# Photocatalytic degradation of MC-LR in water by the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process

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# ABSTRACT

The ultraviolet (UV)/titanium dioxide (TiO<sub>2</sub>)/hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) process (UTHP) has been proven to be effective in removing organics because of its high production of free radicals. In this study, UTHP was further investigated for the photocatalytic degradation of microcystin-LR (MC-LR). Results showed that three mechanisms could realize MC-LR photocatalytic degradation using TiO<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> could effectively inhibit recombination and considerably improve the production of radicals and superoxides. From a correlation of the removal rate with the isomerization and decomposition of MC-LR under UV irradiation it was inferred that isomerization was crucial for MC-LR degradation during photocatalysis given the vulnerability of the exposed conjugated double bonds. The photocatalysis of MC-LR was apparently dependent on pH and MC-LR initial concentration. Under the optimum conditions of pH 3.5, 0.05 g/L TiO2, and 0.05 mmol/L H2O2, 100% MC-LR (308 µg/L) could be removed within 60 min. This process was accompanied by a synergistic effect during the initial 10 min.

Key words | isomerization, MC-LR, photocatalysis, synergistic effect, UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>

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# INTRODUCTION

Population growth, as well as the intensification of agricultural and industrial activities, has increased the incidence of eutrophication in shallow freshwater bodies. Consequently, cyanobacterial blooms have become more prevalent worldwide. Microcystins (MCs), which are a group of cyclic heptapeptides generated by Microcystis aeruginosa, are commonly detected in freshwater bodies (Pinho et al. 2015). The general structure of MCs is cyclo-(D-AlaL-X-MeAsp (iso-linkage)-L-Z-Ad da-D-Glu (iso-linkage)-Mdha), with the ADDA group as one of the key components in biological activities linked with the ADDA side chain (Wu et al. 2012). MCs have over 80 variants, among which, MC-LR, MC-YR, and MC-RR are the three common toxic variants, with MC-LR exhibiting the most toxic effect (Kubwabo et al. 2005). MC-LR can damage the nervous system or the liver, hence, it is harmful to animal and human health (Su et al. 2013). The World doi: 10.2166/ws.2015.110

Health Organization (WHO) has set a provisional guideline value of 1.0 µg/L for MC-LR in drinking water (WHO 1998). Conventional water treatment methods such as flocculation, coagulation, sedimentation, and filtration are ineffective in removing dissolved (extracellular) MC-LR (Su et al. 2013).

Recently, an increasing number of studies have focused on using advanced oxidation processes (AOPs) for ultraviolet (UV)/hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), UV/titanium dioxide (TiO<sub>2</sub>), and visible light-activated TiO<sub>2</sub> photocatalyst to eliminate the aforementioned toxins in raw water. AOPs, which involve generating nonselective OH, O, and H<sub>2</sub>O species, have demonstrated significant promise for MC remediation (Zong et al. 2013). However, UV-C/H<sub>2</sub>O<sub>2</sub> has not been used extensively in disinfection applications (Pablos et al. 2013); moreover, whether the effects of H2O2 on disinfection processes are positive or negative remains unclear. UV/TiO2 exhibits low free radical production because of electron-hole recombination, which results from the lack of a good electron acceptor (Gaya & Abdullah 2008). The visible light-activated TiO<sub>2</sub> photocatalyst, which can utilize visible light and save energy, is time-consuming and cannot degrade MC-LR with high efficiency (Yang *et al.* 2010). To improve AOPs, the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process (UTHP) has been developed recently to realize clean, low-cost, and efficient degradation. Photodegradation using UTHP has been demonstrated to be considerably more effective than that using UV/TiO<sub>2</sub>, and 98% decolorization of 20 mg L<sup>-1</sup> methylene blue can be achieved within 10 s (Zhang *et al.* 2013). A rough comparison shows that using UTHP for the photochemical oxidation of phenol and chlorophenol reduces energy consumption by 40% to 50% compared with using UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> (Dixit *et al.* 2010).

As the combination of UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>, UTHP can generate numerous free radicals and result in high degradation efficiency. In addition, it requires smaller H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> dosages, produces less pollution, and consumes less energy compared with UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>. Although numerous studies have focused on the UTHP process and various experimental conditions have been investigated (Pelaez et al. 2011; Su et al. 2013; Zong et al. 2013), comprehensive research that explains the mechanisms in detail is necessary. The characteristics of TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, UV, pH and MC-LR initial concentration were individually discussed for the photocatalytic degradation of MC-LR, which was extracted from algae. Decomposition and isomerization under UV irradiation were observed in previous studies; the pathways for photocatalytic degradation of MC-LR were analyzed by liquid chromatography mass spectrometry which suggested that isomerization was partly responsible for MC-LR removal (Tsuji et al. 1995; Antoniou et al. 2008a; Jacobs et al. 2013). The correlation of the removal rate with the isomerization and decomposition of MC-LR was also investigated.

# MATERIALS AND METHODS

#### Chemicals and apparatus

A spectrophotometer (DR 5000) was obtained from Hach<sup>®</sup> Company (Colorado, USA). A solid phase extraction (SPE) apparatus (Visiprep<sup>™</sup> disposable liner) was acquired from Supelco (Missouri, USA). Oasis<sup>®</sup> SPE cartridges (6 cc, 500 mg) and a high-performance liquid chromatograph (SUPELCO 2010) were purchased from Waters Corporation (Massachusetts, USA). An illumination incubator (GZX-300BS-III) was bought from Shanghai Touching Technology Company (Shanghai, China).

The Freshwater Algae Culture Collection of the Institute of Hydrobiology (FACHB-Collection, Chinese Academy of Sciences) provided the Microcystis aeruginosa (FACHB-905) with a nutrient medium (BG-11). MC-LR standard sample (>99% purity) was obtained from the Institute of Hydrobiology (Chinese Academy of Sciences). High-performance liquid chromatography (HPLC) grade methanol (CH<sub>3</sub>OH) was obtained from Sigma-Aldrich Corporation (Missouri, USA). Acetonitrile (CH<sub>3</sub>CN, HPLC), analytical reagent (AR)-grade acetic acid (CH<sub>3</sub>COOH), TiO<sub>2</sub> (AR), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, AR), and H<sub>2</sub>O<sub>2</sub> (AR) were purchased from Shanghai Chenyi Corporation (Shanghai, China). Chemically pure trifluoroacetic acid (TFA), sodium hydroxide (NaOH, AR), hydrochloric acid (HCl, AR), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, AR) were bought from Shanghai Chemical Reagent Corporation (Shanghai, China). Ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>, AR) was provided by Sinopharm Chemical Reagent Company.

#### **MC-LR extraction and detection**

MC-LR was detected quantitatively by optimizing SPE and HPLC detection methods.

#### MC-LR SPE

This method was developed and optimized based on the work of previous studies (Lawton *et al.* 1994; Pelaez *et al.* 2011). Mature *Microcystis aeruginosa*, cultured with BG-11 medium, was allowed to melt after being frozen under -20 °C for 12 h, and then frozen again. The process was repeated thee times to ensure that intracellular MC-LR was fully released into the cell sap. The cell sap with MC-LR was then filtered using a microfiltration membrane (0.45 µm, nominal pore size), and then enriched and purified using Oasis<sup>®</sup> SPE cartridges. All SPE cartridges were activated with 10 mL CH<sub>3</sub>OH, followed by 20 mL MilliQ-grade water. The flow rate was  $2.0 \pm 1.0$  mL/min. Each sample was acidized with acetic acid (25:1) and enriched at a flow rate of 5–10 mL/min. Afterward, the cartridge was washed with 10 mL 6% methanol solution. MC-LR was eluted twice with 1.5 mL CH<sub>3</sub>OH. Finally, each sample was transferred to a 250 µL insert.

A recovery test was performed to determine the recovery percentage of MC-LR after SPE. Standard solutions with only MC-LR were prepared. An average recovery rate of 95% was achieved. This recovery rate was verified during the analysis of the samples in each experiment.

# **MC-LR HPLC detection**

MC-LR samples were analyzed using a high-performance liquid chromatograph (SUPELCO 2010). Given that the peak absorbance of MC-LR was at the 238 nm wavelength, 238 nm was employed to determine MC-LR absorption. The analytical conditions were similar to those reported by Antoniou *et al.* (2008a). Samples were filtered prior to analysis. The flow rate was 1 mL/min and the injection volume was 50  $\mu$ L. The mobile phase consisted of CH<sub>3</sub>CN and 0.1% TFA solution according to the volume ratio of 64:36. The chromatographic column temperature was 35 °C.

## **Experimental conditions**

A standard calibration plot was prepared for MC-LR concentrations ranging from 0 to 800 µg/L. The standard plot was prepared before each set of experiments to ensure minimal system errors. The initial concentration of MC-LR was set to 308 µg/L. Preliminary experiments were conducted to determine optimal TiO<sub>2</sub> dosage and H<sub>2</sub>O<sub>2</sub> concentration. The optimal TiO<sub>2</sub> dosage was estimated to be between 0.01 and 0.15 mg/L. The optimal  $H_2O_2$  concentration was between 0.1 and 2 mmol/L. In addition, the concentrations of 0.01, 0.05, 0.10, and 0.15 mg/L were chosen to determine the optimum  $TiO_2$  dosage. Meanwhile, the dosages of 0.1, 0.5, 1 and 2 mmol/L were studied for H<sub>2</sub>O<sub>2</sub> optimum concentration. Then, the required 100 mL solution was transferred to the reactor (Figure 1). Solutions were adjusted to pH 2.5, 3.5, 6.5, and 7.8 with phosphate-buffered saline and to pH 10 with 0.1 mol/L NaOH. The effects of TiO<sub>2</sub> dosage,  $H_2O_2$  concentration and MC-LR initial



Figure 1 | Schematic of the quasi-parallel beam instrument.

concentration were studied at pH 3.5. The UV lamp was placed 50 cm above the reactor. The apparatus was preheated for 5 min. Each sample was stirred with a magnetic stirrer under UV light irradiation. The solution was sampled at 0, 5, 15, 30, 45, and 60 min. Each sample was filtered with a cellulose acetate membrane ( $0.45 \mu m$ , nominal pore size) and quenched with excess Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The concentration of the H<sub>2</sub>O<sub>2</sub> solution was measured via spectrophotometry at 0, 5, 15, 30, 45, and 60 min. The standard plot was also prepared before each set of experiments.

UV with wavelengths of 200–280 nm and over 320 nm were called UV-C and UV-A, respectively. In the experiments, UV-C and UV-A were obtained based on the method presented by Jacobs *et al.* (2013). The mercury UV lamp was customized with a quartz (UV-C) or Pyrex<sup>TM</sup> (UV-A) bulb. The power of the mercury UV lamp was 125 W; its rated working voltage was 220V. The irradiation distance was 50 cm, and the reactor was 10.5 cm in diameter. UV intensity could be kept constant by changing irradiation distance.

## **RESULTS AND DISCUSSION**

# Effect of TiO<sub>2</sub>

To investigate the effect of  $TiO_2$  on the photocatalytic degradation of MC-LR, solutions with different conditions were used (Figure 2). The dark adsorption capability of  $TiO_2$ 



Figure 2 | Effect of TiO<sub>2</sub> on the photocatalytic degradation of MC-LR at pH 3.5 and 308  $\mu$ g/L MC-LR.

was weak, and only 6.4% MC-LR was removed after 60 min, with the adsorption capacity of 0.39 mg/g, which was consistent with the literature (Hsu et al. 2013). MC-LR was rapidly degraded by photolysis (UV-C alone, 0 g/L TiO<sub>2</sub>, Figure 2). According to previous studies (Tsuji et al. 1995; Jacobs et al. 2013), high-energy radiation can decompose MC-LR or induce a structural change in MC-LR molecules; conformational isomers such as 6(Z)-ADDA-MC-LR are typically formed (Figure 3(b)). Although these conformational changes only involve the rotation of the functional groups at carbon 8 of the ADDA group, these isomers cannot be detected by HPLC at the setting peak absorbance wavelength, (i.e., 238 nm); moreover, these isomeric forms do not exhibit mutagenic or carcinogenic properties (Tsuji et al. 1995). Hence, only 65.4% MC-LR could be removed with photolysis after 60 min. In particular, the degradation rates of MC-LR were higher in the photocatalysis with UV-C and TiO<sub>2</sub> catalyst (UV-C/TiO<sub>2</sub>) than in TiO<sub>2</sub> adsorption or photolysis. When the solution with 0.05 g/L TiO<sub>2</sub> was radiated by UV-C, the degradation rate reached its highest (80.3%) after 60 min. Three mechanisms were responsible for the photocatalytic degradation of MC-LR; TiO<sub>2</sub> particles can be photoexcited to form electron donor sites  $e^-$  (i.e. reducing sites - 0.1V) and electron acceptor sites  $h^+$ , (i.e. oxidizing sites +3.1 V), also called electronhole pairs, which provide wide coverage as a redox reagent (Robertson 1996):

- 1. The hole  $(h^+)$  can capture the electron from water molecules  $(H_2O)$ , which in turn produce highly potent hydroxyl radicals (OH) to oxidize MC-LR (Robertson 1996).
- Conduction band electrons (e<sup>-</sup>) may be scavenged by dissolved O<sub>2</sub> molecules, which generate superoxide anion radicals (O<sub>2</sub><sup>-</sup>) that can subsequently lead to the formation of hydroxyl radicals (OH) (Pelaez *et al.* 2011).
- 3. MC-LR adsorbed on the surface of the catalyst may be oxidized directly from holes (h<sup>+</sup>) based on Equations (1) and (2), as follows, and then converted into hydroxyl derivatives (Antoniou *et al.* 2008b):

$$RCOO - +h^+ \rightarrow R \bullet + CO_2$$
 (1)

$$R \bullet + \bullet OH \to ROH.$$
 (2)

Although these possible mechanisms improve the photocatalysis degradation (UV-C/TiO<sub>2</sub>) rate, the improvement is only slightly higher (14.9%) than that of photolysis (UV-C alone) (Figure 2), which is attributed to the recombination of holes and electrons (Zhang *et al.* 2013).



Figure 3 Structures of (a) MC-LR and (b) 6(Z)-ADDA MC-LR



Figure 4 | Effect of H<sub>2</sub>O<sub>2</sub> on the photocatalytic degradation of MC-LR at pH 3.5 and 308  $\mu$ g /L MC-LR.

The catalyst amount plays an important role in the degradation of MC-LR in photocatalysis. Below a certain value (i.e., 0.05 g/L), the degradation rate increases as TiO<sub>2</sub> dosage increases, which implies that all photon energy is utilized. When the dosage is over a certain value, a decline in degradation is observed. An excess in TiO<sub>2</sub> dosage can cause light scattering, which affects light absorption and inhibits the excitation of electron-hole pairs. Therefore, the TiO<sub>2</sub> dosages used for the following experiment in the subsequent sections are all 0.05 g/L.

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

Many studies have focused on reducing the effect of the recombination of charges by applying different techniques (Zhang *et al.* 2013), including the electrochemical method (Yu *et al.* 1997), the surface modification of the photocatalyst (Pablos *et al.* 2013; Su *et al.* 2013), and the addition of an external electron acceptor such as  $H_2O_2$  (Dionysiou *et al.* 2004).  $H_2O_2$  is considered environmentally friendly because it is composed only of oxygen and hydrogen atoms. To verify further the role of  $H_2O_2$  in MC-LR degradation, UV-C/ $H_2O_2$  without TiO<sub>2</sub> was investigated. The result is shown in Figure 4. As a consequence of isomerization and decomposition, 68.2% MC-LR was degraded by UV-C alone. With  $H_2O_2$ , rapid decomposition and conversion to large amounts of hydroxyl radicals (·OH) were realized, and

thus, UV-C/TiO<sub>2</sub> improved degradation to 88.3%. However, the degradation rate of UV-C/H<sub>2</sub>O<sub>2</sub> was only increased by 20.1% compared with that of UV-C alone. By analyzing Figures 2 and 4, we determined that isomerization and decomposition through UV-C alone accounted for most of the removal rate.

For each initial  $H_2O_2$  concentration, the removal rate nearly reached a constant value after 45 min, which implied that  $H_2O_2$  had almost been consumed. The consumption of 0.5 mmol/L  $H_2O_2$  within 60 min is illustrated in Figure 5(a).  $H_2O_2$  was largely consumed (60%) before 15 min and used up after 45 min. This result is consistent with the MC-LR degradation process (Figure 4).

Furthermore, MC-LR reached its highest rate when  $H_2O_2$  concentration was optimized to 0.5 mmol/L. Below the optimal value, the degradation rate increased with increasing concentration. Degradation was decreased beyond this value by adding excess amounts of  $H_2O_2$  to the feed solution, which would diminish the effectiveness of the process because of the favorable inhibiting reactions that scavenge hydroxyl radicals as well as competitive adsorption among  $H_2O_2$ , oxygen, and organic contaminants (Dionysiou *et al.* 2004). Hence, 0.5 mmol/L was selected as the optimal value in the subsequent sections.

## UTHP for MC-LR photocatalytic degradation

The powerful capacity to degrade MC-LR with UTHP is illustrated in Figure 6(a). Over 50% MC-LR was degraded within 5 min, and 100% MC-LR was removed after 60 min. Three major reasons determined the high removal efficiency with the addition of  $H_2O_2$ :

- 1. As discussed in above, H<sub>2</sub>O<sub>2</sub> was rapidly decomposed and converted into large amounts of hydroxyl radicals (OH).
- Meanwhile, H<sub>2</sub>O<sub>2</sub> can capture the conduction band electron (e<sup>-</sup>) of TiO<sub>2</sub> and react with it, as shown in Equation (3) (Dionysiou *et al.* 2004). This process not only reduces the effect of recombination but also improves hydroxyl radical (OH) production.
- Furthermore, the breaking down of H<sub>2</sub>O<sub>2</sub> into water and oxygen facilitates superoxide (O<sub>2</sub><sup>-</sup>) formation.

$$H_2O_2 + e^- \to \bullet OH + OH^- \tag{3}$$



Figure 5 | H<sub>2</sub>O<sub>2</sub> consumption during (a) UV/H<sub>2</sub>O<sub>2</sub> and (b) UTHP degradation processes at pH 3.5 and 308 µg /L MC-LR.

The synergistic effect achieved through the photocatalytic process is shown in Figure 6(b) and Table 1. Many studies have applied the synergistic effect to analyze experimental results (Kim *et al.* 2014). In these studies, Inequation (4) is used either explicitly (the inequation is shown in the paper) or implicitly (the inequation is not shown in the paper) to judge the synergistic effect. We define the synergistic effect factor, i.e., Equation (5) according to Inequation (4) to illustrate the synergistic effect easily and evidently:

$$f_1 + f_2 < f_0 \tag{4}$$

$$F = \frac{f_0}{f_1 + f_2} \tag{5}$$

In Equation (5), *F* is the synergistic effect factor.  $f_0$  is the UV-C/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> average reaction rate, %/min;  $f_1$  is the UV-C/TiO<sub>2</sub> average reaction rate, %/min; and  $f_2$  is the UV/H<sub>2</sub>O<sub>2</sub> average reaction rate, %/min. *F* > 1 demonstrates the synergistic effect, i.e., when the factor is large, the effect is strong. Evidently, the two methods are equivalent when *F* > 1.

The synergistic effect factor *F* decreased rapidly within the initial 15 min and the synergistic effect was observed during the initial 10 min (Figure 6(b)). The  $H_2O_2$  consumption of UTHP is presented in Figure 5(b). Compared with the



Figure 6 | (a) UTHP for MC-LR degradation at pH 3.5 and 308  $\mu$ g/L MC-LR and (b) synergistic effect factor *F* - time curve of UTHP.

 $H_2O_2$  of UV/ $H_2O_2$ , the  $H_2O_2$  of UTHP was largely consumed (70%) within 5 min and used up after 30 min. Given the huge amount of  $H_2O_2$  consumption within a short period, no synergistic effect was exhibited after 10 min and the synergistic factor *F* became a constant in the following reaction.

## Isomerization and decomposition

Compared with UV-C alone (Figures 2, 4, and 6), UTHP increased the removal rate by 30.8% within 60 min. Given

#### Table 1 Calculation of the synergistic effect factor F

	Initial condition			Average reaction rate (%/min)					
	рн	TiO <sub>2</sub> (mg/L)	H <sub>2</sub> O <sub>2</sub> (mmol/L)	Time (min)					
Process				0	5	15	30	45	60
UV-C + TiO <sub>2</sub>	4.69	0.05	_	0	3.86	2.92	2.20	1.75	1.39
$UV-C + H_2O_2$	4.69	_	0.5	0	4.74	3.56	2.69	1.92	1.47
$UV-C+TiO_2+H_2O_2$	4.69	0.05	0.5	0	10.73	4.84	2.93	2.09	1.67
F	-	_	-	-	1.25	0.75	0.60	0.57	0.58

that the removal rate of UV-C alone remained high (76.1%, Figure 4), UV isomerization and decomposition could not be ignored. The effects of isomerization and decomposition on the MC-LR removal rate in UTHP assisted by UV-A and UV-C are presented in Figure 7.

TiO<sub>2</sub> adsorption for MC-LR was nearly the same at 4.1% and 4.6%. MC-LR is known to be resistant to lowenergy radiation (Jacobs *et al.* 2013). It decomposes very slowly when exposed to sunlight (Tsuji *et al.* 1995) and does not absorb irradiation at 365 nm; hence, no direct photolysis was observed at this wavelength (Antoniou *et al.* 2008a). In our experiment, a Pyrex<sup>TM</sup> bulb only allows radiation with wavelengths exceeding 320 nm (UV-A) to pass, and thus, large-scale isomerization and a



Figure 7 | Removal rate of MC-LR during photocatalysis assisted by UV-C and UV-A radiation at pH 3.5 and 308 μg/L MC-LR.

little decomposition occur. The removal rate of UV-C alone was higher than that of UV-A, which implies that UV-C isomerization and decomposition were stronger than those of UV-A. The experiment confirmed that UV-A, which uses lower energy radiation than UV-C, can effectively stimulate TiO<sub>2</sub> photocatalysis, as reported in previous studies (Jacobs et al. 2013). The removal rate of the photocatalysis correlated with the UV-C/TiO2/H2O2 process (U-CTHP) was considerably higher than that of the photocatalysis correlated with the UV-A/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process (U-ATHP) at 100% and 61.0%, respectively, after 60 min. The relationship of the removal rate with the isomerization and decomposition of MC-LR under UV irradiation was observed for the photocatalytic destruction of MC-LR. This finding suggests that isomerization is crucial for efficient removal. As shown in Figure 3, MC-LR isomerization by UV irradiation leads to a space configuration change in MC-LR and C=C conjugated double bonds exposure. Conjugated double bonds were inferred to be more vulnerable to attack and to being broken because exposure weakened the steric effect. This phenomenon also explains why neither UV-C/TiO2 nor UV-C/ H<sub>2</sub>O<sub>2</sub> can increase removal rate significantly.

## Effect of pH

MC-LR was effectively degraded within the pH range of 2.5 to 10. At a pH of 3.5, the maximum value (100%) was reached within 60 min (Figure 8). The effect of pH on the surface charge of TiO<sub>2</sub> is well established (Antoniou *et al.* 2008a), starting from positive at acidic values (pH < 2.6), to neutral at pH 6.4, and to negative under basic conditions (pH > 9.0). The charge for MCs is

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Figure 8 | Effect of pH 2.5, 3.5, 6.5, 7.8, and 10 on the photocatalytic degradation of 308 µg/L MC-LR.

determined by the structure of each derivative. Glutamic acid and methyl aspartic acid (found in nearly all of the MCs, Figure 3(a)) are ionized to anionic carboxylate forms at approximately pH 3 to form two negatively charged ions for the remaining pH range (Feitz et al. 1999). The amino acids in positions 2 and 4, which contain ionizable functional groups, also contribute to the overall charge of the toxin as a function of pH (Antoniou et al. 2008a). In the case of MC-LR, arginine possesses a basic amino group that remains protonated until strong basic conditions (pH > 12) are achieved (Dawson *et al.* 1959). Therefore, MC-LR carries a single negative charge for pH values between 3 and 12 (MC-LRH<sup>-</sup>). By contrast, when the pH value is close to the TiO<sub>2</sub> point of zero charge (6.4), photocatalysis efficiency will decrease because of the accumulation of small TiO2 particles into large particles as a result of the van der Waals force. Thus, the minimum removal rate during the entire photocatalysis process occurs at pH 6.5. In our experiment, pH 3.5 was selected as the most optimal value.

# Effect of MC-LR concentration

The efficiencies of MC-LR photocatalytic removal under different initial concentrations by U-CTHP are shown in Figure 9. Removal efficiency increased when the initial concentration increased from 103 to  $421 \,\mu\text{g/L}$  during the first



Figure 9 | Effect of MC-LR initial concentration on photocatalytic degradation at pH 3.5 and 308 μg/L MC-LR.

5 min. Photocatalysis is generally considered to fit the Langmuir–Hinshelwood kinetics, i.e., Equation (6) when the initial concentration is extremely low (Bacsa & Kiwi 1998):

$$r = kKC \tag{6}$$

where *k* is the true rate, and *K* is the adsorption constant. Equation (6) demonstrates that the rate is proportional to the initial concentration  $C_0$ . Consequently, the reaction rate increases from 5.4 µg/(L•min) to 26.2 µg/(L•min) with increasing initial solution concentration from 103 µg/L to 421 µg/L. However, the reaction rate is no longer associated with concentration when the initial concentration is high. Table 2 shows the average reaction rate during the initial 5 min. When the initial concentration is increased to 421 µg/L, the degradation of large amounts of MC-LR and its intermediates tends to cover the TiO<sub>2</sub> surface and has a negative effect on the absorption of photonic energy, which inhibits the production of hole–electron pairs (Su *et al.* 2013). This phenomenon impedes the formation of OH and the superoxide anion radical ( $O_2^-$ ).

Table 2 | Average reaction rate during the initial 5 min

Concentration (µg/L)	0 min	103	231	308	421	606
	5 min	76	157	189	290	481
Average reaction rate (µg(/L·min))		5.4	14.8	23.8	26.2	25.0

# CONCLUSION

A highly effective degradation of MC-LR in water using UTHP was demonstrated in this study. The photocatalytic destruction of MC-LR was clearly dependent on pH and MC-LR initial concentration. Under optimal conditions (i.e., pH = 3.5, 0.05 g/L TiO<sub>2</sub>, and 0.05 mmol/L H<sub>2</sub>O<sub>2</sub>), 100% MC-LR (308 µg/L) could be removed within 60 min. Three possible mechanisms were responsible for MC-LR removal using TiO<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> could effectively inhibit recombination and significantly improve radical and superoxide production. A synergistic effect was observed within the initial 10 min. A correlation of MC-LR under UV irradiation was observed, which implied that isomerization was important in MC-LR degradation during photocatalysis.

# ACKNOWLEDGEMENTS

This research was supported by China's National Critical Project for Science and Technology on Water Pollution Prevention and Control – Technology Integration and Demonstration of Security of Drinking-Water Source in Lake Tai (No. 2012ZX07403-001) and Suzhou Technology Bureau's Special Project – Biological Stability and Its Control Technology in Drinking-Water Distribution System in Suzhou (No. SS201434).

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First received 12 May 2015; accepted in revised form 7 July 2015. Available online 20 July 2015