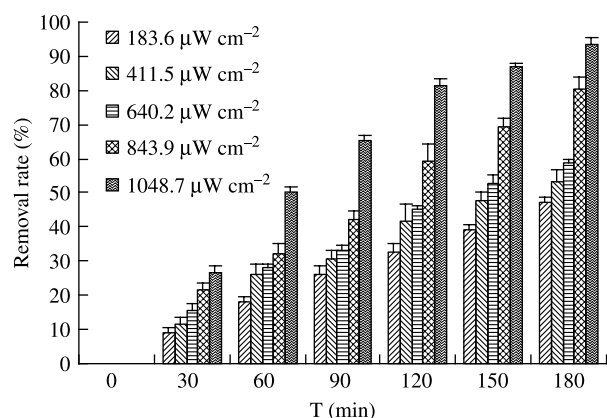


Figure 3 | Effect of UV radiation intensities on TCAA degradation. (Conditions: initial TCAA = $55.7 \pm 0.3 \mu\text{g l}^{-1}$, pH = 7, H_2O_2 dosage = 30 mg l^{-1} . Error bars represent the standard deviation of experimental replicates ($n = 3$)).

411.5, 640.2, 849.3 and $1,048.7 \mu\text{W cm}^{-2}$. UV radiation showed a positive effect on the TCAA removal. Within the 180 min, the final TCAA removal rate increased from 47.1% to 93.4% with the UV radiation intensity increasing from 183.6 to $1,048.7 \mu\text{W cm}^{-2}$. Previous studies showed that yield of hydroxyl radical was limited at low UV radiation intensities, and more hydroxyl radicals were generated at high UV radiation intensity (Chu *et al.* 2009; Gao *et al.* 2009). It can be deduced that the enhancement of removal efficiency is attributed to the strong oxidation strength of numerous hydroxyl radicals produced in the UV/ H_2O_2 /MCA process.

Effect of initial H_2O_2 concentration

H_2O_2 concentration is another parameter in the UV/ H_2O_2 /MCA combination process, which is as important as UV radiation intensity. The effect of H_2O_2 concentration (10, 20, 30, 40 and 50 mg l^{-1}) on the photochemical degradation is shown in Figure 4. The addition of H_2O_2 from 10 to 50 mg l^{-1} enhanced the TCAA degradation rate from 53.5% to 83.9% at 180 min. The enhancement caused by the addition of H_2O_2 was also due to the increased production of the hydroxyl radical. Many studies (for example Kowaska *et al.* 2004; Muruganandham & Swaminathan 2004) have reported that excess hydrogen peroxide would inhibit the oxidation rate. The optimum value for the molar ratio of H_2O_2 concentration to that of target compounds is on the order of several thousands (Aleboyeh *et al.* 2008). When H_2O_2 is used in excess, it acts as a scavenger of hydroxyl radical (Equation (3)):



This phenomenon was observed in our study and differed from the case of DCAA (Chu *et al.* 2009), which showed that the removal rates of different H_2O_2 dosages (30, 40 and 50 mg l^{-1}) were almost marginal at 180 min. This can be explained if the maximum H_2O_2 dosage used to remove TCAA was over the limiting value. Figure 4(b)

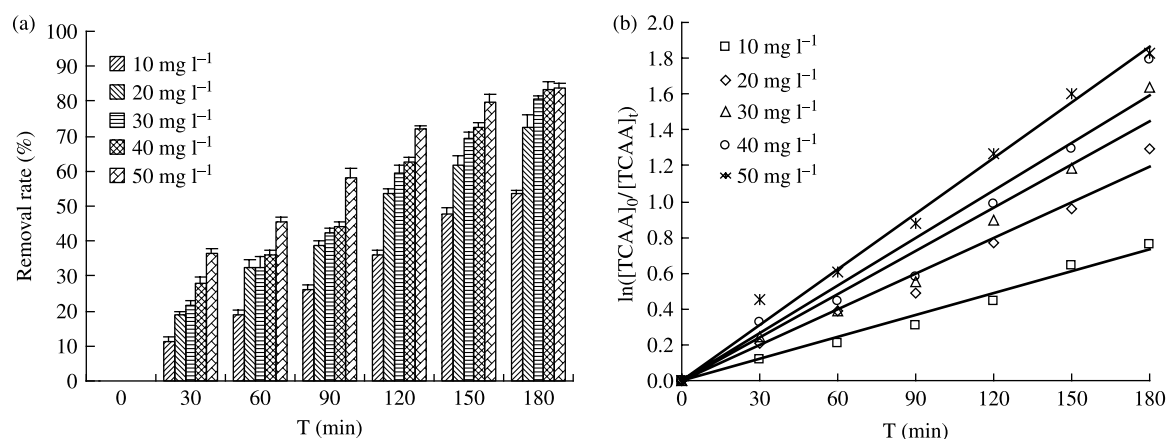


Figure 4 | Effect of initial H_2O_2 concentration on TCAA degradation. (Conditions: initial TCAA = $55.7 \pm 0.3 \mu\text{g l}^{-1}$, pH = 7, UV radiation intensity = $843.9 \mu\text{W cm}^{-2}$ for wavelength = 254 nm and UV radiation intensity = $261.6 \mu\text{W cm}^{-2}$ for wavelength = 185 nm. Error bars represent the standard deviation of experimental replicates ($n = 3$). Fitting curve is enforced to get through zero point).

shows that the TCAA degradation by UV/H₂O₂/MCA under different UV intensities followed a pseudo-first order reaction. With the increasing dosages of H₂O₂ from 10 to 50 mg l⁻¹, the pseudo-first-order rate constants were 0.0041, 0.0066, 0.0081, 0.0088 and 0.010 min⁻¹ ($R^2 > 0.95$), respectively.

Effect of initial TCAA concentration

It is necessary to study the effect of TCAA concentration on the degradation rate in UV/H₂O₂/MCA because the concentrations of TCAA occurring in drinking water vary over a wide range. Experiments were carried out at a UV radiation intensity of 843.9 $\mu\text{W cm}^{-2}$, 30 mg l⁻¹ H₂O₂ and pH 7, with the initial TCAA concentration ranging from 11.2 to 101.2 $\mu\text{g l}^{-1}$.

In general, the TCAA degradation is inhibited by the increasing initial TCAA concentration (Gao *et al.* 2009). This can be explained by the fact that the hydroxyl radical yield was constant under the same UV intensity and H₂O₂ concentration. However, the target (TCAA) concentration was increased, so that the ratio of the oxidized TCAA to total TCAA was smaller at a higher TCAA initial concentration. At the initial concentrations of 11.2, 24.7, 55.7, 77.9 and 101.2 $\mu\text{g l}^{-1}$, the TCAA degradation was a pseudo-first order reaction with the corresponding rate constants of 0.0079, 0.0077, 0.0081, 0.0092 and 0.0086 min⁻¹ ($R^2 > 0.90$). It is worthy of note that the rate constants for the initial concentrations of 11.2, 24.7, 55.7, 77.9 and 101.2 $\mu\text{g l}^{-1}$ were very close, implying that the removal rate was not changed in evidence at an initial TCAA below 100 $\mu\text{g l}^{-1}$.

Effect of initial pH

The effect of different initial pH values (4, 6, 7, 8 and 10) on UV/H₂O₂/MCA was investigated. Figure 5 shows the degradation kinetic characteristics of TCAA at different pH. The TCAA degradation by UV/H₂O₂/MCA at different pH follows pseudo-first-order kinetics. The rank order of pseudo-first-order constants for different pH is: pH 7(0.01439) > pH 6(0.01219) > pH 4(0.0099) > pH 8(0.0081) > pH 10(0.0070) ($R^2 > 0.97$).

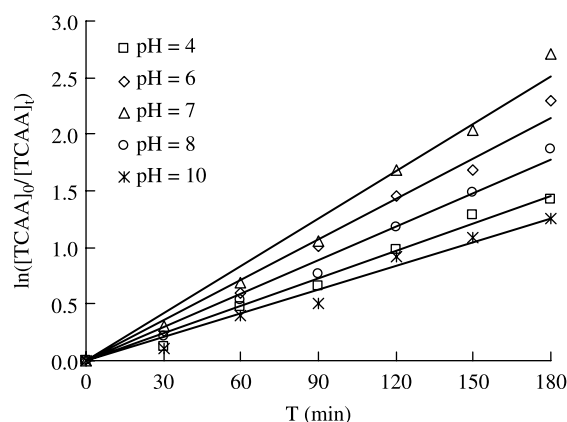


Figure 5 | Effect of initial pH on TCAA degradation. (Conditions: initial TCAA = $55.7 \pm 0.3 \mu\text{g l}^{-1}$, H₂O₂ dosage = 30 mg l⁻¹, UV radiation intensity = 843.9 $\mu\text{W cm}^{-2}$ for wavelength = 254 nm and UV radiation intensity = 261.6 $\mu\text{W cm}^{-2}$ for wavelength = 185 nm. Fitting curve is enforced to get through zero point).



Results also suggest an optimum solution pH of around 7.0 for TCAA degradation in the UV/H₂O₂/MCA combination process. In alkaline and highly acidic conditions, the degradation reaction rate of TCAA was lower than weakly acidic and neutral conditions (pH = 6, 7). In alkaline condition (pH = 8, 10), hydrolysis of H₂O₂ and ozone can generate more hydroperoxide anion (HOO⁻). A mass of hydroxyl radical is captured by HOO⁻ (Andreozzi *et al.* 2004) so that TCAA cannot be degraded effectively. Furthermore, the rate of hydrogen peroxide self-decomposition (Equation (4)) also increases strongly with increasing solution pH (Aleboyeh *et al.* 2008).

TCAA is a weakly acidic material. In strongly acidic condition (pH = 4), ionic forms of TCAA decrease, which weakens the catalytic and promotion actions of oxygen. Therefore, the better degradation effect was achieved in weakly acidic and neutral conditions.

Relationship between pseudo-first order rate constant *k* and factors

The relationship between pseudo-first order rate constant *k* and each operating factor by fitting *k* and the corresponding factor value is presented in Figure 6. The liner relationships between pseudo-first order constant *k* and pH, and between

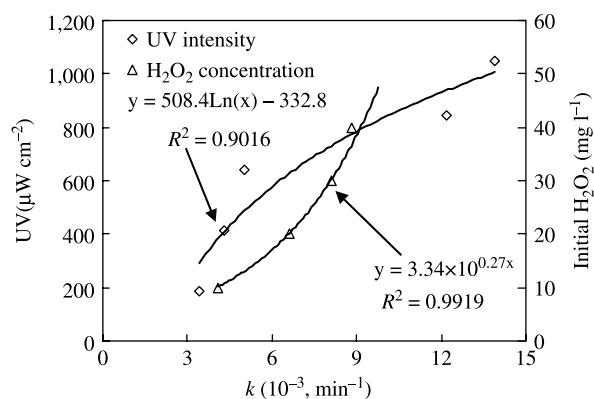
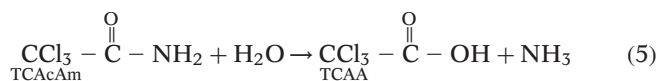


Figure 6 | Relationship between pseudo-rate constant k and each operating factor. (Fitting curve is not enforced to get through zero point).

pseudo-first order constant k and initial TCAA concentration were very poor, while pseudo-first order constant k exponentially increased with increasing H_2O_2 concentration, and was logarithmically enhanced with increased UV intensity, indicating that better removal efficiency could be achieved by improvement of both factors.

Removal of potential TCAA

A new type of halogenated nitrogenous disinfection by-product (N-DBP), haloacetamides (HAcAms), has been identified in drinking water, first quantified as part of the US nationwide DBP occurrence study (Krasner *et al.* 2006). Recently, Plewa reported that the HAcAms were $99 \times$ more cytotoxic than 13 HAAs, $142 \times$ more cytotoxic than the five regulated HAAs, $19 \times$ more genotoxic than 13 HAAs and $12 \times$ more genotoxic than the five regulated HAAs (Plewa *et al.* 2008). Among these HAcAms, trichloroacetamide (TCAcAm) occurs in higher concentrations than other brominated HAcAms and is easy to hydrolyse to form TCAA in drinking water as shown in Equation (5).



TCAA can be removed effectively by UV/ H_2O_2 /MCA, but it could regenerate by hydrolysis of TCAcAm. Therefore, to some extent TCAcAm can be called 'potential TCAA'. Removal efficiencies of TCAcAm by the UV/ H_2O_2 and UV/ H_2O_2 /MCA process were examined as shown in Figure 7.

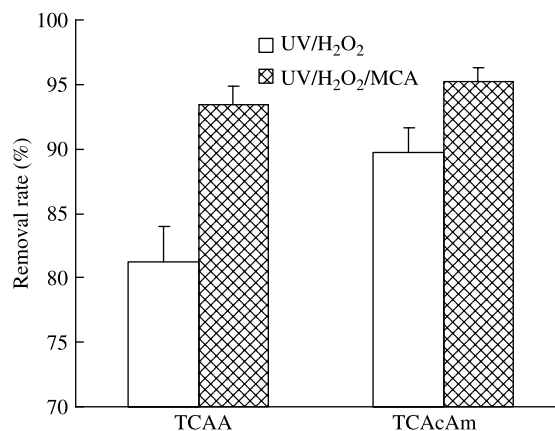


Figure 7 | Removal of potential TCAA (TCAcAm) in UV/ H_2O_2 and UV/ H_2O_2 /MCA process. (Conditions: initial TCAcAm = $35.1 \pm 0.3 \mu\text{g l}^{-1}$, H_2O_2 dosage = 30 mg l^{-1} , pH = 7, reaction time = 120 min, UV radiation intensity = $1,048.7 \mu\text{W cm}^{-2}$ for wavelength = 254 nm and UV intensity = $261.67 \mu\text{W cm}^{-2}$ for wavelength = 185 nm).

This is the first study to investigate the degradation efficiency of TCAcAm by the UV/ H_2O_2 and UV/ H_2O_2 /MCA process. The results show that 89.7% and 95.2% of TCAcAm can be degraded, respectively, by the UV/ H_2O_2 and UV/ H_2O_2 /MCA process within 120 min, which implied that TCAA is more recalcitrant than TCAcAm and difficult to regenerate from TCAcAm after removal.

Preliminary cost analysis

According to the results in Figure 2, a comparison of the projected operating costs between the UV/ H_2O_2 and UV/ H_2O_2 /MCA process for removal of TCAA was carried out as shown in Table 2. The operating costs per unit mass removed TCAA (dollar mg^{-1} TCAA removed) consist of expenditures for power consumption and purchasing H_2O_2 (Gao *et al.* 2009). The estimated unit cost of H_2O_2 and power are 0.00218 dollars g^{-1} (0.495 dollars/lb for 50% purity) (Chemical Market Reporter 2003), and 0.10 dollars kWh^{-1} (Englehardt *et al.* 2006), respectively.

To compare the two individual processes, 62.7% of TCAA removal efficiency, the highest achieved by the UV/ H_2O_2 process within 180 min, was selected as the final removal efficiency. The estimated reaction time required for the UV/ H_2O_2 /MCA process with 30 mg l^{-1} H_2O_2 dosage and $56 \mu\text{g l}^{-1}$ TCAA concentration was about 120 min. It is apparent that introduction of MCA shortened the reaction times through the production of more hydroxyl

Table 2 | Cost comparison between UV/H₂O₂ and UV/H₂O₂/MCA process for removal of TCAA*

Process	UV power (W)	H ₂ O ₂ dosage (mg l ⁻¹)	MCA power (W)	Estimated reaction time (min)	Total cost (dollars)	Cost per unit mass removed TCAA (dollars mg ⁻¹) [†]
UV/H ₂ O ₂	150 [‡]	30 [‡]	0	180	0.0453	1.30
UV/H ₂ O ₂ /MCA	150	30	10	120	0.0323	0.93

*Initial TCAA concentration = 55.7 µg l⁻¹, reaction times were those when 62.7% of TCAA removal efficiencies were achieved (62.7% was the highest removal achieved by UV/H₂O₂ process within 180 min), and the volume of reaction solution was 5 l.

[†]Total power of five UV lamps.

[‡]Assume 0.00218 dollar g⁻¹ H₂O₂, and 0.10 dollar kWh⁻¹.

radicals and synergetic and promotion action. As shown in Table 2, the projected operating cost of the UV/H₂O₂/MCA process was about 0.93 dollars mg⁻¹ TCAA removed, below the projected cost of the UV/H₂O₂ process, 1.30 dollars mg⁻¹ TCAA removed. As a result, the UV/H₂O₂/micro-aeration appeared to be more cost-effective than the UV/H₂O₂ process.

CONCLUSIONS

Compared with direct UV photolysis, H₂O₂ oxidation and MCA processes, the UV/H₂O₂/MCA process was effective at degrading aqueous TCAA and TCACAm. Removal rate of TCAA was strongly affected by UV radiation intensity, H₂O₂ dose and solution pH, but appeared to be slightly influenced by initial TCAA concentration. The degradation of TCAA follows pseudo-first order kinetics and pseudo-rate constant *k* was also affected by UV insensitivity, initial H₂O₂ concentration and solution pH except initial TCAA concentration. There was a logarithmic and exponential relationship, respectively, between rate constant *k* and UV intensity, and between rate constant *k* and initial H₂O₂ concentration, indicating that higher removal capacity can be achieved by improvement of both factors. TCACAm, the potential TCAA, was less recalcitrant than TCAA in the UV/H₂O₂ and UV/H₂O₂/MCA processes, which implied that TCAA cannot regenerate by hydrolysis of TCACAm. Based on a preliminary operating cost analysis, the UV/H₂O₂/MCA process was cost-effective compared with UV/H₂O₂ in degradation of TCAA in drinking water. Therefore, it appears to be a promising technology in the removal of aqueous HAAs.

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