



## Experimental and model comparisons of H<sub>2</sub>O<sub>2</sub> assisted UV photodegradation of Microcystin-LR in simulated drinking water\*

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**Abstract:** The degradation of Microcystin-LR (MC-LR) in water by hydrogen peroxide assisted ultraviolet (UV/H<sub>2</sub>O<sub>2</sub>) process was investigated in this paper. The UV/H<sub>2</sub>O<sub>2</sub> process appeared to be effective in removal of the MC-LR. MC-LR decomposition was primarily ascribed to production of strong and nonselective oxidant-hydroxyl radicals within the system. The intensity of UV radiation, initial concentration of MC-LR, MC-LR purity, dosages of H<sub>2</sub>O<sub>2</sub>, the initial solution pH, and anions present in water, to some extent, influenced the degradation rate of MC-LR. A modified pseudo-first-order kinetic model was developed to predict the removal efficiency under different experimental conditions.

**Key words:** Microcystin-LR (MC-LR), Hydrogen peroxide assisted ultraviolet (UV/H<sub>2</sub>O<sub>2</sub>) process, Hydroxyl radical, Reaction kinetics, Photochemical degradation

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### INTRODUCTION

Eutrophication frequently occurs in lakes and drinking-water reservoirs. Cyanobacterial toxins released by cyanobacteria in freshwater are well documented. There is a group of at least 70 hepatotoxic peptides produced primarily by freshwater cyanobacteria belonging to the genera *Microcystis*, *Anabaena*, *Nostoc* and *Oscillatoria* (Codd, 2000). Among this family of congeners, Microcystin-LR (MC-LR) is the most common and toxic to plants, animals, and humans. MCs can bioaccumulate in various aquatic organisms including mussels, water snails, crusta-

ceans and fish (Amorim and Vasconcelos, 1999; Ozawa *et al.*, 2003), probably leading to the death of these animals and adversely affecting human health. Chronic exposure to these toxins can cause tumor promotion due to the first-pass effect. Acute exposure to MCs causes severe liver damage (e.g., massive intrahepatic haemorrhage, and liver swelling) and even death (Kurki-Helasma and Meriluoto, 1998; Ito *et al.*, 2002). These negative effects of MCs on public health have prompted intensive research on development of effective and reliable technologies to remove them during water purification. MCs are chemically stable under high temperature and at acidic-alkaline condition (Dawson, 1998). In field conditions, chemical or biological degradation of MCs is very slow (Cousins *et al.*, 1996). Conventional water treatment processes cannot adequately remove these toxins. Although a high dose of chlorine can achieve a high removal efficiency of MCs, it brings the increase of chlorination by products, such

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as trihalomethanes (THMs), haloacetic acids (HAAs) halonitromethanes (HNMs), and nitrosodimethyl amines (NDMA) (Lawton and Robertson, 1999). Successful technologies to remove most aqueous organic pollutants, advanced oxidation processes (AOPs) were studied to degrade MCs (Rositano *et al.*, 1998; Gajdek *et al.*, 2001; Liu *et al.*, 2002; Hoeger *et al.*, 2002; Lawton *et al.*, 2003; Qiao *et al.*, 2005; Brooke *et al.*, 2006). Although ozonation is able to rapidly decompose MC-LR, the capital and operational costs are prohibitive, and the risk of bromate production is a concern. Moreover, ozone can only degrade macromolecular organic compounds into small organic molecules; its mineralization ability is lower than other advanced oxidation processes. As a result, ozone oxidation is usually used with the combination of an activated carbon filtration process (Hoeger *et al.*, 2002; Brooke *et al.*, 2006). TiO<sub>2</sub>-catalyzed UV irradiation can quickly remove the MC, but an only slightly decrease of protein phosphatase 1 (PP1) inhibition is up to 20 min reaction time, about 20% inhibition remained after 60 min, and the addition of H<sub>2</sub>O<sub>2</sub> made the PP1 inhibition decrease to 15% of the initial level within 5 min (Lawton *et al.*, 2003). Besides, the separation and reuse of nano-TiO<sub>2</sub> are difficult and uneconomical. Fenton reagents may decompose MCs into a variety of by-products, but the iron sludge produced has to be disposed of and the residual iron ion in water may exceed water quality regulations (Gajdek *et al.*, 2001).

Because of its significantly high disinfection efficacy against a wide range of waterborne pathogens, UV is widely used for water treatment in Europe, and is currently gaining more and more attention in the USA (Qian *et al.*, 2004). Typically, a combined UV/H<sub>2</sub>O<sub>2</sub> process is more practical owing to involving a single-step dissociation of hydrogen peroxide to form two hydroxyl radicals ( $\cdot\text{OH}$ ) (Qiao *et al.*, 2005). The hydroxyl radicals generated can non-selectively oxidize a broad variety of aqueous organic pollutants. Over the past decades, the process has been ascribed to successful decomposition of dyes and pharmaceutical intermediates (Kurbus *et al.*, 2003; Lopez *et al.*, 2003; Shu *et al.*, 2004). Under appropriate conditions, the organic species can be mineralized without any secondary pollution. In addition, the UV/H<sub>2</sub>O<sub>2</sub> system possesses other advantages, such as no phase transfer, no sludge formation, simplicity of operation, and thus low operational costs

(Colonna *et al.*, 1999). Currently, numerous commercial UV/H<sub>2</sub>O<sub>2</sub> processes have been applied to the treatment of drinking water originating from groundwater and reservoirs.

In previous studies, the UV/H<sub>2</sub>O<sub>2</sub> process was demonstrated to effectively degrade MC-LR (Qiao *et al.*, 2005). However, the impacts of several important factors, such as common anions present in water, on the overall treatment efficiency have not been fully evaluated, and appropriate kinetic data has not been well developed. In this study, the effects of the UV radiation intensity, the MC-LR initial concentration, the MC-LR purity, H<sub>2</sub>O<sub>2</sub> dosage, the initial solution pH, and anions present in water on MC-LR degradation were investigated. A modified pseudo-first-order kinetic model was developed to predict the removal efficiency under different experimental conditions.

## EXPERIMENTAL

### Material and analysis

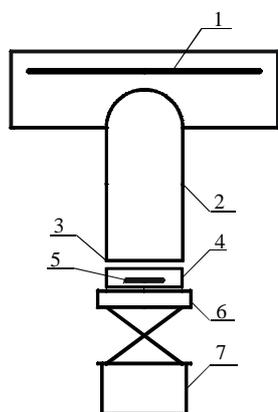
Deionized water was produced using Milli-Q-Water (Millipore, Molsheim, France). H<sub>2</sub>O<sub>2</sub> (30%, v/v) was purchased from Sinopharm Chemical Reagent Co. Ltd., China. AR grade NaOH and HCl were used to adjust the solution pH. The solutions containing different anions including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and SO<sub>4</sub><sup>2-</sup> were made through dissolving AR grade NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> into certain amounts of deionized water, respectively. *Microcystis aeruginosa* was collected from the Lake Taihu in China. The alga solution was centrifuged, dried, and then grounded to powder. The algal powder was dispersed in the deionized water, subsequently frozen in an icebox at -18 °C for 12 h, and thawed at room temperature ((15±2) °C). The freezing and thawing procedure was repeated three times, and the sample was then centrifuged at 10 000 r/min for 10 min (CT15RT, Techcomp, Shanghai, China). The supernatant was filtered through a 0.45-μm cellulose acetate membrane (Xinya, Shanghai, China). The crude MC extract was preconcentrated on a C-18 Sep-pack cartridge under a suction filtration at a rate of 10 ml/min. The cartridge was conditioned with 10 ml of CH<sub>3</sub>OH, followed by 10 ml of deionized water, and then was washed with 10 ml of 5% (v/v) CH<sub>3</sub>OH. The toxin was eluted using 10 ml 100% (v/v) CH<sub>3</sub>OH. The elutant was collected, and then rotary-evaporated to

dryness at 40 °C. Identity was confirmed by high performance liquid chromatography (HPLC) (2010AHT, Shimadzu, Japan) comparison to a standard sample (Sigma-Aldrich). HPLC consists of an SIL-auto-injector auto-sampler with the volume injection set to 100  $\mu$ L, Shimadzu VP-ODS column (250 mm $\times$ 4.6 mm), and a UV detector at 238 nm. The mobile phase consisted of methanol (Sigma-Aldrich, USA) and deionized water with a ratio of methanol/H<sub>2</sub>O (0.05% trifluoroacetic acid, v/v) of 60/40 (v/v). The flow rate was 1 ml/min, and the column temperature was controlled at 40 °C. The solution total organic carbon (TOC) was determined by a TOC-V<sub>CPH</sub> (Shimadzu, Japan). Purities ( $m_{\text{MC-LR}}/\text{TOC}$ , where  $m_{\text{MC-LR}}$  is calculated as the carbon) of crude extracts and solid phase extraction (SPE) purified compound were 0.19% and 4.1% respectively, the colors of the crude extracts and SPE purified solution were slightly blue and yellow, respectively.

### Experimental procedure

The photoreactor was a completely mixed batch reactor. The schematic diagram of the experimental system is shown in Fig.1. The system consisted of a UV lamp (wavelength is 253.7 nm, power is 75 W), lampshade used to parallel the light, baffle, reactor, magnetic stirring apparatus and rest pier. The UV light intensity was controlled by the baffle with helix angle 45°, 90°, 180° and 360° fixed at the bottom of the lampshade. All the experiments were carried out at (15 $\pm$ 2) °C.

This study was conducted in the following



1: UV lamp; 2: lampshade; 3: baffle; 4: reactor; 5: rotator; 6: magnetic stirring apparatus; 7: rest pier

Fig.1 Schematic description of the UV/H<sub>2</sub>O<sub>2</sub> reactor

conditions: (1) side-by-side tests to compare oxidation of MC-LR with UV radiation alone, H<sub>2</sub>O<sub>2</sub> alone, and UV/H<sub>2</sub>O<sub>2</sub>; (2) investigation of effects of different impacting factors, including H<sub>2</sub>O<sub>2</sub> dosage (0~3 mmol/L), MC-LR purity (crude extracts, SPE purified and standard sample), UV intensity (19.12~153  $\mu$ W/cm<sup>2</sup>), anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and SO<sub>4</sub><sup>2-</sup> concentrations of 10 mmol/L), and initial pH (3.13~11.55). Reactions were initiated by adding H<sub>2</sub>O<sub>2</sub> into the photoreaction under the UV irradiation. At the sampling times, 0.5 ml samples were collected for sample analysis in duplicate. Finally, the reactions were quenched by addition of sodium sulfite. The standard deviations of all the measured data were less than 5%.

## RESULTS AND DISCUSSIONS

### Effect of H<sub>2</sub>O<sub>2</sub> dosage

A set of side-by-side tests were conducted to compare the MC-LR removal rates in UV alone, H<sub>2</sub>O<sub>2</sub> alone, and UV/H<sub>2</sub>O<sub>2</sub> (Fig.2). The MC-LR concentration did not decrease when only H<sub>2</sub>O<sub>2</sub> was used, implying that MC-LR was not amenable to the oxidation by H<sub>2</sub>O<sub>2</sub> alone. The UV alone achieved ca. 85% of MC-LR removal within 90 min, while the UV/H<sub>2</sub>O<sub>2</sub> remarkably increased the degradation rate to >95% at 32 min.

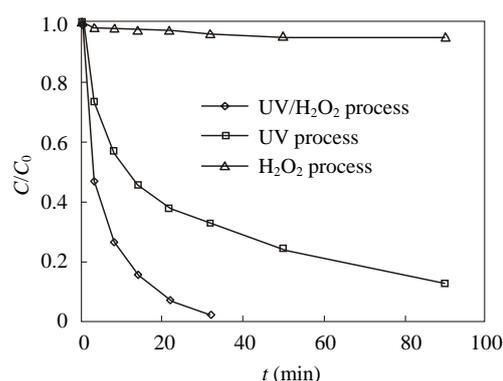
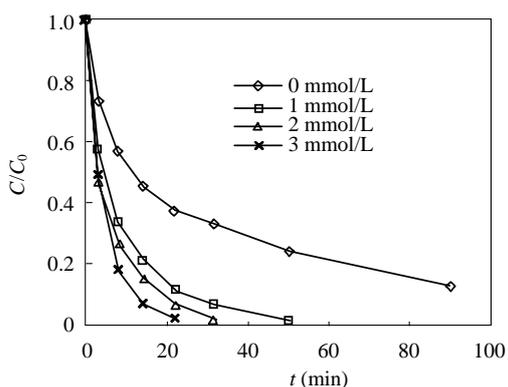


Fig.2 Degradation of MC-LR by UV, H<sub>2</sub>O<sub>2</sub> alone and UV/H<sub>2</sub>O<sub>2</sub> process ( $C_0=0.15$  mg/L, where  $C_0$  is initial MC-LR concentration, UV radiation intensity is 153  $\mu$ W/cm<sup>2</sup>, pH=7.2, H<sub>2</sub>O<sub>2</sub> concentration is 2 mmol/L)

The effect of the H<sub>2</sub>O<sub>2</sub> dosages on the MC-LR degradation is shown in Fig.3. Within 22 min, the residual MC-LR decreased from 0.124 to 0.028 with

the increasing initial  $\text{H}_2\text{O}_2$  concentration from 1 to 3 mmol/L. The degradation of MC-LR was ascribed to the generation of hydroxyl radicals upon photolysis of hydrogen peroxide through Eqs.(1) and (2):



**Fig.3** Effect of different initial concentrations of  $\text{H}_2\text{O}_2$  on the degradation of MC-LR by the UV/ $\text{H}_2\text{O}_2$  process ( $C_0=0.15$  mg/L, UV radiation intensity is  $153 \mu\text{W}/\text{cm}^2$ , pH=7.2)

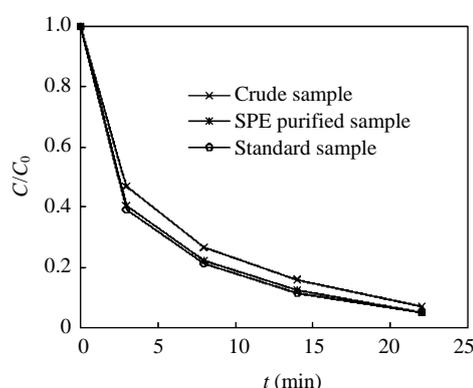
Generally, at a low  $\text{H}_2\text{O}_2$  concentration, the removal efficiency was limited by inadequate hydroxyl radicals produced, while a too high concentration of  $\text{H}_2\text{O}_2$  could inhibit the degradation rate, since excess  $\text{H}_2\text{O}_2$  scavenges hydroxyl radicals produced (Muruganandham and Swaminathan, 2004). In this study, the inhibiting effect of a high  $\text{H}_2\text{O}_2$  dose was not observed, probably because the  $\text{H}_2\text{O}_2$  concentration did not reach the level that can decrease the net amount of hydroxyl radicals.

### Effect of MC-LR purity

A large amount of dissolved pigments contributed to the blue of the crude MC extract solution. In addition, other algae organic materials might exist in the crude MC solution. Therefore, it is necessary to understand the effect of the MC-LR purity on MC-LR degradation. In this study, three samples with different purities of MC-LR were used: crude extracts, SPE purified and standard sample, of which the purities ( $m_{\text{MC-LR}}/\text{DOC}$  (dissolved organic carbon)) were 0.33%, 4.1% and 99.5%, respectively.

The effect of MC-LR purity on the degradation is shown in Fig.4, the initial and residual DOC of crude extracts and SPE purified sample are given in

Table 1. A significant difference in the MC-LR removal rates of the three MC-LR samples was not observed, although they had much different TOC background levels. Within 22 min, the residual MC-LR of the crude sample, SPE purified sample, and standard sample steadily decreased to 0.087, 0.050, to 0.043, respectively. The MC-LR purity did not significantly affect the MC-LR removal rate. It was speculated that the degradation of MC-LR could be enhanced by some algae organic such as phycocyanin pigment (Robertson *et al.*, 1999), while the other compounds inhibited the degradation reaction.



**Fig.4** Effect of MC-LR purity on the degradation by UV/ $\text{H}_2\text{O}_2$  process ( $C_0=0.15$  mg/L, UV radiation intensity is  $153 \mu\text{W}/\text{cm}^2$ ,  $T=(15\pm 2)^\circ\text{C}$ , pH=7.2,  $\text{H}_2\text{O}_2$  concentration is 2 mmol/L)

**Table 1** Initial and residual DOC of crude extracts and SPE purified sample

	Initial DOC (mg/L)	Residual DOC (mg/L)	DOC removal rate
Crude extracts	46.7	41.2	12%
SPE purified sample	3.68	3.69	0%

### Effect of UV radiation intensity

The effect of UV radiation intensity on the degradation of MC-LR is shown in Fig.5. Within 22 min, the residual MC-LR gradually decreased from 0.452 to 0.043 with increasing UV radiation intensity from 19.13 to  $153 \mu\text{W}/\text{cm}^2$ . The observation was attributed to the augmentation in the amount of hydroxyl radicals with the increasing UV intensity. According to Eq.(1), the rate of  $\text{H}_2\text{O}_2$  photolysis was directly related to the UV intensity. High UV intensity caused more hydroxyl radicals to be produced, while low UV intensity limited the photolysis of  $\text{H}_2\text{O}_2$ .

### Effect of initial algae extract concentration

The effect of initial algae extract concentration is shown in Fig.6. When the initial MC-LR concentration increased from 76.1 to 303.4  $\mu\text{g/L}$ , the residual MC-LR was increased correspondingly from 0.058 to 0.368 within 14 min. A high concentration of MC-LR caused a high internal optical density, leading to the high impermeability of the solution to UV radiation. Consequently, less UV light was absorbed by hydrogen peroxide, and fewer hydroxyl radicals were produced (Aleboyeh *et al.*, 2005). The UV transparencies in solutions with different algae extract concentrations are shown in Table 2. Moreover, a high concentration of MC-LR also produced high levels of a variety of intermediate by-products that might greatly compete hydroxyl radicals with MC-LR during the course of the treatment process.

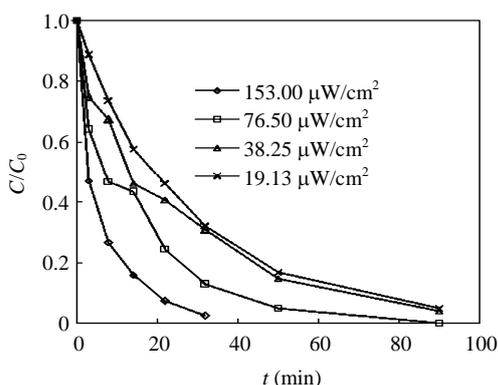


Fig.5 Effect of different intensities of UV radiation on the degradation of MC-LR by UV/H<sub>2</sub>O<sub>2</sub> process ( $C_0=0.15$  mg/L,  $T=(15\pm 2)$  °C, pH=7.2, H<sub>2</sub>O<sub>2</sub> concentration is 2 mmol/L)

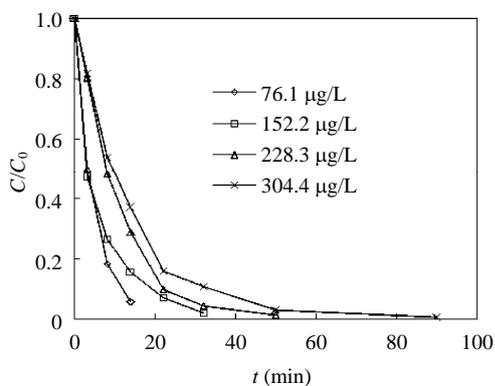


Fig.6 Effect of different initial algal extract concentrations on the degradation of MC-LR by the UV/H<sub>2</sub>O<sub>2</sub> process (UV radiation intensity is 153  $\mu\text{W/cm}^2$ ,  $T=(15\pm 2)$  °C, pH=7.2, H<sub>2</sub>O<sub>2</sub> concentration is 2 mmol/L)

Table 2 The UV transparencies in solutions with different algae extract concentrations

$C_{\text{MC-LR}}$ ( $\mu\text{g/L}$ )	$I_s$ ( $\mu\text{W/cm}^2$ )	$I_b$ ( $\mu\text{W/cm}^2$ )	UV transparency (%)
76.1	153.0	128.2	83.8
152.2	153.0	107.6	70.3
228.3	153.0	90.0	58.8
304.4	153.0	75.6	49.4

$C_{\text{MC-LR}}$ : concentration of MC-LR;  $I_s$ : UV intensity on solution surface;  $I_b$ : UV intensity on solution bottom

### Effects of anions

The effects of the different anions typically found in natural water, including carbonate ( $\text{CO}_3^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ), are shown in Fig.7.  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  obviously slowed the MC-LR degradation, but  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  exhibited a negligible inhibiting effect. Based on the ANOVA analysis, the sequence of significance of the four inorganic anions was  $\text{CO}_3^{2-} > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ .

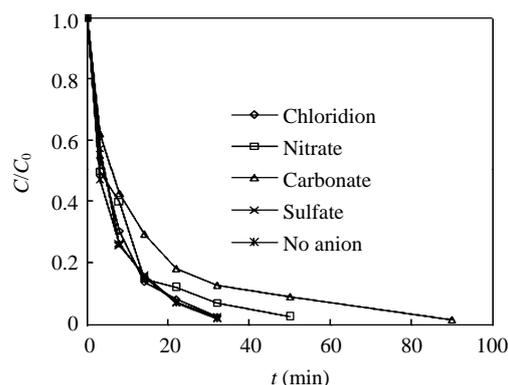
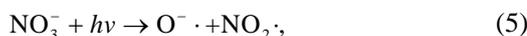
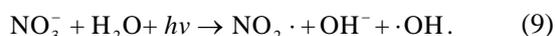


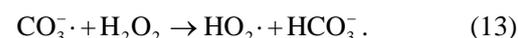
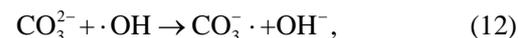
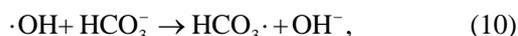
Fig.7 Effect of different anions on the degradation of MC-LR by UV/H<sub>2</sub>O<sub>2</sub> process ( $C_0=0.15$  mg/L, UV radiation intensity is 153  $\mu\text{W/cm}^2$ ,  $T=(15\pm 2)$  °C, pH=7.2, H<sub>2</sub>O<sub>2</sub> concentration is 2 mmol/L, negative ion concentration is 10 mmol/L)

The role of  $\text{NO}_3^-$  in the solution was two-fold. It could produce additional  $\text{HO}\cdot$  under UV irradiation as shown in Eqs.(4)~(9). However, the enhancement effect of  $\text{HO}\cdot$  production became insignificant at the neutral pH used in this study. On the other hand,  $\text{NO}_3^-$  could act as an "inner filter" and reduce the UV light intensity in the photoreactor (Sorensen and Frimmel, 1997). As a result,  $\text{NO}_3^-$  inhibited the MC-LR decomposition rate.





After addition of  $\text{CO}_3^{2-}$  to water, the dominant species would become bicarbonate ( $\text{HCO}_3^-$ ) at equilibrium within the carbonate system. Both bicarbonate and carbonate are well-known scavengers of  $\text{HO} \cdot$  (Liao and Gurol, 1995). They are able to quickly compete hydroxyl radicals with MC-LR, as shown in Eqs.(10)~(13). Consequently, the MC-LR degradation was slowed.

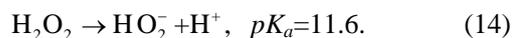


### Effect of pH

The effect of initial solution pH on the degradation of MC-LR is illustrated in Fig.8. Within 22 min, the residual MC-LR was increased from 0.019 to 0.258 with the increasing pH from 3.13 to 11.55. Particularly, the solution pH slightly dropped over the reaction time as shown in Fig.9. The extent of pH drop within 50 min decreased with the decreasing initial pH. The maximum pH drop of ca. 1.00 occurred at the initial pH of 11.47, while the minimum pH drop was almost zero at the initial pH of 3.13. The negative effect of high pH on MC-LR decomposition may be ascribed to the following aspects.

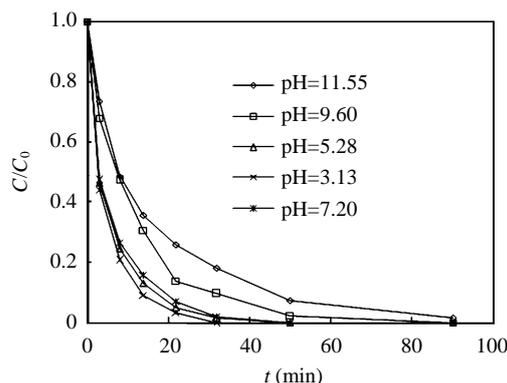
(1) High alkalinity at high pH could inhibit MC-LR degradation since high concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  would rapidly compete hydroxyl radicals as the scavengers (Eqs.(10)~(13)).

(2) At alkaline conditions, the level of  $\text{HO}_2^-$  and the conjugate base of  $\text{H}_2\text{O}_2$  increased and can be expressed as Eq.(14):

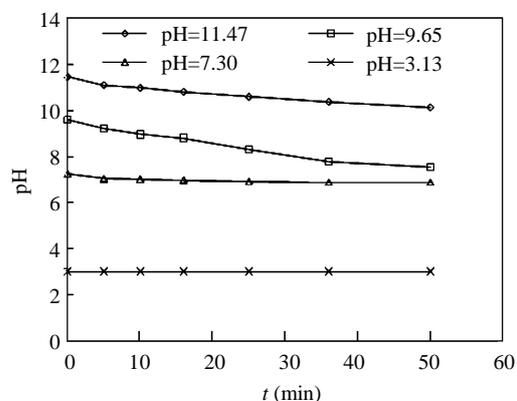


Although  $\text{HO}_2^-$  had a higher cross-section (240 mol/cm) at 254 nm than that of  $\text{H}_2\text{O}_2$  (18.6 mol/cm), which favored the absorption of UV light by the re-

active species and enhanced production of  $\text{OH} \cdot$ ,  $\text{HO}_2^-$  could rapidly react with  $\text{OH} \cdot$  and played a stronger  $\text{OH} \cdot$  scavenger than  $\text{H}_2\text{O}_2$  (Eqs.(15) and (16)) (Beltran *et al.*, 1996).



**Fig.8** Effect of pH on the degradation of MC-LR by UV/ $\text{H}_2\text{O}_2$  process ( $C_0=0.15$  mg/L, UV radiation intensity is  $153 \mu\text{W}/\text{cm}^2$ ,  $T=(15 \pm 2)^\circ\text{C}$ ,  $\text{pH}=7.2$ ,  $\text{H}_2\text{O}_2$  concentration is 2 mmol/L)



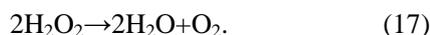
**Fig.9** pH change of the solution with the time

(3) de Maagd *et al.*(1999) reported that relative hydrophobicity of MC-LR depends on pH, with the compound having greater  $\text{lg}_{\text{Dow}}$  (octanol/water distribution ratio) values under acidic conditions. The removal rate (with 22 min) and hydrophobicity ( $\text{lg}_{\text{Dow}}$ ) of MC-LR were listed in Table 3. It was observed that the fastest degradation occurs under the acidic condition (Table 3). It may be explained that the MC-LR could be more easily localized at the surface of other organic compounds such as pigments in acidic condition and more easily give access to the hydroxyl radicals generated by the photocatalysis.

**Table 3** Degradation rates and  $\lg_{\text{Dow}}$  of MC-LR at various solution pH

pH of the solution	Removal rate (%)	$\lg_{\text{Dow}}$
3.13	98.1	1.1
5.28	97.2	-0.1
7.20	96.5	-1.1
9.60	86.3	-1.7

(4) High pH can accelerate the self-decomposition of  $\text{H}_2\text{O}_2$  into water and oxygen.



In practice,  $\text{H}_2\text{O}_2$  is supplied at slightly acid condition (pH=5) because an alkaline condition causes its rapid self-decomposition. For example, the first order reaction rate constants of  $\text{H}_2\text{O}_2$  self-decomposition were determined to be  $2.29 \times 10^{-2}$  and  $7.40 \times 10^{-2} \text{ min}^{-1}$  at pH=7 and 10.5, respectively (Chu, 2001).

### Kinetics model of the MC-LR degradation

Hydroxyl radicals produced within the UV/ $\text{H}_2\text{O}_2$  system can react with MC-LR,  $\text{H}_2\text{O}_2$ , and other species such as some intermediates. Therefore, the  $\cdot\text{OH}$  concentration can be expressed as (Benitez *et al.*, 1996)

$$c_{\cdot\text{OH}} = \frac{\varphi' W'_{\text{abs}}}{k_i c_{\text{MC-LR}} + k_h c_{\text{H}_2\text{O}_2} + k_s c_s}, \quad (18)$$

where  $c_{\text{MC-LR}}$ ,  $c_{\text{H}_2\text{O}_2}$ ,  $c_{\cdot\text{OH}}$ ,  $c_s$  are the molar concentrations of MC-LR,  $\text{H}_2\text{O}_2$ ,  $\cdot\text{OH}$  and S, S is all the other species within the UV/ $\text{H}_2\text{O}_2$  system that can react with  $\cdot\text{OH}$ ;  $\varphi'$  is the quantum yield of hydrogen peroxide disappearance;  $W'_{\text{abs}}$  is the rate of light absorption of hydrogen peroxide;  $k_i$ ,  $k_h$ , and  $k_s$  are the reaction rate constants of the reactions of MC-LR,  $\text{H}_2\text{O}_2$ , and S with  $\cdot\text{OH}$ .

The MC-LR removal rate in a completely mixed batch reactor (CMBR) can be expressed in the following ordinary differential equation:

$$-\frac{dc_{\text{MC-LR}}}{dt} = k c_{\cdot\text{OH}}^m c_{\text{MC-LR}}^n, \quad (19)$$

where  $k$  is the overall rate constant;  $m$  and  $n$  is the reaction order for  $\cdot\text{OH}$  and MC-LR, respectively.

Since  $\cdot\text{OH}$  is highly reactive, its concentration can change rapidly in response to solution conditions. In such situation,  $\cdot\text{OH}$  is assumed under a pseudo steady state, that is,  $m=0$ . Therefore, Eq.(19) can be transformed into:

$$-\frac{dc_{\text{MC-LR}}}{dt} = k_1 c_{\text{MC-LR}}^n. \quad (20)$$

In this study, three kinetics models were used to fit the experimental data. First, the pseudo-first-order model ( $n=1$ ) is shown in Eq.(21).

$$-\frac{dc_{\text{MC-LR}}}{dt} = k_1 c_{\text{MC-LR}}. \quad (21)$$

After integration, we have

$$c_{\text{MC-LR}} = c_{0\text{MC-LR}} e^{-k_1 t}. \quad (22)$$

Then, the second order model ( $n=2$ ) is shown as

$$-\frac{dc_{\text{MC-LR}}}{dt} = k_2 c_{\text{MC-LR}}^2. \quad (23)$$

After integration, we obtain

$$\frac{1}{c_{\text{MC-LR}}} = k_2 t + \frac{1}{c_{0\text{MC-LR}}}. \quad (24)$$

Third, a modified first-order model ( $n=1$ ), in which the rate constant  $k$  in the pseudo-first-order reaction was decreased with the reaction time, because of the gradual decrease of  $\text{H}_2\text{O}_2$  dosage and the accumulation of hydroxyl radical scavengers such as the carbonate (or bicarbonate) and intermediate oxidation products. In this study,  $k$  was assumed to linearly decrease with the reaction time  $t$ , and a modified first-order kinetics equation was established as

$$\frac{dc_{\text{MC-LR}}}{dt} = -(a - bt) c_{\text{MC-LR}}, \quad (25)$$

here,  $a$  and  $b$  are constants.

After integration, we have

$$c_{\text{MC-LR}} = c_{0\text{MC-LR}} e^{-k_3 t(1-k_4 t)}, \quad (26)$$

where  $k_3=a$ ,  $k_4=b/(2a)$ .

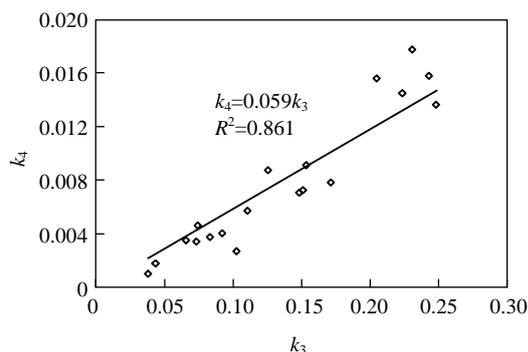
In the third model, the overall reaction rate was determined by two constants,  $k_3$  and  $k_4$ .  $k_3$  represented the initial reaction rate constant which was positively related to UV density, initial  $\text{H}_2\text{O}_2$  dosage, and initial solution pH.  $k_4$  represented the decrease extent of the reaction rate with time, which was affected by decrease of the  $\text{H}_2\text{O}_2$  dosage, accumulation of hydroxyl radical scavengers such as the carbonate (or bicarbonate) and intermediate oxidation products. It seems that when  $k_3$  is relatively low, the consumption rate of

$\text{H}_2\text{O}_2$  and the accumulation rate of  $\text{CO}_3^{2-}$  ( $\text{HCO}_3^-$ ) intermediate oxidation products are consequently low. So, it assumed that there is some positive correlation between  $k_3$  and  $k_4$ . Kinetic parameters in the three kinetics models were computed based on the kinetic data under different reaction conditions, as summarized in Table 4.

The mean  $R^2$  in the three models are 0.927, 0.827, and 0.982, respectively. Apparently, the modified pseudo-first-order kinetic model best fits the experimental model due to its highest mean  $R^2$ . In the UV/ $\text{H}_2\text{O}_2$  system, the plot of  $k_3$  and  $k_4$  is shown in Fig.10. As assumed, a linear relationship of  $k_3$  and  $k_4$  was observed with the equation of  $k_4=0.0595k_3$  ( $R^2=0.861$ ).

**Table 4 Determination of kinetic parameters within different models**

Factor	Reaction condition	$c_{\text{MC-LR}} = c_{0\text{MC-LR}} e^{-k_3 t}$		$\frac{1}{c_{\text{MC-LR}}} = k_2 t + \frac{1}{c_{0\text{MC-LR}}}$		$c_{\text{MC-LR}} = c_{0\text{MC-LR}} e^{-k_3 t(1-k_4 t)}$		
		$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\times 10^{-6} \text{min}^{-1}$ )	$R^2$	$k_3$ ( $\text{min}^{-1}$ )	$k_4$ ( $\text{min}^{-1}$ )	$R^2$
UV alone								
UV intensity ( $\mu\text{W}/\text{cm}^2$ )	153.00	0.0266	0.8121	2.75	0.9847	0.0450	0.0056	0.9378
	76.50	0.0203	0.5250	1.50	0.8738	0.0407	0.0050	0.9202
	38.25	0.0143	0.8099	0.84	0.9627	0.0250	0.0059	0.9861
UV/ $\text{H}_2\text{O}_2$								
$\text{H}_2\text{O}_2$ dosage (mmol/L)	1	0.0844	0.9578	28.23	0.7581	0.1101	0.0058	0.9833
	2	0.1238	0.9687	38.69	0.7433	0.1505	0.0073	0.9756
	3	0.1664	0.9542	50.18	0.8914	0.2425	0.0158	0.9998
MC-LR purity	Crude extract	0.1238	0.9687	38.69	0.7433	0.1505	0.0073	0.9756
	SPE purified	0.1451	0.9447	31.50	0.9154	0.2048	0.0156	0.9826
	Standard sample	0.1544	0.9327	36.31	0.9386	0.2300	0.0178	0.9869
MC-LR concentration ( $\mu\text{g}/\text{L}$ )	76.1	0.2060	0.9975	70.42	0.8707	0.2474	0.0137	0.9999
	228.3	0.0911	0.9937	27.47	0.7412	0.1021	0.0027	0.997
	304.4	0.0597	0.9604	18.82	0.7890	0.0825	0.0038	0.9983
Initial pH	11.55	0.0481	0.9558	8.261	0.8851	0.0650	0.0036	0.9900
	9.60	0.0764	0.9822	22.74	0.7657	0.0915	0.0041	0.9919
	5.28	0.1354	0.9740	54.69	0.7623	0.1712	0.0079	0.9900
	3.13	0.1629	0.9646	42.06	0.8632	0.2226	0.0145	0.9934
Inorganic anions	$\text{Cl}^-$	0.1158	0.9647	27.37	0.8090	0.1529	0.0092	0.9882
	$\text{NO}_3^-$	0.0814	0.8773	20.30	0.8583	0.1250	0.0087	0.9638
	$\text{CO}_3^{2-}$	0.0488	0.8725	15.53	0.8112	0.0740	0.0047	0.9566
	$\text{SO}_4^{2-}$	0.1205	0.9759	36.50	0.7641	0.1481	0.0071	0.9875
UV intensity ( $\mu\text{W}/\text{cm}^2$ )	153.00	0.1238	0.9687	38.69	0.7433	0.1505	0.0073	0.9756
	76.50	0.0625	0.9758	11.20	0.8310	0.0726	0.0035	0.9826
	38.25	0.0373	0.9841	8.32	0.8149	0.0430	0.0018	0.9899
	19.12	0.0346	0.9980	6.72	0.8270	0.0374	0.0011	0.9996



**Fig.10** Relationship between  $k_3$  and  $k_4$  in the modified pseudo-first-order model

## CONCLUSION

Based on this study, the UV/H<sub>2</sub>O<sub>2</sub> process appeared to be a very promising technology to remove MC-LR from water, compared with H<sub>2</sub>O<sub>2</sub> or UV alone. A high degradation rate of MC-LR could be achieved at the low MC-LR concentration, high H<sub>2</sub>O<sub>2</sub> dosage, high UV intensity, or low solution pH. Anions present in water, to different degrees, slowed the MC-LR degradation, among which CO<sub>3</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> greatly reduced the oxidation, but Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> seemed not to have significant inhibiting effects. The presence of pigments and other algae organic materials played a dual role, which could enhance the oxidation, but might compete hydroxyl radicals to decrease the overall treatment efficiency. Furthermore, a modified pseudo-first-order kinetic model was developed to predict the removal efficiency under different experimental conditions.

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