



Oxidation of microcystin-LR by the Fenton process: Kinetics, degradation intermediates, water quality and toxicity assessment



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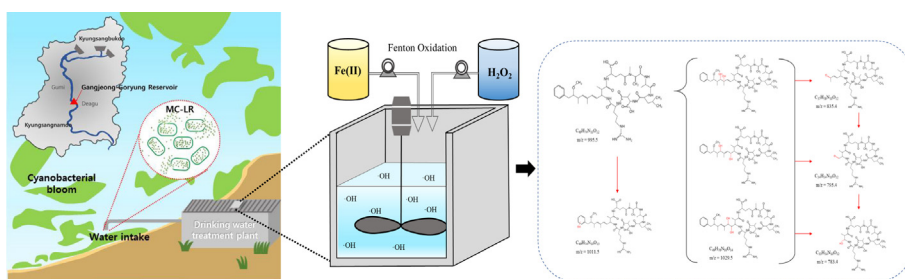
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HIGHLIGHTS

- The Fenton process is a cost-effective method for removing MC-LR.
- Degradation of MC-LR is a fast reaction that completed mostly within 5 min.
- Degradation intermediates of MC-LR are mainly related to diene bond of Adda chain.
- Degradation of MC-LR was reduced by presence of NOM, T&O compounds, and high pH.
- No acute toxicity was observed by application of the Fenton process using *D. magna*.

GRAPHICAL ABSTRACT



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ABSTRACT

The Fenton process was assessed as a cost-effective technology for the removal of Microcystin-LR (MC-LR) among UV, UV/H₂O₂, and Fenton process according to efficiency and electrical energy per order (EE/O). The determined practical concentrations of the Fenton reagents were 5 mg/L Fe(II) and 5 mg/L H₂O₂, respectively. The Fenton process is a fast reaction, completed within 5–30 min (Fe(II), H₂O₂ = 0.2–10 mg/L; MC-LR₀ = 200 µg/L). The degradation intermediates of MC-LR by the Fenton process were firstly reported as *m/z* 1029.5, 1011.5, 835.5, 795.4, and 783.4, associated with the diene bond in the Adda chain, then alleviate their toxicity. The effects of organic matter were examined in the range of Nak-Dong River water, as a drinking water source, monitored for six months in 2015. Fulvic acid was affected more than humic acid and natural organic matter (NOM). The degradation efficiency in the raw water was lower than that of distilled water because of the competing effect of NOM, geosmin, and 2-methylisoborneol, and the higher pH (7.64), furthermore, dissolved organic matter, geosmin, and 2-methylisoborneol was removed 7.39%, 4.28% and 12.30% after the Fenton process in the river water. The final concentration of MC-LR after treatment was under the drinking water guideline level with initial MC-LR concentration of 2 µg/L. No acute toxicity was observed to *Daphnia magna* (TU = 0) after the Fenton process.

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1. Introduction

Algal bloom is caused by excessive algal growth due to increasing amounts of nutrients, including nitrogen and phosphorus. Cyanobacteria, including *Anabaena*, *Microcystis*, *Nodularia*, and

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Cylindrospermopsis, are predominant organisms that cause harmful algal blooms (HABs) in surface water with the production of harmful toxins [1]. Some cyanobacteria species are known to produce toxins that are harmful to humans and the environment; these toxins are primarily hepatotoxins (microcystin) and neurotoxins (anatoxin-a) [2,3]. Microcystin-LR (MC-LR) is one of the most commonly observed and studied hepatotoxins in surface water [4,5], which had a LD₅₀ of 122 µg/kg in rats and tolerable daily intake value of 0.04 µg/kg/day for humans [6,7]. Thus, the World Health Organization recommended a provisional guideline value of 1 µg/L MC-LR for drinking water [8].

Cyanobacteria are ubiquitous in surface water, and they are not problematic in conventional water treatment when the number of cells is low. HABs occur seasonally with a rapid growth of cyanobacteria, possibly causing a decrease in the efficiency of water treatment [9]. The American Water Works Association Research Foundation (AWWARF) survey on 667 sample sources of drinking water from 24 public water systems in the United States and Canada from 1996 to 1998 revealed that microcystin was observed in 80% of the samples, and 4.3% were above 1 µg/L, including 2 samples obtained from treated drinking water [10]. In 2014, in the city of Toledo, Ohio, the concentration of microcystins increased to 2.5 µg/L in treated drinking water due to HABs in the source water of Lake Erie [11].

Two strategies exist for the removal of MC-LR in the presence of HABs: one is the removal of intact cyanobacteria cells before they release toxins (intracellular) and another is the treatment of the dissolved toxins (extracellular). Conventional water treatment processes, including coagulation, flocculation, and sedimentation, are effective for intracellular MC-LR; however, they are not sufficient for removing extracellular MC-LR. Thus, additional chemical treatment processes are required [12].

Advanced oxidation processes (AOPs) are generally more effective for the reduction of extracellular MC-LR than conventional oxidation processes, and a variety of AOPs have been studied, such as UV/H₂O₂ [13–16], the Fenton process (Fe(II)/H₂O₂) [17–21], UV/O₃ [22,23], TiO₂ photocatalysis [24–27], and ultrasonication [28]. The Fenton oxidation process is an attractive method in AOPs to remove MC-LR in DWTP as H₂O₂ is an environmentally friendly oxidant because it decomposes into water and oxygen, and iron is highly abundant and low toxicity [21,29]. In addition, the Fenton process is easily incorporated into drinking water treatments because an H₂O₂ solution could be added to the coagulation with iron salt, which is already used as a coagulant for drinking water [20]. H₂O₂ is commonly used chemical for disinfection in water treatment plants, and has recently been used for suppressing the population of cyanobacteria in surface water [29–31]. Although these advantages, limited studies have been conducted using the Fenton process to remove MC-LR, and evaluated degradation efficiency only in distilled water [17–21].

Thus, more research is required to improve our knowledge to remove MC-LR using the Fenton oxidation process in drinking water source. The aim of this research was to: 1) compare the degradation efficiencies and energy consumption by UV, UV/H₂O₂, and Fenton process, 2) determine the practical concentration of Fe(II) and H₂O₂ for the removal of MC-LR, 3) investigate the impact of water quality parameters including initial MC-LR concentration, solution pH, and organic matter fractions in synthetic water, 4) observe the main degradation intermediates of MC-LR during Fenton process using kinetic degradation analysis, 5) monitor the Nak-dong river water samples from a drinking water treatment plant (DWTP) for six months, used as water matrix for the removal of MC-LR, 6) apply the Fenton process to evaluate the degradation efficiency in the river water, and 7) conduct an acute toxicity assessment with *Daphnia magna* due to generate possible toxic by-product after the application of the Fenton process in drinking water source.

2. Materials and methods

2.1. Chemicals

MC-LR (MW 995.2 g/L, L30244) was purchased from Enzo Life Science (Lausen, Switzerland), hydrogen peroxide (35% v/v) and deionized-distilled (DI) water were obtained from OCI (Seoul, Korea), and a Milli-Q Water system was obtained from Millipore (Bedford, MA, USA). All of the other chemicals, including FeCl₂·4H₂O (98%), ammonium formate (≥99% HPLC grade), acetonitrile solution (0.1% v/v formic acid), catalase from bovine liver (2000–5000 µ/mg), para-chlorobenzoic acid (pCBA), geosmin (2 mg/ml) and 2-Methylisoborneol (2-MIB) (10 mg/mL), were purchased from Sigma Aldrich (St. Louis, MO, USA). Suwannee River natural organic matter (NOM) (RO isolation), humic acid standard II, and fulvic acid standard II were taken by International Humic Substances Society (IHSS).

2.2. Detection of MC-LR and its intermediates by LC/MS/MS

MC-LR was quantified by chromatographic separation using a ultra-performance liquid chromatography (UPLC) (Agilent 1290 Infinity series, Agilent Technology, Waldbronn, Germany) equipped with a triple-quadrupole mass spectrometer (6460 Jet Stream series, Agilent Technologies). An eclipse XDB-C₁₈ column (5 µm particle size, 4.6 × 150 mm) was utilized as a stationary phase. The mobile phase was composed of 20 mmol/L ammonium formate and 0.1% formic acid in acetonitrile solution at a ratio of 90:10 (v/v), with a flow rate of 1 mL/min. The analysis was performed under isocratic conditions with an injection volume of 10 µL, a source voltage of 3.5 kV and a column temperature of 35 °C. Under these conditions, MC-LR eluted at approximately 4.3 min. The reaction intermediates were analyzed during the Fenton process (Fe(II) = 5 mg/L, H₂O₂ = 5 mg/L) (5–30 min) with an initial MC-LR concentration of 2 mg/L. The data were obtained in positive ion mode by full scanning from *m/z* 600–1100. The detection limit is 0.02 µg/L.

2.3. Comparative studies for UV, UV/H₂O₂, and Fenton process

For the comparison of UV, UV/H₂O₂, Fenton water treatment process, the MC-LR removal efficiency and electrical energy per order (EE/O) have been investigated. The EE/O values (kWh/m³) can be calculated as following (Eq. (1)) [32]:

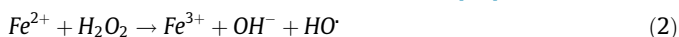
$$EE/O = P_{el} \times t \times 1000 / \left(V \times 60 \times \log \frac{C_0}{C_t} \right) \quad (1)$$

where P_{el} is the electric power (kW), t is the reaction time (min), V is the reaction volume (L), C_0 is the initial concentration, C_t is concentration at time t .

The photochemical reactor equipped with 254 nm wavelength UV-C lamp and quartz reactor that UV intensity was determined as 0.29 mW/cm² according to Bolton et al. [33]. Samples were completely mixed by stirring with magnetic bar. The initial concentration of MC-LR was spiked as 100 µg/L in DI water, and reaction time was 5 min (total UV dose = 87 mJ/cm²). The initial concentration of Fe(II) and/or H₂O₂ were 5 mg/L for UV/H₂O₂ and Fenton (Fe(II)/H₂O₂) processes. The pH values were ranged 5.2–5.6.

2.4. Evaluation of Fenton process for the removal of MC-LR in synthetic water

The Fenton reaction is known as follows [34]:



A standard solution of MC-LR (1000 mg/L) was diluted with DI water to adjust to the desired initial concentration (2–200 µg/L). The Fenton process was started by mixing premeasured Fe(II) and

H₂O₂ solutions in 50 mL polypropylene conical tubes. A catalase solution was added to the sample to quench residual H₂O₂ at a pre-determined time (5–30 min) before analysis [35]. The initial concentration of H₂O₂ was measured by a Hach hydrogen peroxide test kit (Model HYP-1 kit, Hach, Loveland, Colorado, USA). The concentration of Fe(II) before and after the Fenton reaction was determined by the ferrozine method [36,37]. The sample (1 mL) was mixed with 2 mL of 10 mM ferrozine in 1 M tris buffer (pH 7) and was measured using a UV–vis spectrophotometer (Optizen POP QX, Mecasys, Korea) at a wavelength of 562 nm. The hydroxyl radical concentration (M) at steady state ($\cdot\text{OH}_{ss}$) was determined by pCBA degradation [38]. Simply, the degradation amount of pCBA can be converted to OH radical concentration during same reaction time (5 min) for different Fe(II) and H₂O₂ concentration. The concentration of pCBA was analyzed by HPLC with UV/vis detection (PerkinElmer, Flexar, PDA plus Detector, PerkinElmer, USA) at 240 nm. An acetonitrile solution/1% phosphoric acid at a ratio of 40:60 ((v/v) mixture) was used as the mobile phase (flow rate = 1 ml/min) with column (5 μm particle size, 4.6 \times 150 mm, Agilent Technology, Waldbronn, Germany). All of the experiments were conducted at room temperature and at pH values of 4.5–5.2 without adjusting the pH, except for the fifth set of experiments.

The first set of experiments was performed to observe the effect of the initial H₂O₂ concentration on the degradation of MC-LR (MC-LR₀ = 200 $\mu\text{g/L}$; initial Fe(II) concentration = 0.2 mg/L; initial H₂O₂ concentration = 0.01–1 mg/L). In addition, the degradation efficiency of MC-LR was observed only with H₂O₂ (2, 3, 5, and 10 mg/L) for comparison with the Fenton reaction.

The second set of experiments was performed to examine the effect of the initial Fe(II) concentration on the Fenton reaction ((MC-LR₀ = 200 $\mu\text{g/L}$; initial Fe(II) concentration = 0.05–0.5 mg/L; initial H₂O₂ concentration = 0.2 mg/L).

The third set of experiments was conducted to determine the optimum concentration for the Fenton reaction for the degradation of MC-LR by increasing the initial concentration of Fe(II) and H₂O₂ using kinetic analysis. The concentrations of Fe(II) and H₂O₂ ranged from 0.2 to 10 mg/L and 0.2–50 mg/L, respectively.

The fourth set of experiments was performed to examine the effect of the initial concentration of MC-LR on the Fenton reaction with a reaction time of 0–30 min. The initial concentration of MC-LR was varied at 2, 20, and 200 $\mu\text{g/L}$ with same initial Fe(II) and H₂O₂ concentrations of 5 mg/L.

The fifth set of experiments was conducted to observe the effect of solution pH (3, 5, 7, 9 and 11) adjusted using 0.1 M H₂SO₄ and 0.1 M NaOH solutions on the Fenton reaction. The experiments were conducted with 5 mg/L of Fe(II) and H₂O₂, respectively, for 5 min. The pH was measured with a pH probe (9107BN, Thermo Scientific, Waltham, MA, USA) before and after the reaction. The sixth set of experiments was examined the effect of organic matter using natural organic matter (NOM), humic acid (HA), and fulvic acid (FA) by adding respectively in the DI water. The concentration of NOM, HA, and FA were adjusted 2–5 mg/L according to raw river water range monitored by this study.

2.5. Application of the Fenton process in drinking water source

The Nak-Dong river water, a source of drinking water, was obtained from a DWTP in Daegu, South Korea. The Nak-Dong River is the second largest river, and supplies drinking water resource to two big cities in South Korea, Busan and Daegu. The Nak-Dong river has suffered from cyanobacterial blooms during hot summer seasons (June–September), the water quality parameters such as total MC-LR concentration, dissolved organic carbon (DOC), SUVA₂₅₄ value, pH and turbidity had been monitored during the period June 2015–December 2015 prior to application of Fenton process. The sampling site was Ganjeong–Goryung reservoir in

Nak-Dong River, Dalseong-gun, Daegu, Korea. The samples were sonicated for 5 min (VCX-750, Sonics and Materials, USA), and filtered through 0.22 μm filter only for determining the total MC-LR concentration. The river water samples had the following characteristics for application of Fenton process: DOC = 4.06 mg/L, SUVA value = 2.64 L/mg-m, turbidity = 0.78 NTU, color = 7 Pt-Co unit, Fe(III) = 0.23 mg/L, pH = 7.64, electrical conductivity (EC) = 475 $\mu\text{S/L}$, geosmin = 23.10 ng/L, and 2-MIB = 25.60 ng/L. The river water was filtered through a Whatman™ 1822-047 grade GF/C filter (diameter: 4.7 cm, pore size: 1.2 μm) prior to experiments. The initial concentration of MC-LR was 0.06 $\mu\text{g/L}$ in raw water; therefore, MC-LR was added to meet the desired concentration (2, 20, and 200 $\mu\text{g/L}$) for application of the Fenton process.

2.6. Toxicity assessment

Acute toxicity tests were performed to determine the adverse effect to *D. magna* neonates (age, <24 h) from any by-products after the Fenton process in raw water. Five neonates were placed in 50 mL solutions, each containing 5 different concentrations (100, 50, 25, 12.5, and 6.25%) of sample after the Fenton process. The experiments was conducted as quintuplicate. The numbers of mobile and immobile neonates were observed 24 h after contact with the sample solutions at 20 \pm 1 °C.

3. Results and discussion

3.1. Degradation of MC-LR by UV, UV/H₂O₂ and Fenton process

The water treatment process was evaluated by two aspects, efficiency and cost. The degradation of MC-LR and EE/O values were examined by different processes with 5 min reaction (Fig. 1). The degradation efficiency of MC-LR was the highest using UV/H₂O₂ process (72.1 \pm 1.1%) followed by Fenton process (Fe(II)/H₂O₂) (65.8 \pm 3.7%), and UV (64.7 \pm 2.3%) process. MC-LR was least degraded by direct UV irradiation, and mostly degraded by the combination of direct UV photolysis and formation of hydroxyl radicals reacted between UV and H₂O₂, although, differences among these processes were quite low. Momani et al. [21] compared the a variety of processes including O₃, O₃/H₂O₂, and O₃/Fe(II) and Fenton process that the Fenton process was achieved 100% degradation efficiency of MC-LR and microcystin-RR (MC-RR) for 1 min. Therefore, the removal efficiency of MC-LR by Fenton process was high among various processes, even similar to that of UV-combined process.

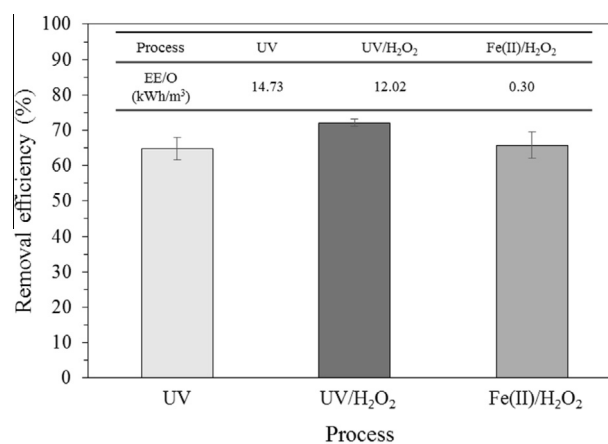


Fig. 1. Removal efficiencies and EE/O values for removal of MC-LR (MC-LR₀ = 100 $\mu\text{g/L}$) using UV, UV/H₂O₂ (5 mg/L), and Fenton process (Fe(II) = 5 mg/L, H₂O₂ = 5 mg/L) at pH 5–5.2. Error bars represent standard deviation of the mean (n = 3).

The operational cost is another important factor to determine the MC-LR removal efficiency that EE/O value was shown in Fig. 1. The cost of Fenton process can be considered as electric energy to apply the EE/O value that 1 kg of H_2O_2 was equivalent to 0.17 kW/min [39]. Also, 1 kg of Fe(II) was equivalent to

5.6 kW/min according to the cost (Table S1). Among the treatment processes, the EE/O value of UV and UV/ H_2O_2 process are 14.73 and 12.02 kWh/ m^3 , respectively, which means each process requires quite more electrical energy than Fenton process (0.30 kWh/ m^3). Generally, an EE/O value under 2.5 kWh/ m^3 is considered practical

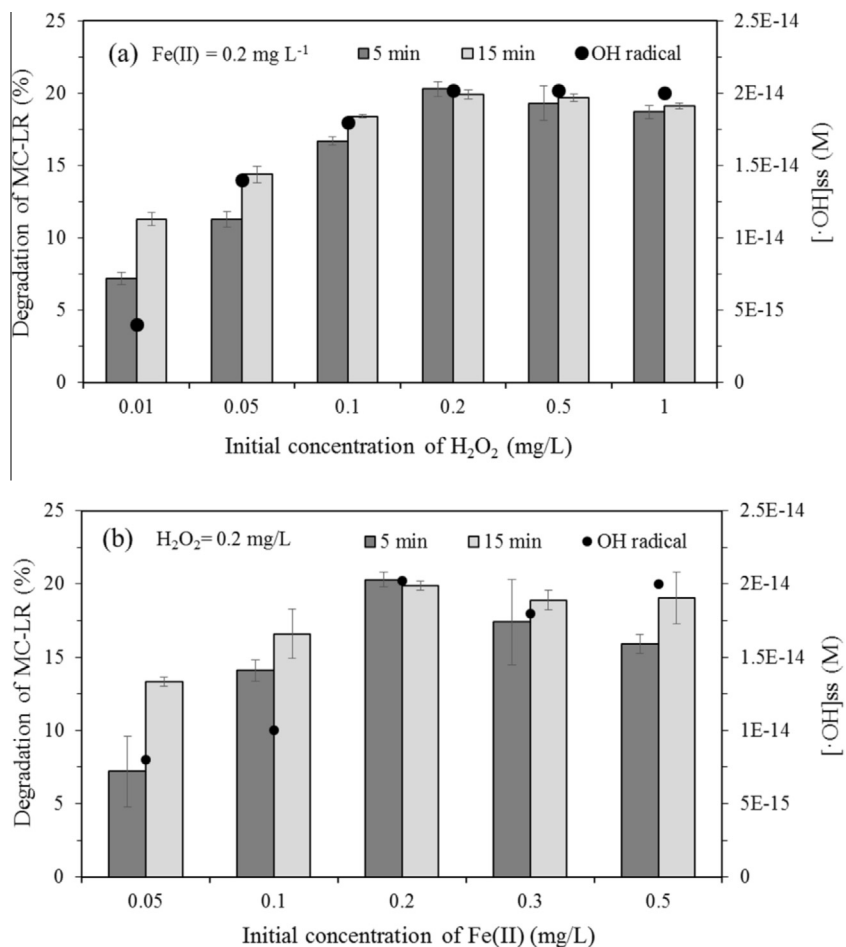


Fig. 2. Relative concentration of MC-LR ($\text{MC-LR}_0 = 200 \mu\text{g/L}$): (a) effect of initial H_2O_2 concentration (0.01–1 mg/L); (b) effect of initial Fe(II) concentration (0.05–0.5 mg/L) at pH 4.5–5.2. Error bars represent standard deviation of the mean ($n = 3$).

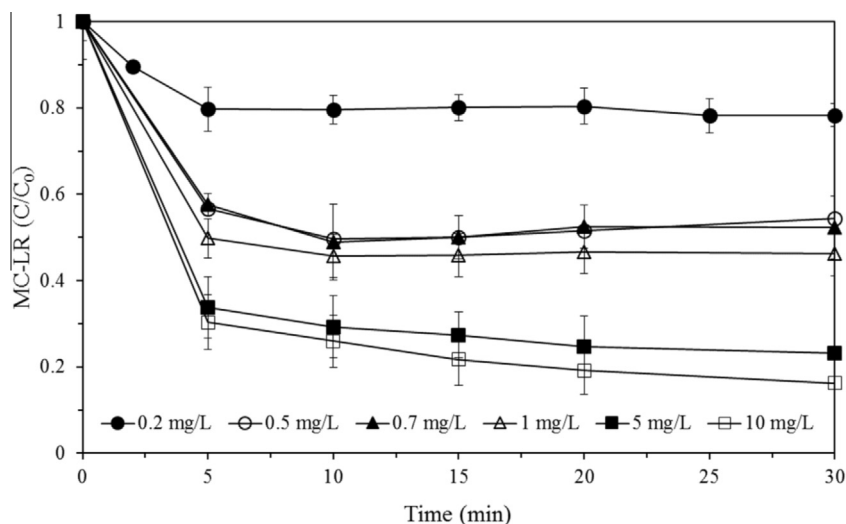


Fig. 3. Relative concentration of MC-LR (initial conc. = $200 \mu\text{g/L}$) using various concentrations (0.2–10 mg/L) of Fe(II) and H_2O_2 at a ratio of 1:1 at pH 4.6–5.1. Error bars represent standard deviation of the mean ($n = 3$).

Table 1

The $[\text{OH}]_{\text{ss}}$ produced by using various initial concentrations of Fe(II) and H_2O_2 (initial conc. of MC-LR = 200 $\mu\text{g/L}$).

Initial H_2O_2 conc. (mg/L)	Initial Fe(II) conc. (mg/L)	$[\text{OH}]_{\text{ss}}$ (M)
0.2	0.2	2.0×10^{-14}
0.5	0.5	3.8×10^{-14}
0.7	0.7	6.2×10^{-14}
1	1	9.0×10^{-14}
5	5	4.1×10^{-13}
10	10	4.3×10^{-13}

process, moreover, below 1 kWh/m³ is feasible process in Europe due to higher price of electric energy [40,41]. Saritha et al. [42] also found that the operational cost per kg of waste water was quite higher using UV (250.5 \$), and UV/ H_2O_2 (58.6 \$) processes than the Fenton process (7.4 \$). Hence, the Fenton process can be considered as a cost-effective process for removing MC-LR.

3.2. Effect of initial H_2O_2 and Fe(II) concentrations

Even at a high concentration (2–10 mg/L) of H_2O_2 , H_2O_2 alone did not efficiently degrade MC-LR, with a less than 5% of efficiency (Fig. S1). Similarly, in previous studies, no considerable MC-LR degradation was observed by adding H_2O_2 [17,20,21,43].

The concentration ratio of $[\text{Fe(II)}]:[\text{H}_2\text{O}_2]$ is important in the Fenton process, and various initial Fe(II) and H_2O_2 concentrations were examined in the low range of 0.05–0.5 mg/L, and 0.01–1 mg/L, respectively (Fig. 2). The removal rate of MC-LR increased from 7.2 to 20.3% by increasing the concentration of H_2O_2 (0.01–0.2 mg/L) and then slightly decreased to 18.7% ($\text{H}_2\text{O}_2 = 1$ mg/L) with the addition of 0.2 mg/L (Fe(II)) for 5 min (Fig. 2a). The degradation efficiency corresponded to the $[\text{OH}]_{\text{ss}}$ generation. The highest removal rate of MC-LR was 20.3% with the highest $[\text{OH}]_{\text{ss}}$ value of 2.02×10^{-14} M (Fe(II) = 0.2 mg/L, $\text{H}_2\text{O}_2 = 0.2$ mg/L, MC-LR = 200 $\mu\text{g/L}$) at 5 min. Concentrations of H_2O_2 above 0.2 mg/L did not enhance the degradation of MC-LR due to the scavenging effect of H_2O_2 . Zhong et al. [44] reported a similar trend in which a higher H_2O_2 dosage inhibited the generation of hydroxyl radicals, thus reducing the oxidation efficiency of MC-RR.

In addition, an initial Fe(II) concentrations ranging from 0.05 to 0.5 mg/L at a fixed H_2O_2 concentration of 0.2 mg/L (Fig. 2b) was used. Over the low dose range (0.05–0.2 mg/L Fe(II)), the degradation efficiency of MC-LR increased with increasing Fe(II) concentra-

tion because more hydroxyl radicals were produced. The MC-LR degradation efficiency slightly decreased above 0.2 mg/L Fe(II) because the excess Fe(II) reacted with the hydroxyl radicals to form the oxidized Fe(III) [44]. Therefore, both the initial Fe(II) and H_2O_2 concentrations were important parameters for the degradation of MC-LR. A concentration of 0.2 mg/L for both Fe(II) and H_2O_2 were selected as the favorable condition based on these experiments.

3.3. Effect of reaction times for degradation of MC-LR by the Fenton process

To increase the degradation efficiency of MC-LR, the concentrations of Fe(II) and H_2O_2 were increased at a ratio of 1:1 with various reaction times (Fig. 3). The Fenton process is a fast reaction the comes to completion within 5–30 min because of the initial surge of hydroxyl radicals when the Fe(II) and H_2O_2 are brought into contact [17]. The $[\text{OH}]_{\text{ss}}$ are shown in Table 1. The degradation of MC-LR was enhanced by increasing the Fe(II) and H_2O_2 concentration. After a 30-min reaction, 76.77–83.82% of MC-LR was reduced at Fe(II) and H_2O_2 concentrations above 5 mg/L. The degradation efficiency of MC-LR is closely related to $[\text{OH}]_{\text{ss}}$. An increase in the initial amounts of both H_2O_2 and Fe(II) led to an increased $[\text{OH}]_{\text{ss}}$ from 2.02×10^{-13} to 4.28×10^{-13} M, which enhanced the degradation efficiency of MC-LR. However, a slight amount of $[\text{OH}]_{\text{ss}}$ increased with 10 mg/L compared to 5 mg/L of both Fe(II) and H_2O_2 because of the both scavenging effect of an excessive dose of Fe(II) and H_2O_2 , and iron hydroxide yellow precipitation. The precipitation was observed only when 10 mg/L of both Fe(II) and H_2O_2 was reacted. From an economic perspective to generate $[\text{OH}]_{\text{ss}}$, the appropriate initial concentration of Fe(II) and H_2O_2 was 5 mg/L for MC-LR degradation.

In the previous literature, different concentrations of Fe(II) and H_2O_2 were used to degrade microcystins (MC-LR, MC-RR) (Table 2). The range of the $[\text{H}_2\text{O}_2]:[\text{Fe(II)}]$ weight ratio was 0.4–12, demonstrated as favorable condition for the removal of microcystins in each experiments. Most of the previous studies used high amount of H_2O_2 (>50 mg/L) to focus on obtaining high removal efficiency. Thus, different weight ratios (1:1, 1:5, and 1:10) were further examined in the range of 0.5–5 mg/L (Fe(II)) and 5–50 mg/L (H_2O_2) (Fig. S2), and it was found that a $[\text{H}_2\text{O}_2]:[\text{Fe(II)}]$ weight ratio of 1 was the best condition for MC-LR degradation. Therefore, further experiments were conducted using 5 mg/L of both Fe(II) and H_2O_2 in consideration of both cost and degradation efficiency.

Table 2

Removal rates of microcystin (MC-LR, MC-RR) by the Fenton process reported in the literature.

Type of microcystin	Initial Fe(II) (mg/L)	Initial H_2O_2 (mg/L)	Weight ratio $[\text{H}_2\text{O}_2]:[\text{Fe(II)}]$	Initial microcystin ($\mu\text{g/L}$)	Water	pH	Reaction time (min)	Removal rate (%)	Reference
MC-RR	5.6	51	9.11	1450	DI	3–4	30	99	Zhong et al. [44]
MC-LR	83.78	510	6.09	2,99,000	DI	–	30	100	Gajdek et al. [20]
MC-LR, MC-RR	0.02	0.05	0.40	1000–1500	PBS	7	1.5	100	Momani et al. [21]
MC-LR	140	170	1.21	4000	DI	<5	15	61	Bandala et al. [17]
MC-LR	0.14	0.51	3.64	500	DI	3	4	18	Bober et al. [18]
MC-LR	667	8000	11.99	–	DI	2	30	90>	Chen [19]
MC-LR	5	5	1	2	DI	5.2	30	92	This study
MC-LR	5	5	1	20	DI	5.2	30	80	This study
MC-LR	5	5	1	200	DI	5.2	30	77	This study
MC-LR	5	5	1	2	River water	7.6	30	30	This study
MC-LR	5	5	1	20	River water	7.6	30	38	This study
MC-LR	5	5	1	200	River water	7.6	30	53	This study

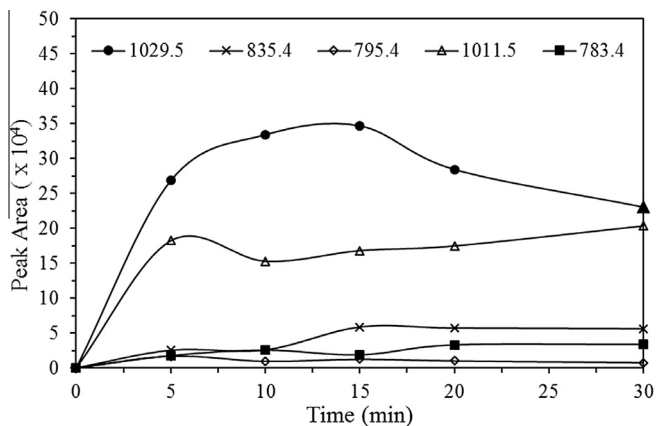


Fig. 4. Abundance curve of MC-LR intermediates for the Fenton process (Fe(II) = 5 mg/L; H₂O₂ = 5 mg/L; MC-LR₀ = 2 mg/L; pH 5.2).

3.4. MC-LR degradation intermediates and pathways

Many previous studies have been identified the degradation pathways of MC-LR during oxidation such as chlorination [45,46], TiO₂ photocatalytic oxidation [47,48], O₃ [49], UV/O₃ [22], and UV/H₂O₂ [50]. However, degradation intermediates of MC-LR by the Fenton process are not yet reported. Degradation intermediates of MC-LR by Fenton process, firstly reported in this study, include five degradation intermediates identified with *m/z* 1029.5, 1011.5, 835.4, 795.4, and 783.4 (Table S2). The hydroxyl radical is the predominant oxidant in the Fenton process, and it generally reacts via three types of competing pathways: hydroxyl addition, hydrogen abstraction, and electron abstraction [28,48,51]. The five intermediates appeared within 5 min related with Adda groups, and generally increased by increasing oxidation time, except the peak at *m/z* 1029.5 (Fig. 4). The major intermediates were *m/z* 1029.5 and

1011.5 caused by double hydroxyl addition on the conjugated diene bond of Adda, and single hydroxyl substitution, respectively. This ion product (*m/z* 1029.5) is reported as the primary breakdown product of MC-LR by hydroxyl radicals in many previous studies [48–50,52]. The second oxidation route tends to remove the Adda chain followed by diene bond cleavage through ·OH attack. The *m/z* 835.4, 795.4 and 783.4 were observed during the Fenton process, which supported the bond cleavage mechanistic steps. The proposed degradation pathway of MC-LR by Fenton process is shown in Fig. 5. The toxicity of microcystin-LR is associated with the diene bond in the Adda chain [53]; thus, cleavage of this bond would be anticipated to alleviate toxicity.

3.5. Effect of the initial MC-LR concentration

The efficiency of MC-LR degradation generally decreased by increasing the concentration of MC-LR (2–200 µg/L) (Fig. 6). At all of the initial MC-LR concentrations, approximately 65% of MC-LR was reduced within 5 min. The efficiency of MC-LR degradation was 92.06 ± 0.89% after the Fenton reaction for 30 min with an initial MC-LR concentration of 2 µg/L; however, this value slightly decreased to 80.00 ± 2.73% and 76.77 ± 7.09% due to an increase in the initial concentration of MC-LR to 20 and 200 µg/L, respectively. Momani et al. [21] showed similar results in which 75% of MC-LR was degraded with an initial MC-LR concentration of 1 mg/L, while 97% of MC-LR was reduced with an initial MC-LR concentration of 0.5 mg/L.

3.6. Effect of initial pH

The removal efficiencies of MC-LR at different pH values ranging from 3 to 11 are shown in Fig. 7. The removal efficiency gradually increased with decreasing pH, however, an initial pH of 3–7 yields a good MC-LR removal efficiency (>54.19%). Zhong et al. [44] determined that pH 3–6.84 was appropriate for MC-LR removal. The

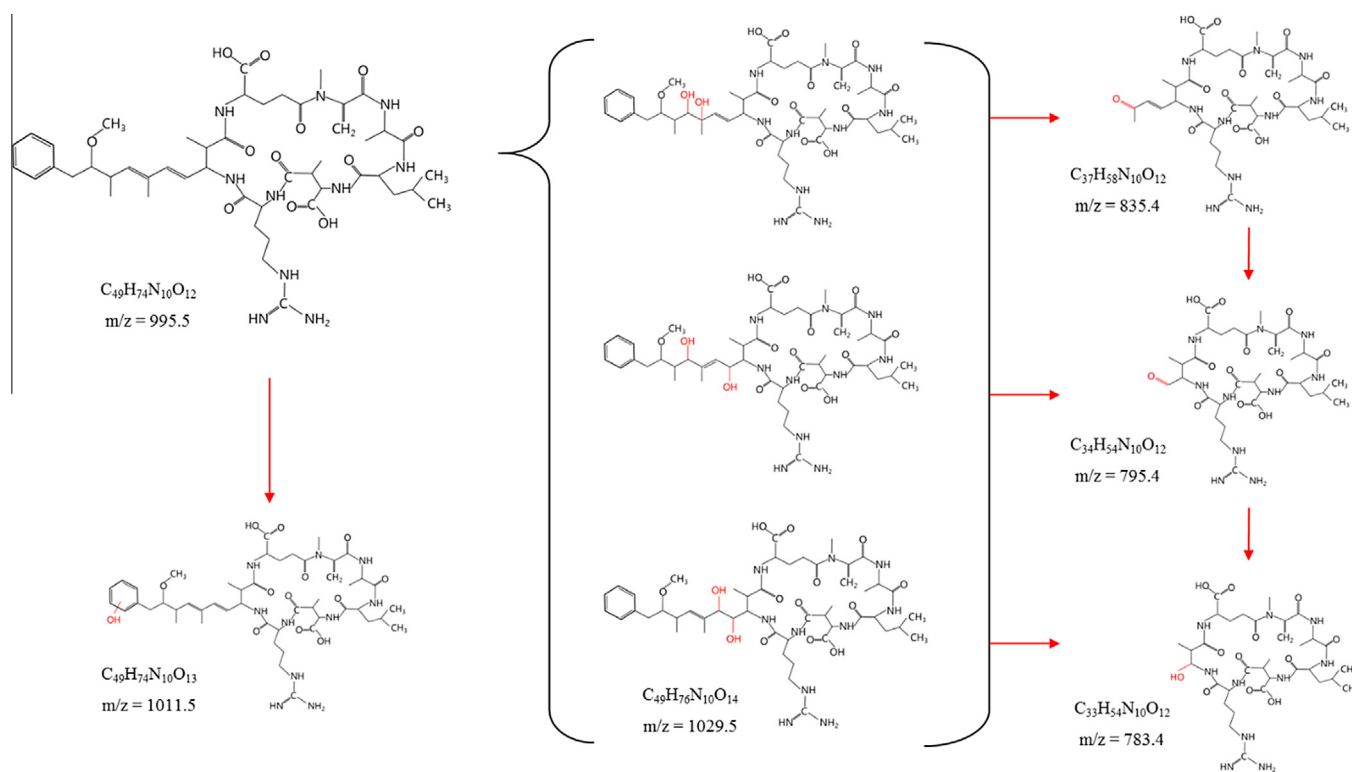


Fig. 5. Proposed degradation pathways of MC-LR by the Fenton process.

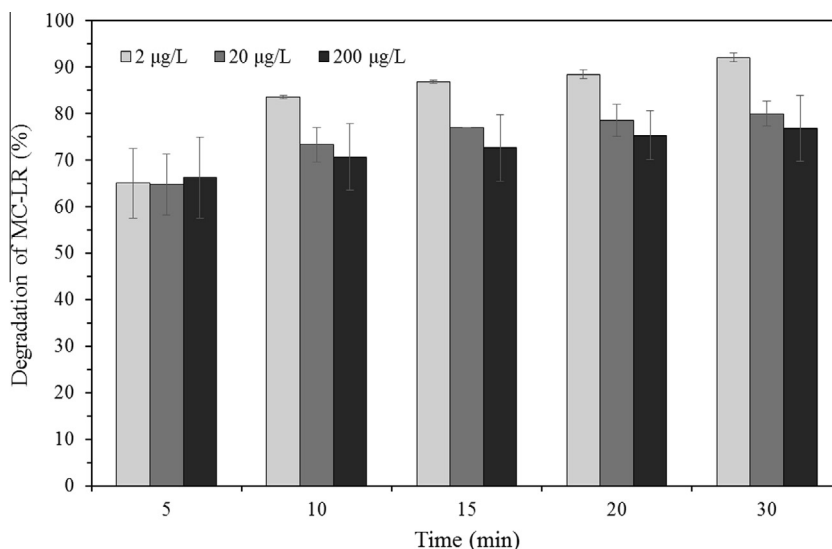


Fig. 6. The effect of the initial concentration of MC-LR (Fe(II) = 5 mg/L; H₂O₂ = 5 mg/L; MC-LR₀ = 200 µg/L; pH 5.2). Error bars represent standard deviation of the mean (n = 3).

removal efficiency was highest (77.27%) at pH 3, according to the highest [·OH]_{ss} (4.2 × 10⁻¹³ M). Under strong basic condition (pH 9–11), the removal efficiency was less than 10% because of a decrease in the Fe(II) concentration due to the formation of Fe(OH)₃, Fe(OH)⁺, Fe(OH)₂⁺ and iron hydroxide precipitation, as calculated using Visual MINTEQ version 3.1. The pH values were slightly decreased to an acidic condition after the Fenton reaction in the initial pH from 5.2 to 4.4, from 6.6 to 5.1, and from 8.7 to 6.7, while initial pH values of 3 and 11 were unchanged. Many previous studies investigated the optimal pH range of 2–4.5 for the Fenton process in which the presence of not only Fe(II) but also H⁺ can enhance the generation of hydroxyl radicals by H₂O₂ decomposition [18]. The removal efficiency was 68.23% within 5 min of reaction without adjusting the pH (approximately 5). Controlling the pH under highly acidic conditions (>pH 3) is expensive and laborious because initial pH is around pH 7, and requires a neutralizing chemical, such as NaOH, for coagulation process and consumer in drinking water treatment plants; thus, further experiments with raw water were conducted without adjusting the pH.

3.7. Effect of organic matter

The presence of organic matter had a significant effect on the degradation of MC-LR (Fig. 8). The degradation efficiency of MC-LR decreased by increasing NOM concentration. The differences

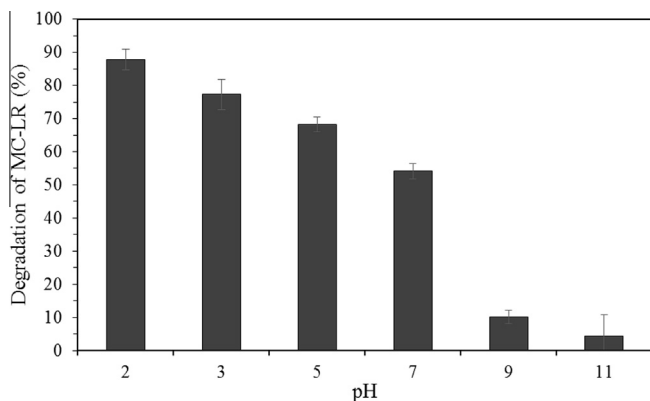


Fig. 7. The effect of pH (3–11) on the degradation of MC-LR (Fe(II) = 5 mg/L; H₂O₂ = 5 mg/L; MC-LR₀ = 200 µg/L; reaction time = 5 min). Error bars represent standard deviation of the mean (n = 3).

of MC-LR degradation rate between DI water and NOM (5 mg/L) were varied 14.8–25.0%, and the differences reduced gradually during 30 min reaction. Aquatic NOM is consisted of both hydrophobic, and hydrophilic components, and major one is humic substances, which are mainly divided into humic acids (HA), and fulvic acid (FA) [54]. Comparing with characteristic of organic mat-

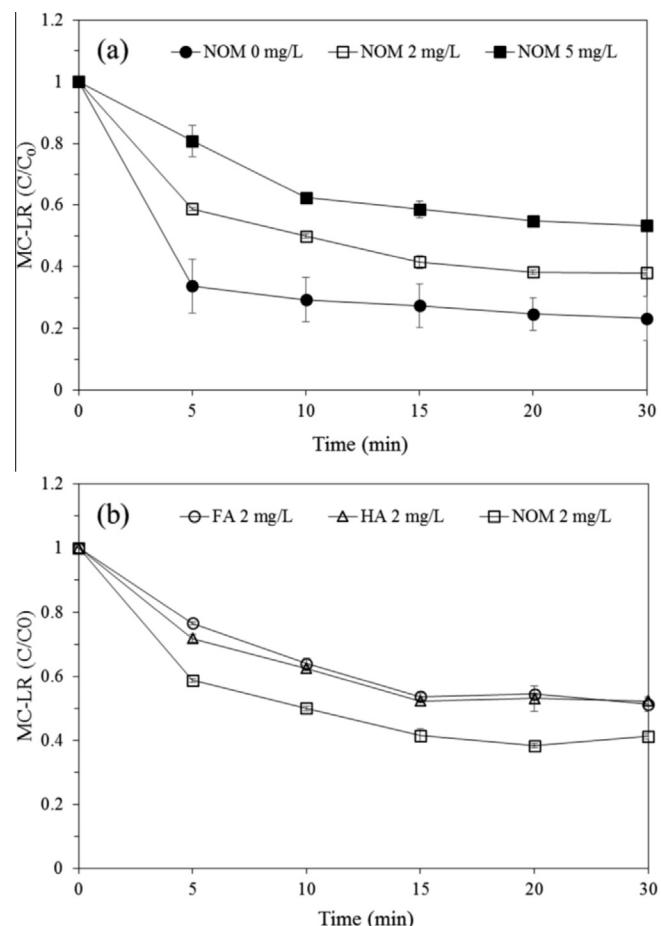


Fig. 8. The effect of organic matter on the degradation of MC-LR (Fe(II) = 5 mg/L; H₂O₂ = 5 mg/L; MC-LR₀ = 200 µg/L; pH 5.2). Error bars represent standard deviation of the mean (n = 3).

ter, the degradation efficiency of MC-LR was slightly decreased in the following order NOM, HA, and FA. The presence of organic matter reduced MC-LR removal efficiency due to scavenging of $\cdot\text{OH}$ during Fenton process [13].

3.8. MC-LR degradation in river water and its toxicity

For application in the DWTP in Nak-dong River in Korea, the characteristics of the river water including total MC-LR concentra-

tion, dissolved organic carbon (DOC), SUVA_{254} value, pH and turbidity was observed during the sampling period (June – December, 2015). The pH ranged from 6.21 to 8.50, and turbidity varied from 1.69 to 4.04 NTU. The DOC was observed around 2.42–4.07 mg/L, the highest value was obtained on September as presented in Fig. S3. Volk et al. [55] suggested that high DOC values are due to algae blooms on the surface water during summer time. The concentration of total MC-LR ranged from 0.03 to 0.53 $\mu\text{g/L}$ during six months, and the higher value was observed during sum-

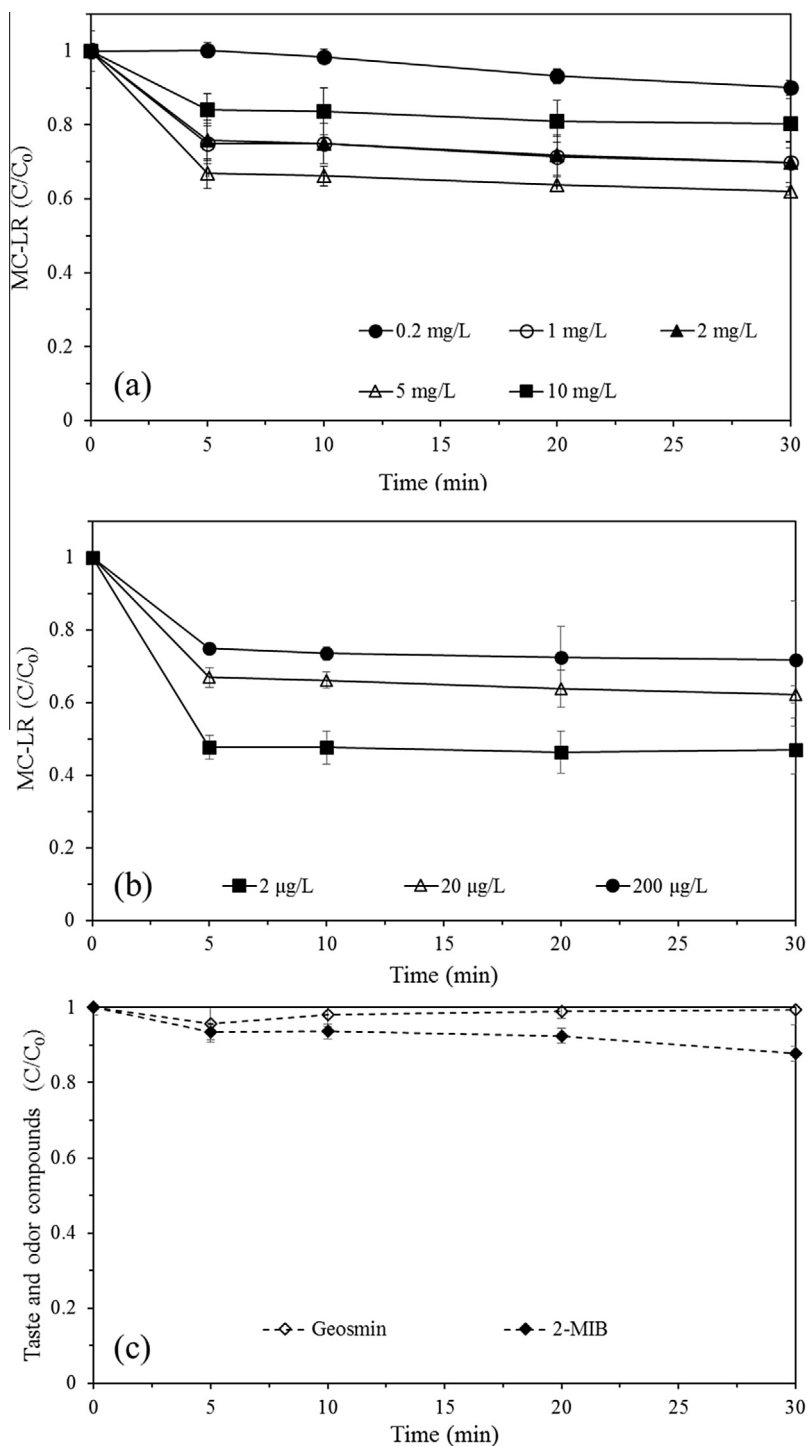


Fig. 9. Relative concentration of MC-LR, geosmin, and 2-MIB in river water under the Fenton process at pH 7.6: (a) various conc. of Fe(II) and H₂O₂ at a ratio of 1:1 (0.2–10 mg/L) with MC-LR₀ (20 $\mu\text{g/L}$); (b) various MC-LR conc. (2–200 $\mu\text{g/L}$) (Fe(II) = 5 mg/L; H₂O₂ = 5 mg/L); (c) relative concentration of geosmin, and 2-MIB (geosmin₀ = 23.10 ng/L, and 2-MIB₀ = 25.60 ng/L) (Fe(II) = 5 mg/L; H₂O₂ = 5 mg/L). Error bars represent standard deviation of the mean (n = 3).

mer (July = 0.41 µg/L, September = 0.53 µg/L). The highest total MC-LR concentration did not exceed the WHO guideline limit (1 µg/L) for drinking water during the period, however, further long-term investigation should be performed to protect the public health from toxin exposure derived from HABs during the summer.

The application of the Fenton process using the river water is presented in Fig. 9 as a function of reaction time. The various concentrations of Fe(II) and H₂O₂ at a ratio of 1:1 were applied to the river water with an initial MC-LR concentration of 20 µg/L (Fig. 9a), which is typically found in natural water [46]. The best degradation efficiency (33.13%) was found with 5 mg/L of Fe(II) and H₂O₂, respectively, for a 5-min reaction in the river water.

The degradation efficiency was lower than that of DI water because of the effect of the water matrix, mainly affected by initial pH of the river water (7.64), and the presence of DOC (4.06 mg/L). From the experiments with synthetic water, pH over 7 and high concentration of NOM (5 mg/L) was reduced the degradation efficiency as mentioned before. The consumption of H₂O₂ was 46%, Fe(II) was not observed due to the conversion of all Fe(II) to Fe(III), and the color and DOC value was decreased from 7 to 5 Pt-Co units, 4.06 to 3.76 mg/L after the Fenton process in the river water.

The effect of the initial MC-LR concentration was also examined using the river water (Fig. 9b). Most of the MC-LR degradation was completed after 5 min. In addition, another concern of HABs, geosmin and 2-MIB, as taste and odor compounds, were analyzed before and after the Fenton process, showing that geosmin and 2-MIB were slightly degraded 4.28% and 12.30% within 30 min, respectively (Fig. 9c). The experimental results evidenced that hydroxyl radicals produced by the Fenton process participate in a non-selective reaction that reduces the MC-LR removal efficiency due to the competing effect of NOM, geosmin, and 2-MIB in the river water.

Although the MC-LR degradation efficiency in natural water was lower than that of DI water in every initial MC-LR concentration by the adverse effect of water quality parameters, the degradation efficiency was over 52.30% with an initial MC-LR concentration of 2 µg/L within 5 min. Therefore, the final concentration of MC-LR was below the WHO drinking water guideline value (1 µg/L) when the initial MC-LR concentration of 2 µg/L in the river water. In the acute toxicity tests before and after the Fenton process, *D. magna* was unaffected (immobilization = 0%, TU = 0) in all of the samples indicating that no toxic by-product was produced by the Fenton process (Table S3). Thus, the Fenton process is feasible for DWTP for the removal of MC-LR when the initial concentration is below 2 µg/L.

4. Conclusion

The Fenton process was found to be a cost-effective method to degrade MC-LR. The degradation of MC-LR by the Fenton process was fast reaction. The degradation intermediates of MC-LR by the Fenton process were result from oxidation of the diene bond in the Adda chain that would be expected to be less toxic than MC-LR. The degradation efficiency of MC-LR was reduced when was applied in the Nak-Dong River water from DWTP due to the competing effect of other compounds (NOM, geosmin, and 2-MIB) and the higher pH; however, the Fenton process is still a promising non-toxic and simple method for MC-LR removal for water purification. Therefore, this study provided knowledge of the Fenton process for use as an alternative method to remove MC-LR in drinking water source.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.10.083>.

References

- [1] H.W. Walker, Harmful Algae Blooms in Drinking Water: Removal of Cyanobacterial Cells and Toxins, CRC Press, New York, USA, 2015.
- [2] B. Hawkins, S. Bosch, M. Odin, D. Odin, D. Wohlers, Toxicological Reviews of Cyanobacterial Toxins: Anatoxin-a (External Review Draft), U.S. Environmental Protection Agency, Washington, DC, NCEA-C-1743, USA, 2006.
- [3] B. Hawkins, H. Carlson-Lynch, M. Ordin, J. Stickney, Toxicological Reviews of Cyanobacterial Toxins: Microcystins LR, RR, YR and LA (External Review Draft), U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-06/139, USA, 2006.
- [4] E.R. Weiner, Application of environmental aquatic chemistry: A Practical guide, 3rd ed., New York, 2012.
- [5] J. Burns, Toxic cyanobacteria in Florida waters, in: H.K. Hudnell (ed.), Cyanobacterial Harmful Algal Blooms: State of the Science and Research Needs, Advances in Experimental Medicine and Biology, New York, USA, 2008.
- [6] I. Chorus, J. Bartram, Toxic cyanobacteria in water. A guide to public health consequences, monitoring and management, London, E & FN Spon, World Health Organization, London, 1999.
- [7] G.A. Miura, N.A. Robinson, W.B. Lawrence, J.G. Pace, Hepatotoxicity of microcystin-LR in fed and fasted rats, Toxicol 29 (1991) 337–346.
- [8] WHO, Guidelines for Drinking-Water Quality, 4th ed., World Health Organization, Geneva, Switzerland, 2011.
- [9] B. Ghernaout, D. Ghernaout, A. Saiba, Algae and cyanotoxins removal by coagulation/flocculation: A review, Desalination Water Treat. 20 (2010) 133–143.
- [10] W.W. Carmichael, Assessment of Blue-Green Algal Toxins in Raw and Finished Drinking Water, American Water Works Association, USA, 2001.
- [11] USEPA, Drinking Water Health Advisory for the Cyanobacterial Microcystin Toxins, U.S. Environmental Protection Agency, Washington DC, USA, 2015.
- [12] AWWA, Draft white paper on cyanotoxin treatment, American Water Works Association Research Foundation, Ohio, USA, 2015.
- [13] X. He, M. Pelaez, J.A. Westrick, K.E. O'Shen, A. Hiskia, T. Triantis, T. Kaloudis, M. I. Stefan, A.A. de la Cruze, D.D. Dionysiou, Efficient removal of microcystin-LR by UV-C/H₂O₂ in synthetic and natural water samples, Water Res. 46 (2012) 1501–1510.
- [14] X. He, A.A. de la Cruze, A. Hiskia, T. Kaloudis, K.E. O'Shen, D.D. Dionysiou, Destruction of microcystins (cyanotoxins) by UV-254 nm-based direct photolysis and advanced oxidation processes (AOPs): influence of variable amino acids on the degradation kinetics and reaction mechanisms, Water Res. 74 (2015) 227–238.
- [15] L. Li, N.Y. Gao, Y. Deng, J.J. Yao, K.J. Zhang, Experimental and model comparisons of H₂O₂ assisted UV photodegradation of Microcystin-LR in simulated drinking water, J. Zhejiang Univ. Sci. A. 10 (2009) 1660–1669.
- [16] R.P. Qiao, N. Li, X.H. Qi, Q.S. Wang, Y.Y. Zhuang, Degradation of microcystin-RR by UV radiation in the presence of hydrogen peroxide, Toxicol 45 (2005) 745–752.
- [17] E.R. Bandala, D. Martinez, E. Martinez, D.D. Dionysiou, Degradation of microcystin-LR toxin by Fenton and photo-Fenton process, Toxicol 43 (2004) 829–832.
- [18] B. Bober, K. Pudas, Z. Lechowski, J. Bialczyk, Degradation of microcystin-LR by ozone in the presence of Fenton reagent, J. Environ. Sci. Health A 43 (2008) 186–190.
- [19] Y.P. Chen, Study on the kinetics of removal of microcystin-LR by Fenton reagent, Safety Environ. Eng. 4 (2006) 012.
- [20] P. Gajdek, Z. Lechowski, T. Bochnia, M. Kepczynski, Decomposition of microcystin-LR by Fenton oxidation, Toxicol 39 (2001) 1575–1578.
- [21] F.A. Momani, D.W. Smith, M.G. El-Din, Degradation of cyanobacteria toxin by advanced oxidation processes, J. Hazard. Mater. 150 (2008) 238–249.
- [22] J. Chang, Z.L. Chen, Z. Wang, J. Kang, Q. Chen, L. Yuan, J.M. Shen, Oxidation of microcystin-LR in water by ozone combined with UV radiation: the removal and degradation pathway, Chem. Eng. J. 276 (2015) 97–105.
- [23] G. Zhu, X. Lu, Z. Yang, Characteristics of UV-MicroO₃ reactor and its application to microcystins degradation during surface water treatment, J. Chem. 2015 (2015) 1–9.
- [24] H. Choi, M.G. Antoniou, M. Pelaez, A.A. de la Cruz, J.A. Shoemaker, D.D. Dionysiou, Mesoporous nitrogen-doped TiO₂ for the photocatalytic destruction of the cyanobacterial toxin microcystin-LR under visible light irradiation, Environ. Sci. Technol. 41 (2007) 7530–7535.
- [25] B.J.P.A. Cornish, L.A. Lawton, P.K.J. Robertson, Hydrogen peroxide enhanced photocatalytic oxidation of microcystin-LR using titanium dioxide, Appl. Catal. B 25 (2000) 59–67.
- [26] L.A. Lawton, P.K.J. Robertson, B.J.P.A. Cornish, I.L. Marr, M. Jaspars, Processes influencing surface interaction and photocatalytic destruction of microcystins on titanium dioxide photocatalysts, J. Catal. 213 (2003) 109–113.

- [27] G.S. Shephard, S. Stockenstrom, D. de Villiers, W.J. Engelbrecht, G.F.S. Wessels, Degradation of microcystin toxins in a falling film photocatalytic reactor with immobilized titanium dioxide catalyst, *Water Res.* 36 (2002) 140–146.
- [28] W. Song, A.A. de La Cruz, K. Rein, K.E. O'Shea, Ultrasonically induced degradation of microcystin-LR and -RR: identification of products, effect of pH, formation and destruction of peroxides, *Environ. Sci. Technol.* 40 (2006) 3941–3946.
- [29] H.C.P. Matthijs, P.M. Visser, B. Reeze, J. Meeuse, P.C. Slot, G. Wijn, R. Talens, J. Huisman, Selective suppression of harmful cyanobacteria in an entire lake with hydrogen peroxide, *Water Res.* 46 (2012) 1460–1472.
- [30] D.J. Barrington, A. Ghadouani, Application of hydrogen peroxide for the removal of toxic cyanobacteria and other phytoplankton from wastewater, *Environ. Sci. Technol.* 42 (2008) 8916–8921.
- [31] X. Huo, D.W. Chang, J.H. Tseng, M.D. Burch, T.F. Lin, Exposure of *Microcystis aeruginosa* to hydrogen peroxide under light: kinetic modeling of cell rupture and simultaneous microcystin degradation, *Environ. Sci. Technol.* 49 (2015) 5502–5510.
- [32] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures of merit for the technical development and application of advanced oxidation processes, *J. Adv. Oxid. Technol.* 1 (1996) 13.
- [33] J.R. Bolton, K.G. Linden, Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments, *J. Environ. Eng.* 129 (2003) 209–215.
- [34] H.J.H. Fenton, Oxidation of tartaric acid in presence of iron, *J. Chem. Soc.* 65 (1894) 899–910.
- [35] W. Liu, S.A. Andrews, M.I. Stefan, J.R. Bolton, Optimal methods for quenching H_2O_2 residuals prior to UFC testing, *Water Res.* 37 (2003) 3697–3703.
- [36] L.L. Stookey, Ferrozine-A new spectrophotometric reagent for iron, *Anal. Chem.* 42 (1970) 779–781.
- [37] Y.H. Jung, H.K. Kim, H.M. Park, Y.C. Park, K. Park, J.H. Seo, K.H. Kim, Mimicking the Fenton reaction-induced wood decay by fungi for pretreatment of lignocellulose, *Bioresour. Technol.* 179 (2015) 467–472.
- [38] M. Elovitz, U. von Gunten, Hydroxyl radical/ozone ratios during the ozonation processes, I The Rct Concept, *Ozone Sci. Eng.* 21 (1999) 239–260.
- [39] J.P. Müller, M. Jekel, Comparison of advanced oxidation processes in flow-through pilot plants (Part I), *Water Sci. Technol.* 44 (2001) 303–309.
- [40] J.R. Bolton, S.R. Cater, Homogeneous Photodegradation of Pollutants in Contaminated Water: An Introduction, CRC Press, Boca Raton, FL, USA, 1994.
- [41] K. Zoschke, N. Dietrich, H. Börnick, E. Worch, UV-based advanced oxidation processes for the treatment of odour compounds: efficiency and by-product formation, *Water Res.* 46 (2012) 5365–5373.
- [42] P. Saritha, C. Aparna, V. Himabindu, Y. Anjaneyulu, Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol, *J. Hazard. Mater.* 149 (2007) 609–614.
- [43] A.M. de Freitas, C. Sirtori, C.A. Lenz, P.G.P. Zamora, Microcystin-LR degradation by solar photo-Fenton, UV-A/photo-Fenton and UV-C/ H_2O_2 : a comparative study, *Photochem. Photobiol. Sci.* 12 (2013) 696–702.
- [44] Y. Zhong, X. Jin, R. Qiao, X. Qi, Y. Zhuang, Destruction of microcystin-RR by Fenton oxidation, *J. Hazard. Mater.* 167 (2009) 1114–1118.
- [45] W. Zong, F. Sun, H. Pei, W. Hu, R. Pei, Microcystin-associated disinfection by-products: the real and non-negligible risk to drinking water subject to chlorination, *Chem. Eng. J.* 279 (2015) 498–506.
- [46] Y. Zhang, Y. Shao, N. Gao, W. Chu, Z. Sun, Removal of microcystin-LR by free chlorine: identify of transformation products and disinfection by-products formation, *Chem. Eng. J.* 287 (2016) 189–195.
- [47] Y. Su, Y. Deng, Y. Du, Alternative pathways for photocatalytic degradation of microcystin-LR revealed by TiO_2 nanotubes, *J. Mol. Catal. A-Chem.* 373 (2013) 18–24.
- [48] M.G. Antoniou, J.A. Shoemaker, A.A. de La Cruz, D.D. Dionysiou, Unveiling new degradation intermediates/pathways from the photocatalytic degradation of microcystin-LR, *Environ. Sci. Technol.* 42 (2008), 8877–8833.
- [49] J. Chang, Z.L. Chen, Z. Wang, J.M. Shen, Q. Chen, J. Kang, L. Yang, X.W. Liu, C.X. Nie, Ozonation degradation of microcystin-LR in aqueous solution: intermediates, byproducts and pathways, *Water Res.* 63 (2014) 52–61.
- [50] W. Zong, F. Sun, X. Sun, Oxidation by-products formation of microcystin-LR exposed to UV/H_2O_2 : toward the generative mechanism and biological toxicity, *Water Res.* 47 (2013) 3211–3219.
- [51] T. Fotiou, T.M. Triantis, T. Kaloudis, K.E. O'shea, D.D. Dionysiou, A. Hiskia, Assessment of the roles of reactive oxygen species in the UV and visible light photocatalytic degradation of cyanotoxins and water taste and odor compounds using C- TiO_2 , *Water Res.* 90 (2016) 52–61.
- [52] I. Liu, L.A. Lawton, P.K.J. Robertson, Mechanistic studies of the photocatalytic oxidation of microcystin-LR: an investigation of byproducts of the decomposition process, *Environ. Sci. Technol.* 37 (2003) 3214–3219.
- [53] R.M. Dawson, The toxicology of microcystins, *Toxicol.* 36 (1998) 953–962.
- [54] A. Matilainen, E.T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, M. Sillanpää, An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment, *Chemosphere* 83 (2011) 1431–1442.
- [55] C. Volk, L.A. Kaplan, J. Robinson, B. Johnson, L. Wood, H.W. Zhu, M. Lechevallier, Fluctuations of dissolved organic matter in river used for drinking water and impacts on conventional treatment plant performance, *Environ. Sci. Technol.* 39 (2005) 4258–4264.