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# Microcystin-RR degradation by ozonation

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ABSTRACT

Bench-scale tests were conducted to investigate the ozonation of Microcystin (MC)-RR obtained from cyanobacterial blooms in this study. The effects of ozone dose, initial MC-RR concentration, solution pH, and coexisting anions on the MC-RR ozonation kinetics were evaluated. Results showed that the MC-RR ozonation well followed the pseudo-first-order degradation kinetics under different experimental conditions. At pH 7 and 461.5 μg/L MC-RR, the degradation rate constant dramatically increased from 0.0125 to 0.0623 $min^{-1}$ with the increase of the ozone dose from 0.31 to 1.35 mg/L, but was not significantly affected by the initial MC-RR concentration. Typically, an acidic condition favored the MC-RR degradation. As the pH increased from 3.1 to 10.1, the rate constant decreased from 0.1906 to 0.0102 $min^{-1}$ at an $O_3$ dose of 0.82 mg/L. Different inorganic anions exhibited different behaviors in the MC-RR degradation. $NO_3^-$ slightly enhanced the decomposition, while $SO_4^{2-}$, $Cl^-$, and $CO_3^{2-}$ slowed the degradation to different degrees. Particularly, the inhibiting effect of $CO_3^{2-}$ was significant, probably due to its scavenging effect. These results demonstrated that ozonation appears to be a promising treatment method in the removal of MC-RR from water sources.

*Keywords:* Anions; Kinetics; Microcystin-RR; Ozonation

## 1. Introduction

With the dramatic increase of population and consequent intensification of agricultural and industrial activities, eutrophication frequently occurs in surface water worldwide as a result of cyanobacteria blooms. Microcystins (MCs) are cyclic non-ribosomal peptides produced by cyanobacteria, and can be very toxic for plants and animals [1,2]. Medical studies have shown that MCs in drinking water would cause human liver organ lesions, tumors, and even cancer [3]. Particularly, they are recognized internationally as one of the three major factors leading to liver cancer. Therefore, these toxins have received great attention due to their serious risks in the public health [4–7]. Currently, some countries such as Brazil, New Zealand, and United Kingdom have set up the criteria of MCs in drinking water to lower the chronic exposure of MCs and the World Health Organization has set a provisional guideline limit of 1 μg/L for MC-LR in drinking water.

MCs are mainly produced by freshwater cyanobacteria species such as Microcystis, Oscillatoria, Nostoc, and Anabaena [8,9]. Among the 80 known MC

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variants, MC-RR is one of the most two common variants (the other is MC-LR). Occasionally, the level of MC-RR in water sources is greater than that of MC-LR [10–12]. However, conventional drinking water treatment appears to be ineffective for the removal of MC-RR [13,14]. MC-RR ($C_{49}H_{75}N_{13}O_{12}$), consists of seven amino acids, including five D-amino acids and two unusual amino acids namely the N-methyldehydroalanine (Mdha) and hydrophobic b-aminoacid, 3-amino-9-methoxy-2, 6, 8-trimethyl-10-phenyldeca-4,6-dienoic acid (Adda). The reported semi-lethal intravenous ($LD_{50}$) injection of MC-RR for mice is 600 μg/kg [15]. Its toxicity is partly due to the Adda moiety, because the big ring and interval double bond in the molecule have higher thermal stability [9,16] Moreover, MC is readily soluble because multiple carboxyls, amino, amido,and other polar functional groups exist in its molecular structure.

Over the past years, different advanced methods have been studied to remove MCs from water sources, including membrane processes [17,18], Fenton oxidation [19], ozonation [20–22], ferrate oxidation [23], oxidation by chlorine, chlorine dioxide and permanganate [24], $TiO_2$ catalyzed photo-oxidation [25–30], and direct UV radiation [31,32]. Among these methods, ozonation shows promising results due to its strong oxidizing capacity. In a typical ozonation, ozone can directly attack organic molecules in the C–C, C–N, N–N, and other double bonds, aromatic rings, and amino [33], and also produce hydroxyl radicals (•OH) that are able to rapidly degrade most of organic molecules [34]. Although there are numerous studies on MC ozonation, most of them focus on MC-LR. Miao [22] found that MC-RR destruction was mainly involved in the attack of ozone on Adda side chain, involving the following sequent steps. First, the conjugated diene structure of Adda moiety was attacked by •OH to produce dihydroxylated products, then the hydroxylated 4–5 and/or 6–7 bond of Adda was cleaved into aldehyde or ketone peptide residues, and finally the residues were oxidized into the corresponding carboxylic acids. Moreover, the fragmentation of the Mdha-Ala peptide bond of MCs also contributed positively to the oxidation process. In the aspect of toxicity evaluation, they observed that the MC-RR degradation products had no adverse effects *in vivo* and *in vitro*. However, this study only emphasized the degradation pathway and toxicity evaluation during MC-RR ozonation. Until now, there has been a poor understanding of MC-RR ozonation kinetics and of the effects of different operating factors in the MC-LR ozonation.

The overall objective of this study is to assess the oxidation kinetics of MC-RR by ozone under various operational conditions. More specifically, effects of the ozone dose, initial MC-RR level, solution pH, and coexisting inorganic anions (nitrate, sulfate, chloride, and carbonate) on the MC-RR ozonation were evaluated.

## 2. Materials and methods

### 2.1. Ozonation experiment

The schematic diagram of the ozonation system is shown in Fig. 1. $O_3$ was produced by an ozone generator (SK-CFG-10) fed with the pure oxygen supplied from an oxygen cylinder. The pure oxygen was measured accurately by a gas flow indicator outfitted on the pipelines. Five hundred milliliter of algal toxin-containing solution was dispensed in a 500 mL conical flask. $O_3$ was fed to the reactor through a water injector Venturi, and the $O_3$ tail gas was finally absorbed by 2% KI solution. Once $O_3$ feeding was completed, the reactor was sealed. All the tests were run at 12 ± 3°C. One reactor was scarified at each designated sampling time for sample analysis. The samples were quenched with excess sodium sulfite before the MC-RR analysis.

### 2.2. Chemicals

The standard concentrate of MC-RR (CAS number: 111755-34-7, purity > 99%, molecular formula shown in Fig. 2) was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences, and was used to produce the standard curves for the qualitative and quantitative analysis by high-performance liquid chromatography (HPLC, Shimadzu LC-2010AHT). During the blue-green algae outbreak in the Taihu Lake in Wuxi, China in 2007, blue-green algae were collected, dried, milled into powders, and then stored at −20°C. Two gram dry algae powder was accurately weighed, and then dissolved in 100 mL deionized water with magnetic stirring for 30 min at room temperature. The solution was cooled in a freezer at −20°C for 12 h, placed at room temperature until melt, and then frozen at −20°C for 12 h again. The freezing—thawing procedure was repeated thrice. Subsequently, the algae solution was centrifuged at 7,000 rpm for 10 min, and then the supernatant was collected. Thereafter, the rest of the solution was centrifuged again. The procedure was repeated thrice. Finally, all the supernatants were collected together, and then filtrated by acetic acid fiber filters (0.45 μm) to obtain the MC extract. 0.69 mg MC-RR could be extracted from 1 g dry algae powder through this method. When the extract was not further purified by solid-phase extraction (SPE), the extraction liquid was blue. The

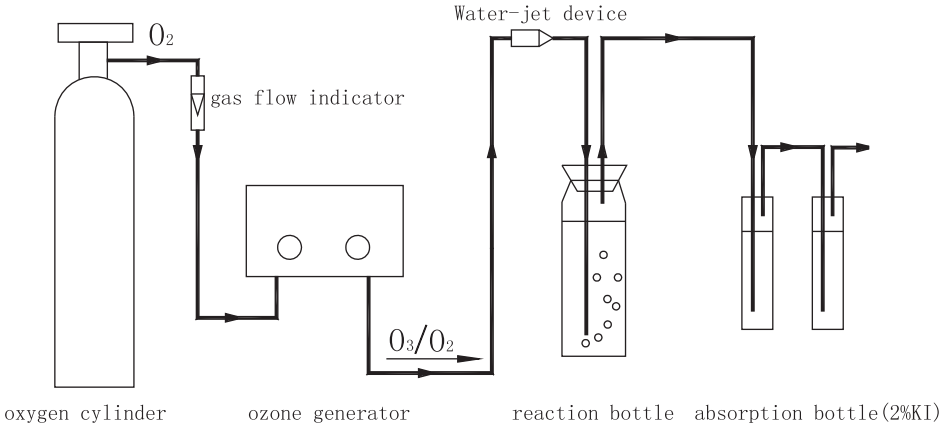


Fig. 1. Schematic diagram of the ozonation system.

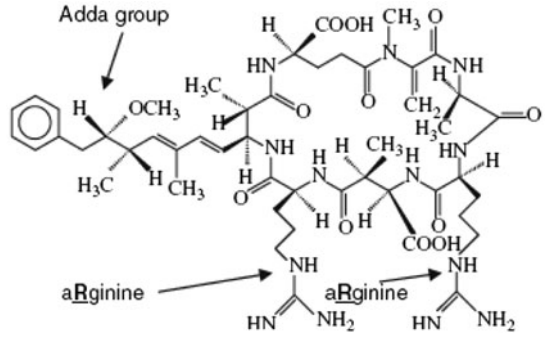


Fig. 2. Molecular structure of MC-RR.

prepared algal toxin solution was diluted to 500 mL with deionized water. The solution pH was approximately 6.5. If necessary, the solution pH could be further adjusted to the desirable levels with 1 M HCl and 1 M NaOH. $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$, and $NO_3^-$ were added with their respective sodium salts to achieve their final concentrations of 10 mmol/L.

### 2.3. Sample extraction

In sample analysis, solid-phase extraction (SPE column, ENVI-18, Supeco) with a concentration factor of 20 was used if the MC-RR level in the sample was less than the HPLC detection limit (~10 μg/L). The SPE column was first activated successively by 10 mL dichloromethane and 15 mL methanol, and then washed by 20 mL Milli-Q water. Thereafter, 20 mL sample passed through the SPE at a 3 mL/min flow rate. Finally, the chromatography elute was washed out with 1.00 mL methanol (HPLC pure) and analyzed by HPLC. Recovery rates of this method ranged within 84–92% in this study.

### 2.4. Analytical methods

Ozone concentration in water was determined by indigo disulfonate spectrophotometry [35]. Solution pH was measured by a pH meter (PHS-3C). MC-RR was quantified by HPLC (Shimadzu LC-2010AHT) using the column of BDS-C18 reversed phase column (5 μm, 150 × 4.6 mm). The test conditions were as follows: flow rate 0.8 mL/min, mobile-phase methanol: phosphate buffer solution (pH 3) = 57:43 (*v*:*v*), UV detection wavelength 238 nm, column temperature 40℃, analysis time 15 min, and MC-RR response time of 12.5 min.

## 3. Results and discussion

### 3.1. Ozonation kinetics

MC-RR removal by ozonation with time (MC-RR = 461.5 μg/L, pH 7.0, and initial $O_3$ = 0.82 mg/L) is shown in Fig. 3. Typically, MC-RR removal was increased with time. Within 90 min, 85% of the MC-RR could be decomposed, thus suggesting that ozonation is very effective for MC-RR control.

Our observation in the high treatment efficiency of MC-RR degradation by ozone agrees with several previous reports. Momani [36] found that 1.0 mg/L $O_3$ sufficiently reduced 1.0 or 1.5 mg/L MC-RR to an undetectable level (<0.2 μg/L). Miao [22] reported that the removal rate of MC-RR with an initial concentration of 50 mg/L increased from 25.0 to 82.4% with the increase of $O_3$ molar ratio from 1 to 6.

Typically, two primary reactions (Eqs. (1) and (2)) occur during ozonation in drinking water treatment [37]: direct $O_3$ oxidation (Eq. (1)) and indirect oxidation by hydroxyl radicals (•OH) (Eq. (2)).

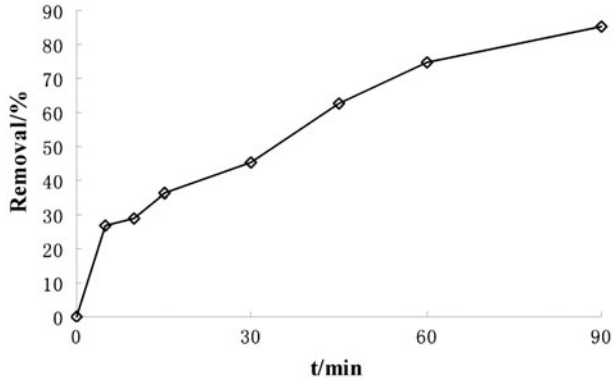


Fig. 3. MC-RR removal by ozonation vs. reaction time (pH: 7.0 ± 0.1; MC-RR initial concentration: 461.5 μg/L; $O_3$ concentration: 0.82 mg/L).

$$O_3 + OH^- - HO_2^- + O_2 \quad (1)$$

$$O_3 + HO_2^- - OH^{\cdot} + O_2^{\cdot -} + O_2 \quad (2)$$

Therefore, MC-RR degradation can be expressed as Eq. (3):

$$-\frac{d[\text{MC-RR}]}{dt} = k_{O_3}[\text{MC-RR}][O_3] + k_{OH^{\cdot}}[\text{MC-RR}][OH^{\cdot}] \quad (3)$$

where

$k_{O_3}$ and $k_{OH}$: reaction rate constants of ozone direct oxidation and indirect oxidation,

[MC-RR]: concentration of MC-RR,

$[O_3]$: concentration of ozone,

$[OH^{\bullet}]$: concentration of $OH^{\bullet}$,

$t$: reaction time.

von Gunten [37] presumed $[OH^{\bullet}]:[O_3]$ was constant at a specific pH, which can be denoted by $R_c$ as follows:

$$R_c = [OH^{\cdot}]/[O_3] \quad (4)$$

Substituting Eq. (4) in Eq. (3), it yields:

$$-\frac{d[\text{MC-RR}]}{dt} = (k_{O_3} + k_{OH^{\cdot}} R_C)[\text{MC-RR}][O_3] \quad (5)$$

In this study, the ozone level was much higher than the MC-RR concentration. Hence, Eq. (5) can be rewritten as follows:

$$-\frac{d[\text{MC-RR}]}{dt} = k[\text{MC-RR}] \quad (6)$$

where $k$ is an apparent rate constant ($k = (k_{O_3} + k_{OH^{\cdot}} R_C)[O_3]$). Therefore, MC-RR ozonation is regarded as a pseudo-first-order reaction. The rate constant $k$ in Eq. (6) can be determined by Eq. (7):

$$k = -\frac{1}{t}\ln\left\{\frac{[\text{MC-RR}]_t}{[\text{MC-RR}]_0}\right\} \quad (7)$$

where

$[\text{MC-RR}]_t$: concentration of MC-RR at the time of $t$,

$[\text{MC-RR}]_0$: initial concentration of MC-RR,

$t$: reaction time.

As shown in Fig. 4, our experimental data well exhibited a pseudo-first-order reaction kinetics behavior ($R^2 = 0.9853$), suggesting that MC-RR ozonation could be appropriately described by Eq. (6).

### 3.2. Effect of ozone dose

The effect of the ozone dose is shown in Fig. 5 and Table 1. Typically, all the degradations exhibited pseudo-first-order reaction behavior ($R^2 > 0.95$), and the pseudo-rate constant ($k$) increased from 0.0125 to 0.0623 $min^{-1}$ when the initial $O_3$ dose increased from 0.31 to 1.35 mg/L. Obviously, a high ozone dose increased the probability of ozone molecule attacking the double bonds and amino. Additionally, more hydroxide radicals were produced from Eq. (2). Of note, as shown in Table 1, when the initial $O_3$ dose was increased from 0.82 to 1.35 mg/L, the MC-RR degradation rate constant tripled from 0.0203 to 0.0623 $min^{-1}$. The observation suggested that increase in the initial $O_3$ dose may be a very effective method in MC-RR degradation.

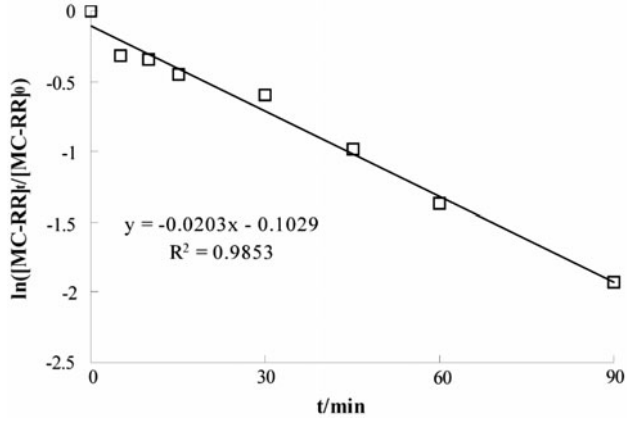


Fig. 4. Pseudo-first-order kinetic plot of MC-RR oxidation reaction (pH: 7.0 ± 0.1; MC-RR initial concentration: 461.5 μg/L; $O_3$ concentration: 0.82 μg/L).

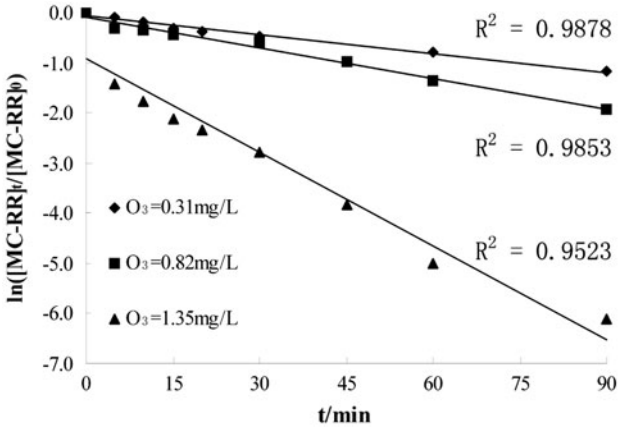


Fig. 5. Effect of the initial $O_3$ dose on the MC-RR degradation (pH: 7.0 ± 0.1; MC-RR initial concentration: 461.5 μg/L; $O_3$ concentrations:0.31, 0.82 and 1.35 mg/L).

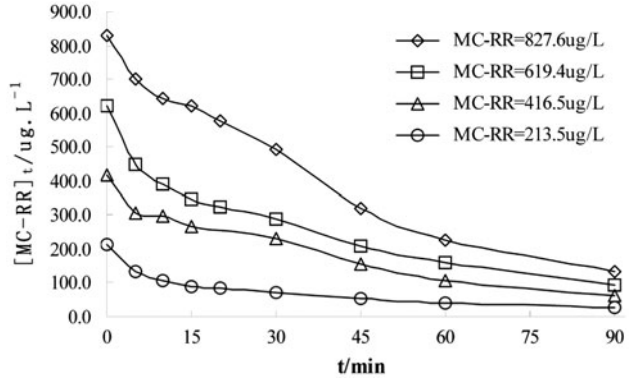


Fig. 6. Variation of residual of MC-RR with reaction time under different initial concentrations (pH: 7.0 ± 0.1; $O_3$ concentration: 0.82 mg/L; MC-RR initial concentrations: 213.5, 416.5.0, 619.4, and 827.6 μg/L).

Table 1
Fitting parameters of kinetics models (pseudo-first-order) on the MC-RR ozonation at different initial $O_3$ doses

| Ozone concentration (mg/L) | $k$ ($min^{-1}$) | $t_{1/2}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 0.31 | 0.0125 | 55.44 | 0.9878 |
| 0.82 | 0.0203 | 34.14 | 0.9853 |
| 1.35 | 0.0623 | 11.12 | 0.9523 |

Table 2
Fitting parameters of kinetics models (pseudo-first-order) on the MC-RR ozonation with different initial MC-RR concentrations

| MC-RR concentration (μg/L) | $k$ ($min^{-1}$) | $t_{1/2}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 213.5 | 0.0207 | 33.49 | 0.9228 |
| 416.5 | 0.0203 | 34.15 | 0.9853 |
| 619.4 | 0.0195 | 35.55 | 0.9784 |
| 827.6 | 0.0204 | 33.98 | 0.9923 |

### 3.3. Effect of the initial MC-RR concentration

The effect of the initial MC-RR concentration on MC-RR ozonation is shown in Fig. 6 and Table 2. When the initial MC-RR ranged within 213.5–827.6 μg/L, the MC-RR ozonation was of a pseudo-first-order reaction ($R^2 > 0.92$). For a particular $O_3$ dose, a higher remaining MC-RR level was found in the solution at a higher initial MC-RR concentration. Interestingly, the degradation rate constant was regardless of the initial MC-RR, almost stabilizing at 0.02 $min^{-1}$.

### 3.4. Effect of solution pH

The effect of solution pH is shown in Fig. 7 and Table 3. Over a broad pH range of 3.1–10.1, MC-RR ozonation still exhibited a pseudo-first-order degradation behavior. As seen, acidic condition favored the MC-RR ozonation. The highest rate constant of 0.19 $min^{-1}$ occurred at pH 3.1. With the pH increase from 3.1 to 10.1, the rate constant gradually decreased to 0.01 $min^{-1}$.

Algal toxins could be favorably decomposed by ozone in an acidic condition, which agreed with the previous findings of Momani [36] and Shawwa, and Smith [38]. This observation may be due to the following two reasons. First, in the molecular structures of algal toxins, double bonds and amino are more readily attacked by direct ozone oxidation, rather than indirect oxidation by $OH^{\bullet}$. Solution pH plays an important role in determining whether direct or indirect reaction during ozonation predominates [39]. Normally, the direct pathway dominates under acidic conditions (pH < 4.0), while the indirect one gradually prevails with the increase in solution pH because hydroxide ion ($OH^-$) is the initiator of $OH^{\bullet}$. Second, the oxidation potential of $O_3$ is much higher under acidic conditions (2.07 V) than under alkaline conditions (1.24 V).

### 3.5. Effects of different inorganic anions

Effects of four inorganic anions, $NO_3^-$, $Cl^-$, $SO_4^{2-}$, and $CO_3^{2-}$, on MC-RR ozonation are shown in Fig. 8 and Table 4. In the presence of different anions, the MC-RR ozonation was still a pseudo-first-order

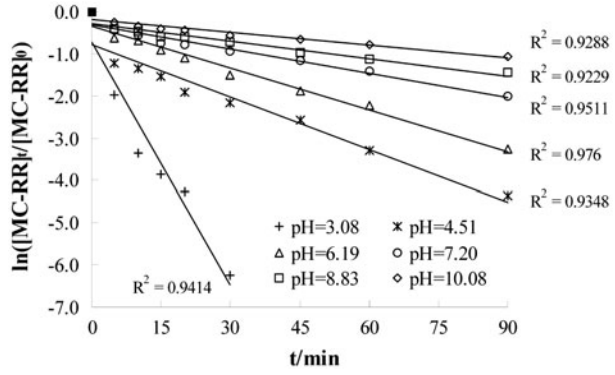


Fig. 7. Effect of solution pH on the MC-RR ozonation (MC-RR initial concentration: 416.5 μg/L; $O_3$ concentration: 0.82 mg/L; pH: 3.08, 4.51, 6.19, 7.20, 8.83, and 10.08).

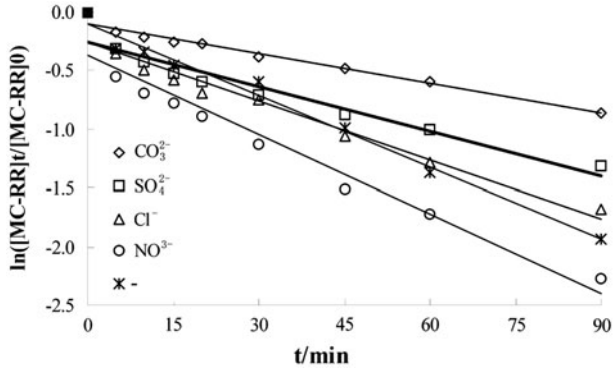


Fig. 8. Effects of anions on the degradation of MC-RR by Ozonation (pH: 7.0 ± 0.1; MC-RR initial concentration: 416.5 μg/L; $O_3$ concentration: 0.82 mg/L; the concentrations of $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$ and $NO_3^-$: 10 mmol/L).

Table 3
Fitting parameters of kinetics models (pseudo-first-order) on the MC-RR ozonation under different solution pH values

| pH | $k$ ($min^{-1}$) | $t_{1/2}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 3.08 | 0.1906 | 3.65 | 0.9414 |
| 4.51 | 0.0416 | 16.90 | 0.9348 |
| 6.19 | 0.0332 | 21.00 | 0.9760 |
| 7.20 | 0.0193 | 36.47 | 0.9511 |
| 8.83 | 0.0139 | 53.31 | 0.9229 |
| 10.08 | 0.0102 | 69.30 | 0.9288 |

Table 4
Fitting parameters of kinetics models (pseudo-first-order) on the MC-RR ozonation in the presence of different anions

| Anions | $k$ ($min^{-1}$) | $t_{1/2}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| $CO_3^{2-}$ | 0.0086 | 80.58 | 0.9760 |
| $SO_4^{2-}$ | 0.0128 | 54.14 | 0.9236 |
| $Cl^-$ | 0.0168 | 41.25 | 0.9543 |
| $NO_3^-$ | 0.0226 | 30.66 | 0.9475 |
| – | 0.0203 | 34.14 | 0.9853 |

reaction. Compared to the control group (no addition of any anion) ($k = 0.020\ min^{-1}$), $NO_3^-$ was a little more conducive to the MC-RR degradation ($k = 0.023\ min^{-1}$), $SO_4^{2-}$ and $Cl^-$ had a slightly inhibiting effect ($k = 0.013$ and $0.017\ min^{-1}$), and $CO_3^{2-}$ greatly slowed the MC-RR removal ($k = 0.009\ min^{-1}$).

Once $CO_3^{2-}$ was added to the solution, chemical equilibrium between $CO_3^{2-}$ and $HCO_3^-$ would be reached. Either of $CO_3^{2-}$ and $HCO_3^-$ is a well-known radical scavenger, capable of competing $OH^\bullet$ produced with MC-RR, producing inert inorganic radicals, thus interrupting free radical chain reaction and reducing the ability of the oxidation. The scavenging reaction caused by $CO_3^{2-}$ is shown in Eq. (8) [40].

$$OH^\cdot + CO_3^{2-} \rightarrow CO_3^{\cdot-} + OH^- \quad (8)$$

$NO_3^-$ played a synergistic role in promoting the MC-RR ozonation, because N in $NO_3^-$ is its oxidation state, and has a pro-electric effect on double bonds [41]. The slight inhibiting effects of $Cl^-$ and $SO_4^{2-}$ on the MC-RR ozonation are due to their scavenging reactions with hydroxyl radicals. $Cl^-$ can compete with organic species for $OH^\bullet$ ($k = 4.3 \times 10^9\ M^{-1}\ s^{-1}$), to form less reactive chloride radicals that may continue to scavenge $OH^\bullet$ [42]. Similarly, $SO_4^{2-}$ can scavenge $OH^\bullet$ and form unreactive iron–sulfato ($SO_4^{\cdot-}$) complexes [43].

## 4. Conclusion

Our study demonstrated that ozonation is an effective technology to remove MC-RR from drinking water sources. MC-RR degradation by ozone could be well described in pseudo-first-order kinetics models ($R^2 > 0.96$). In this study, we used an initial ozone dose much higher than the initial MC-RR concentration, and found that the MC-RR ozonation rate was not influenced by the initial MC-RR level. On the other side, ozone dosage and solution pH significantly affected the degradation rate. High ozone dose and acidic pH favored the MC-RR degradation. Furthermore, different species of co-existing anions exhibited different behaviors. $NO_3^-$ was conducive to MC-RR

removal; $SO_4^{2-}$ and $Cl^-$ had a slightly inhibiting effect; and $CO_3^{2-}$ significantly hinders MC-RR degradation.

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