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# Degradation and formation of wood odorant β-cyclocitral during permanganate oxidation

Ke-jia Zhang[a], Nai-yun Gao[a], Hung-Kai Yen[b], Yi-Ting Chiu[b], Tsair-Fuh Lin[b,*]

[a] State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai City 200092, China
[b] Department of Environmental Engineering and Sustainable Environment Research Center, National Cheng Kung University, Tainan City 70101, Taiwan

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ABSTRACT

The effect of permanganate oxidation on the formation and degradation of wood odorant β-cyclocitral in water was investigated. Oxidation experiments were conducted for β-cyclocitral prepared from pure chemicals and extracted from *Microcystis aeruginosa*. The data were simulated with appropriate kinetic rate models. The formation and degradation of β-cyclocitral during the oxidation of β-carotene were also monitored and modeled. The degradation of β-cyclocitral prepared from pure chemicals followed second-order kinetics with a rate constant of $91.7 \pm 2.4\ M^{-1}\ s^{-1}$, and that of the β-cyclocitral precursor, β-carotene, followed first-order kinetics with a rate constant of $0.0054 \pm 0.0004\ min^{-1}$. During the oxidation of β-carotene, β-cyclocitral was produced. The formation and degradation can both be simulated by first-order kinetics with respect to β-carotene and β-cyclocitral concentrations, respectively. The degradation rate of β-cyclocitral produced from β-carotene was found to be much slower than that for β-cyclocitral obtained from pure chemicals, very likely due to a mass transfer limitation. The kinetic models were further employed to simulate the oxidation of β-cyclocitral in the presence of β-carotene and for β-cyclocitral extracted from *M. aeruginosa*, respectively. The models well predict/fit the experimental data, with rate constants similar to other experiments, indicating that the models may be used for simulating the formation and degradation of β-cyclocitral in water treatment systems.



## 1. Introduction

Cyanobacteria-related taste and odour (T&O) chemicals in drinking water have received increasing attention during the last few decades [1–3]. Among T&O compounds, a wooden-odour chemical commonly present with *Microcystis* sp., called β-cyclocitral (2,2,6-trimethyl-1-cyclohexene-1-carboxaldehyde), has been detected in many lakes and reservoirs [4–7]. The concentrations detected were in the range of 100–3000 ng $L^{-1}$, which is on the same level or higher than the odour threshold concentration (OTC) of β-cyclocitral (~500 ng $L^{-1}$ in water) [4,6]. Juttner and Hoflacher [5] discovered that β-cyclocitral forms after *Microcystis* cells rupture. The chemical is the product of an oxidative cleavage reaction of β-carotene, catalyzed by β-carotene oxygenases bound on *Microcystis* cells under aerobic conditions. In a laboratory culture study of *Microcystis aeruginosa*, Rashash et al. [8] found that the production quota of β-cyclocitral was about 10.5 fg $cell^{-1}$. In a study of field samples, Jones and Korth [4] detected a very similar level (10 fg $cell^{-1}$) for *Microcystis* bloom.

Permanganate oxidation is a common process employed in drinking water treatment plants (DWTPs), often for the control of dissolved manganese, T&O, color, and biological growth [9]. It produces fewer disinfection byproducts (DBPs) [9] than do chlorine-based oxidants and is therefore considered to be more environmentally benign. Therefore, permanganate oxidation is used as an alternative pretreatment process of eutrophic raw water in DWTPs [2,10].

Unlike the oxidation of other T&O compounds, such as geosmin, that of β-cyclocitral has been rarely studied. Dietrich et al. [11] showed that chlorine at 1 and 3 mg $L^{-1}$ dosages and permanganate at 0.25 and 1 mg $L^{-1}$ dosages has very little effect on the odour characteristics of β-cyclocitral in water. The results were based entirely on a sensory evaluation, called flavour-profile analysis; no chemical analysis was performed. Based on chemical analysis, Lin et al. [7] confirmed that chlorine at up to a 10 mg $L^{-1}$ dosage and 60 min of contact time was not able to destroy β-cyclocitral. However, in their study, the permanganate oxidation of β-cyclocitral was not evaluated. In addition to direct oxidation, the presence of β-carotene may affect the β-cyclocitral concentration during oxidation processes. β-Carotene is known to be an important pigment component of many algae and cyanobacteria [12]. During the pre-oxidation of cyanobacteria-laden water, β-carotene may be present in the water and may interact with oxidants. Sommerburg et al.

* Corresponding author. Tel.: +886 6 2364455; fax: +886 6 2752790.
*E-mail address:* tflin@mail.ncku.edu.tw (T.-F. Lin).

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[13] examined the effect of chlorination on β-carotene cleavage, and observed that β-cyclocitral is one of the oxidation products. Although there have been no reports on permanganate oxidation with β-carotene and β-cyclocitral, it is speculated that permanganate may have an impact on the destruction of β-carotene and the formation and destruction of β-cyclocitral.

Permanganate is a common (pre-)oxidant employed in many DWTPs with eutrophic raw water. Therefore, the chances of permanganate contacting cyanobacteria cells and associated β-carotene, and β-cyclocitral are expected to be high. To better understand the formation and removal of β-cyclocitral in permanganate oxidation processes, the aims of this study are: (1) to characterize the reaction kinetics of β-cyclocitral and β-carotene with permanganate, (2) to understand the kinetics of formation and subsequent destruction for β-cyclocitral during β-carotene oxidation, and (3) to compare the effect of β-cyclocitral sources (pure chemicals and cyanobacteria cells) on the reaction kinetics.

## 2. Materials and methods

### 2.1. Oxidation of β-cyclocitral

Batch-type experiments were conducted for permanganate oxidation. In the experiments, 1-L glass reactors, each with a Teflon-coated magnetic stirrer, were maintained at 25 °C. The dose of permanganate was controlled between 1.0 mg $L^{-1}$ (6.3 μM) and 16.0 mg $L^{-1}$ (100.8 μM), and the concentrations of β-cyclocitral (analytical grade, Sigma–Aldrich) were controlled at 400 ng $L^{-1}$ (0.0026 μM), 800 ng $L^{-1}$ (0.0053 μM) and 1800 ng $L^{-1}$ (0.0118 μM), respectively. During the reaction, the pH was maintained at 7.4 with phosphate buffered saline solution (140 mM NaCl, 10 mM phosphate buffer, and 3 mM KCl) (Merck, Germany). Samples were collected at predetermined time intervals for the analysis of β-cyclocitral and residual permanganate. Before the analysis of β-cyclocitral, the samples were quenched with sodium thiosulfate (reagent grade, Baker, USA) to avoid further reaction.

### 2.2. Oxidation of β-carotene

The procedures and conditions for the oxidation experiments of β-carotene are similar to those of β-cyclocitral. Because β-carotene is photo-sensitive, the experiments were considered in darkness. The concentration of β-carotene (analytical grade, Fluka) was controlled at 1600 μg $L^{-1}$ (2.98 μM). In nature, β-carotene is present in particle form due to its low water solubility. For analysis, the β-carotene particles in water were first collected with centrifugal filter devices (0.22 μm) (Ultrafree-MC, Millipore) and then dissolved with furan (GR grade, Fluka) before analysis.

### 2.3. Oxidation of β-cyclocitral extracted from M. aeruginosa

Another set of oxidation experiments was conducted for β-cyclocitral extracted from a laboratory cultured cyanobacterium, *M. aeruginosa*. In the experiments, *M. aeruginosa PCC 7820* obtained from Pasteur Culture Collection of Cyanobacteria, France, was used. The cyanobacterium was cultured in BG11 media at 25 °C under constant light flux. After a stationary phase (~$3.2 \times 10^6$ cells $mL^{-1}$) was reached, the samples were used for the extraction experiments. In the experiments, β-cyclocitral was first extracted from *M. aeruginosa* (PCC 7820) with 100% furan, filtered with a 0.20-μm filter, and then diluted 10,000× with the phosphate buffered saline (Merck). The experiments were then conducted at two doses of permanganate (8 mg $L^{-1}$ and 16 mg $L^{-1}$) with an initial β-cyclocitral concentration of 0.0033 μM.

### 2.4. Analysis

A portable spectrophotometer (Hach, DR/2010, US) was used to determine the concentration of the residual permanganate in water by measuring its absorbance at 525 nm. Before measurements, a 0.10-μm nylon filter was used for separating the solution and manganese dioxide particles. The analysis results showed that the calibration curves are linear, with regression coefficients >0.999. In addition, the replicates and spike concentrations have errors of less than 5%. Although in some of the samples, the cyanobacteria associated pigments, such as β-carotene, may potentially interfere with the measurement of permanganate concentrations, preliminary experiments indicated that the influence was less 5–10% in this study.

β-Cyclocitral was quantified using headspace solid-phase microextraction (HSPME) coupled with a gas chromatograph (GC, Agilent 6890) and a mass spectrometer (MS, Agilent 5973). A commercially available fiber (30/50 μm DVB/CAR/PDMS (No. 57328-U)) and a manual fiber holder (No. 57330-U), both from Supelco (Bellefonte, PA, USA), were used for the extraction of the odorants. The chemicals trapped in the fiber were quantified using GC/MS. The procedure for odorant analysis was similar to that prescribed in *Standard Methods* 6040D (2000) for 2-methylisoboroneol (2-MIB). Detailed analytical procedures can be found elsewhere [14,15]. For β-cyclocitral analysis, the MS was set to selected ion monitoring (SIM) mode at $m/z$ = 137. As HSPME was operated at 65 °C for 0.5 h, thermal decomposition of β-carotene may be of concern for producing β-cyclocitral during the analysis processes. In fact, Kanasawud and Crouzet [16] showed that the production of β-cyclocitral from thermal decomposition of beta-carotene was trivial, only <0.1 μg of β-cyclocitral being produced per 50 mg of β-carotene under 97 °C for 3 h. Therefore, it is expected that production of β-cyclocitral from thermal decomposition of β-carotene can be neglected during the analysis processes.

β-Carotene analysis was carried out using a liquid chromatograph (LC) equipped with two identical pumps (LC-10AD, Shimadzu, Japan), a reverse phase C18 analytical column (100 mm × 4.6 mm i.d.) (Chromolith Performance RP-18e, Merck, Germany), and a mass spectrometer (2010EV, Shimadzu, Japan). As described in Section 2.2, β-carotene particles were first separated from the water using filtration. The particles were then dissolved into furan for LC/MS analysis. The mobile phase consisted of acetonitrile/LC water with 0.05% trifluoroacetic acid (TFA) (80/20, v/v). The injection volume was set to 10 μL, the flow rate was set to 1.0 mL, and the column temperature was set to 35 °C. For β-carotene analysis, the MS was set in SIM mode at $m/z$ = 538.4.

## 3. Results and discussion

### 3.1. Reaction kinetics of β-cyclocitral under permanganate oxidation

To determine the reaction kinetics, a series of experiments were conducted at various permanganate and β-cyclocitral concentrations, with the pH controlled at 7.0. Fig. 1 shows the concentration change with time for β-cyclocitral after reacting with permanganate. In the experiment, the initial dose of permanganate was set to 2 mg $L^{-1}$ (12.6 μM), and the concentration of β-cyclocitral was between 0.0026 and 0.0118 μM. Since the dose of permanganate is much larger than that of β-cyclocitral, permanganate concentration is expected to be almost constant within the experimental time. Permanganate concentrations for the three experimental runs changed by only 2–11%. Previous studies led to the conclusion that the reaction of permanganate with several organic compounds, such as trichloroethylene (TCE) [17], methyl *tert*-butyl

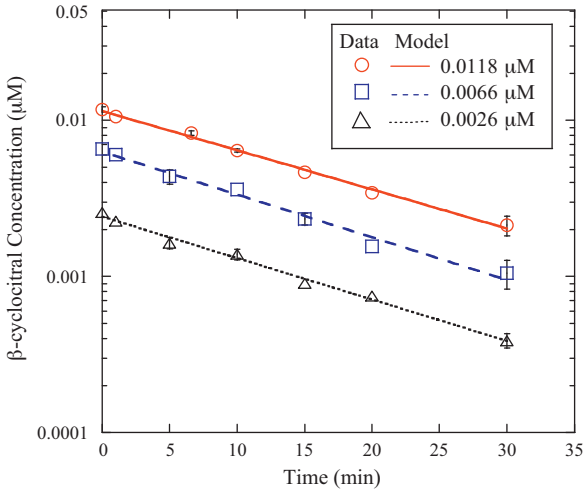


**Fig. 1.** Degradation of β-cyclocitral with permanganate oxidation for various β-cyclocitral concentrations (initial dose of permanganate = 2 mg $L^{-1}$ (12.6 μM)).

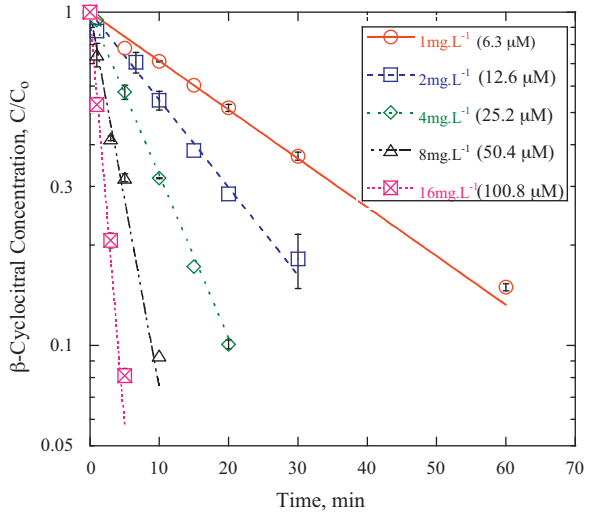


**Fig. 2.** Effect of permanganate dose on the degradation of β-cyclocitral (initial β-cyclocitral concentration = 1800 ng $L^{-1}$ (0.0118 μM)).

**Table 1**
Kinetic rate constants for permanganate oxidation of β-cyclocitral under various experimental conditions.*

| $[\beta\text{-Cyclocitral}]_0$ (μM) | $[KMnO_4]_0$ (μM) | $k_{obs}$ ($min^{-1}$) | $k_{CM}$ ($s^{-1}$ $M^{-1}$) | $R^2$ |
|---|---|---|---|---|
| 0.0026 | 12.6 | 0.061 | 81 | 0.986 |
| 0.0066 | 12.6 | 0.063 | 83 | 0.992 |
| 0.0118 | 12.6 | 0.061 | 81 | 0.982 |
| 0.0118 | 6.3 | 0.034 | 90 | 0.990 |
| 0.0118 | 25.2 | 0.11 | 73 | 0.996 |
| 0.0118 | 50.4 | 0.26 | 86 | 0.991 |
| 0.0118 | 100.8 | 0.57 | 94 | 0.995 |

* Temperature was controlled at 25 °C.

ether (MTBE) [18], microcystin-RR [10], and microcystin-LR (MC-LR) [19] is second order (first order with respect to each reactant). Therefore, in the current set of experiments, the reaction rate of β-cyclocitral with permanganate may follow a pseudo-first-order reaction, as expressed in Eqs. (1) and (2).

$$\frac{d[C_{\beta\text{-cyclocitral}}]}{dt} = -k_{obs}[C_{\beta\text{-cyclocitral}}] \quad (1)$$

$$k_{obs} = k_{CM}[C_{KMnO_4}]_0 \quad (2)$$

where $t$ is the time (min), $k_{obs}$ ($min^{-1}$) is the pseudo-first-order rate constant for β-cyclocitral and $[C_{KMnO_4}]_0$ is the initial concentration of permanganate, which can be considered constant in this case.

As shown in Fig. 1, the pseudo-first-order rate model well fits the experimental data for the permanganation of β-cyclocitral. The model fits the experimental data very well (correlation coefficients, $R^2 > 0.98$) for all the three cases examined. The extracted $k_{obs}$ values and their $R^2$ values are listed in the first three rows of Table 1. The three $k_{obs}$ values are almost identical, suggesting that $k_{obs}$ is independent of β-cyclocitral concentration. Fig. 2 shows another set of data for five permanganate doses. Again, the pseudo-first-order kinetic model well fits all the data, with all $R^2$ values >0.98. The extracted $k_{obs}$ values increase with increasing permanganate dose.

To obtain the rate model for the reaction between β-cyclocitral and permanganate, the extracted $k_{obs}$ values were plotted versus permanganate doses. Fig. 3 shows a linear relationship between $k_{obs}$ and permanganate dose with $R^2 = 0.99$. This implies that the reaction rate is first order with respect to permanganate concentration. From Eq. (2), the rate law of β-cyclocitral in the reaction with permanganate may be expressed as Eq. (3), with a second-order rate constant ($k_{CM}$) of $91.7 \pm 2.4$ $M^{-1}$ $s^{-1}$.

$$\frac{d[C_{\beta\text{-cyclocitral}}]}{dt} = -k_{CM}[C_{\beta\text{-cyclocitral}}][C_{KMnO_4}] \quad (3)$$

This rate constant is lower than those for MC-RR ($469 \pm 37$ $M^{-1}$ $s^{-1}$) [10] and for MC-LR ($357.2 \pm 17.5$ $M^{-1}$ $s^{-1}$) [19], but higher than that for other organic compounds, including trichloroethylene ($0.067 \pm 0.03$ $M^{-1}$ $s^{-1}$) [17] and methyl *tert*-butyl ether ($6.2 \times 10^{-5}$ $M^{-1}$ $s^{-1}$) [18].

The relatively high value of $k_{CM}$ suggests that permanganate is a suitable oxidant for the degradation of β-cyclocitral in drinking water treatment processes. This result is different from that obtained by Dietrich et al. [11], who reported that permanganate had very little effect on the removal of the odour produced by β-cyclocitral. In their study, the results were based entirely on a sensory evaluation, which is not able to determine the degradation of β-cyclocitral. Lin et al. [7] studied the chlorination of β-cyclocitral in de-ionized water. They observed that for chlorine at a concentration of 10 mg $L^{-1}$ and a contact time of 60 min, the oxidant was not able to destroy β-cyclocitral. This may be attributed to

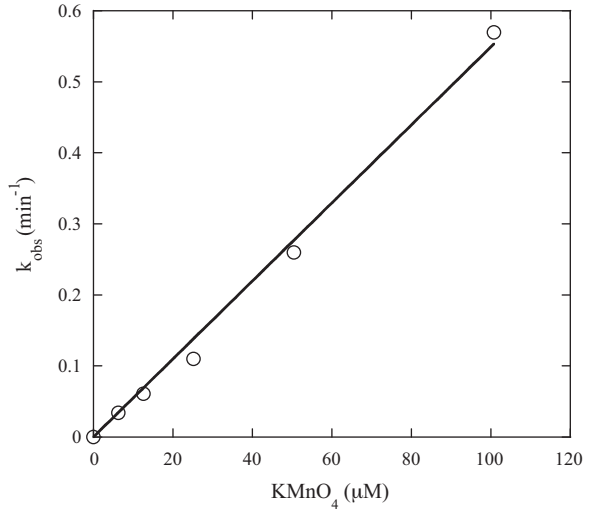


**Fig. 3.** Relationship between pseudo-first-order rate constants for β-cyclocitral degradation and permanganate concentration.

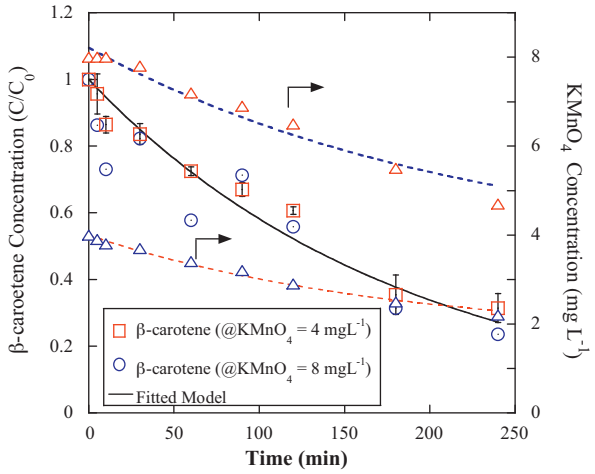


**Fig. 4.** Degradation of β-carotene under permanganate oxidation (initial β-carotene concentration = 1600 μg $L^{-1}$ (2.98 μM)).

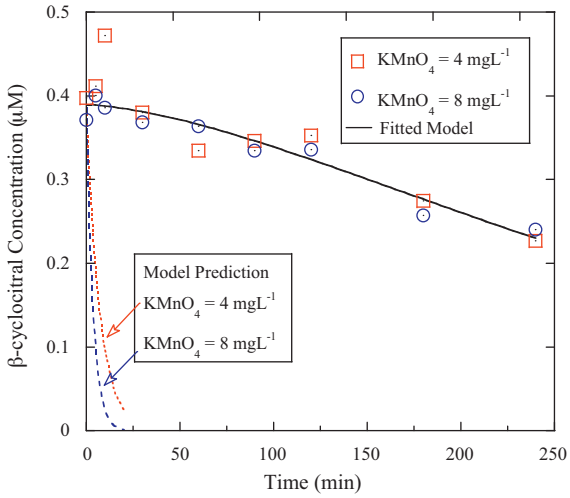


**Fig. 5.** Concentration change of β-cyclocitral during oxidation of β-carotene (initial β-carotene concentration = 1600 μg $L^{-1}$ (2.98 μM)).

the lower oxidation potential of hypochloric acid (1.49 V) compared to that of permanganate (1.68 V). For the ozonation of β-cyclocitral, a second-order rate constant of $3890 \pm 140\ M^{-1}\ s^{-1}$ was determined [20]. Although the rate constant of β-cyclocitral for ozone reaction is much higher than that for permanganate oxidation, ozone can penetrate or lyse the cells, resulting in more toxins and odorants being released into the water [19].

### 3.2. Degradation of β-carotene under permanganate oxidation

To clarify the effect of permanganate on the degradation of β-carotene, and the formation and subsequent degradation of β-cyclocitral, oxidation experiments of β-carotene were conducted with two permanganate doses (25.2 and 50.4 μM). In the experiments, β-carotene concentrations were initially set to 2.98 μM. Fig. 4 shows the experimental data for β-carotene. Unlike the kinetics observed for β-cyclocitral, the rate of β-carotene degradation is independent of the initial permanganate dose. The two sets of data are very similar when plotted in dimensionless concentrations for β-carotene. As shown in Fig. 4, two datum points are slightly away from the trend for the case of 25.2 μM permanganate. Considering that the analysis of β-carotene is difficult, this discrepancy is acceptable. Therefore, the kinetic data suggest that the reaction rate for β-carotene did not follow second-order kinetics as observed for common organics under permanganate oxidation. Instead, it is assumed that the reaction of β-carotene with permanganate follows a pseudo-first-order rate law. The rate of β-carotene oxidation can be expressed as Eq. (4).

$$\frac{d[C_{\beta\text{-carotene}}]}{dt} = -k_{\beta\text{-carotene}}[C_{\beta\text{-carotene}}] \quad (4)$$

where $k_{\beta\text{-carotene}}$ [$min^{-1}$] is the pseudo-first order rate constant for β-carotene.

Fig. 4 shows a good fit between the experimental data and the curve derived from the first-order rate model with $k_{\beta\text{-carotene}} = 0.0054 \pm 0.0004\ min^{-1}$. Note that the experimental data were obtained under two permanganate doses. The correlation coefficient is 0.88, suggesting that the fitting is reasonable.

β-Carotene is known to be humidity, heat and light sensitive [21]; one of its by-products is β-cyclocitral [22]. Although all the experiments were carried out in darkness, β-cyclocitral was observed at the beginning. The concentration is about 0.37–0.40 μM, which is about 1/9 that of β-carotene. Fig. 5 shows the concentration change of β-cyclocitral after the oxidation of β-carotene. If no other sources of β-cyclocitral are present, the concentration profiles of β-cyclocitral should follow the two dashed lines (shown in the figure) predicted using $k_{CM} = 91.7\ M^{-1}\ s^{-1}$ obtained in Section 3.1 under the two permanganate doses. However, the experimental results show that the β-cyclocitral concentration did not quickly disappear. The slow reaction rate may be attributed to two reasons: the presence of additional sources of β-cyclocitral in the system and/or a slow mass transfer rate. Sommerburg et al. [13] found that one major by-product during chlorination of β-carotene is β-cyclocitral. Therefore, it is assumed that β-cyclocitral is also produced during the permanganate oxidation of β-carotene. Similar to the degradation of β-carotene, the formation of β-cyclocitral is assumed to follow first-order kinetics with respect to β-carotene. Although the degradation of β-cyclocitral obtained from pure chemicals follows second-order kinetics, as shown in Section 3.1, the degradation of carotene-associated β-cyclocitral is different (discussed below). Therefore, first-order kinetics with respect to β-cyclocitral is also assumed. Eq. (5) expresses the formation and subsequent degradation of β-cyclocitral during the oxidation of β-carotene.

$$\frac{d[C_{\beta\text{-cyclocitral}}]}{dt} = k_1[C_{\beta\text{-carotene}}] - k_2[C_{\beta\text{-cyclocitral,C}}] \quad (5)$$

where $C_{\beta\text{-cyclocitral,C}}$ is the β-cyclocitral concentration associated with β-carotene, $k_1$ [$min^{-1}$] is the rate constant for the formation of β-cyclocitral from β-carotene, and $k_2$ [$min^{-1}$] is the rate constant for the destruction of β-carotene-associated β-cyclocitral by permanganate.

In Eq. (5), the formation of β-cyclocitral is assumed to be from the cleavage of β-carotene by permanganate. However, β-cyclocitral is not the only product of the reaction. During oxidation (e.g., chlorination), other chemicals, such as 5,6-epoxi-β-ionone, ionene, β-ionone, and dihydroactinidiolide may also be generated [13]. β-Ionone was also detected in the samples of β-carotene oxidation, although at a concentration much lower than that of β-cyclocitral (data not shown). Since cleaving one mole of β-carotene produces at most two moles of β-cyclocitral, $k_1$ should be less than $2 \times k_{\beta\text{-carotene}}$ (the rate constant of β-carotene degradation). For $k_2$, another rate constant in the equation, it should be theoretically equal to $k_{CM}$ $[KMnO_4]_0$ and similar to $k_{obs}$. However, if a portion of the β-cyclocitral is not present in the dissolved phase, $k_2$ may be different from $k_{CM}$ $[KMnO_4]_0$. Fig. 5 shows the experimental data and model fits from Eq. (5) for the change of β-cyclocitral concentration during the oxidation of β-carotene. Matlab (Math Works Company, USA) was used to fit the models to the data.

The best fitted kinetic parameters are 0.00070 $min^{-1}$ for $k_1$ and 0.0057 $min^{-1}$ for $k_2$. As mentioned, $k_1$ should be less than $2 \times k_{\beta\text{-carotene}}$. The $k_1$ obtained here is about 13% of $k_{\beta\text{-carotene}}$, suggesting that cleavage of one mole of β-carotene molecules approximately forms 0.1 moles of β-cyclocitral. The $k_2$ values may be transformed to $k_{CM}$ after accounting for $[KMnO_4]_0$. $k_{CM}$ is estimated to be 3.8 and 1.9 $M^{-1}\,s^{-1}$ for the two permanganate doses applied in the experiments, respectively. These $k_{CM}$ values are much smaller than that obtained for the direct oxidation of β-cyclocitral (91.7 $M^{-1}\,s^{-1}$) (see Eq. (3)). This discrepancy in $k_{CM}$ values for the two sets of experiments suggests that the β-cyclocitral produced from β-carotene may react slower with permanganate. Although the possibility of different reactivities for the two forms of β-cyclocitral cannot be ruled out, it is more likely that the different reaction rates are caused by a mass transfer limitation. β-Carotene is known to be insoluble in water [23]. Therefore, it is suspected that β-carotene hydrosols (particles) are present in the experimental system. When reacting with permanganate, β-cyclocitral produced from β-carotene may still remain in the particle phase, prohibiting the quick contact of β-cyclocitral with permanganate and thus lowering the reaction rate. Similar results were obtained by Wache et al. [23] who found that the co-oxidation of β-carotene in biphasic media containing hexane or benzene was facilitated by enzyme-produced free radicals. The cleaved product from β-carotene, β-ionone, accumulating in the organic phase prohibited the contact of radicals with itself and resulted in a much slower degradation rate compared with that in the aqueous phase. In addition, as for β-carotene during permanganate oxidation, a first-order rate law best describes β-carotene-associated β-cyclocitral in the oxidation.

To further support the hypotheses that different degradation rates were present for β-cyclocitral in the dissolved phase and that produced from β-carotene, two more experiments were conducted. The first one, referred to as Case C1, was the oxidation of 1.49 μM β-carotene with 8 mg $L^{-1}$ (50.4 μM) of permanganate. In the second experiment, referred to as Case C2, similar experimental conditions were adopted except that an additional 0.14 μM β-cyclocitral was added into the system. The change of β-cyclocitral concentrations in the two cases is shown in Fig. 6. The initial concentration of β-cyclocitral in Case C1 is about 10% that of β-carotene. A small, sudden increase of β-cyclocitral concentration, followed by a gradual decrease, was then observed. This may be linked to the production of β-cyclocitral from the oxidation of β-carotene. At the same time, β-cyclocitral, including that originally present with β-carotene and that formed from oxidation, was further degraded by permanganate. For Case C2, a very rapid reduction was found right after oxidation. β-Cyclocitral in this case includes three sources, two associated with β-carotene as in Case C1 (referred to as β-carotene-associated β-cyclocitral) and the addition of β-cyclocitral obtained from pure chemicals (referred to as chemical β-cyclocitral). It is expected that chemical β-cyclocitral is in the dissolved phase, while β-carotene-associated β-cyclocitral binds with small β-carotene particles. Therefore, the concentration difference of β-cyclocitral between the two cases may represent the change of chemical β-cyclocitral in the system. Fig. 7 plots the concentration change of chemical β-cyclocitral. The data are well fit with the first-order kinetics in Eqs. (1) and (2). A rate constant ($k_{CM}$) of 69 $M^{-1}\,s^{-1}$ and a high correlation coefficient ($R^2 = 0.99$) were obtained in the simulation. This $k_{CM}$ is only 25% lower than that obtained in Eq. (3), suggesting that the degradation of chemical β-cyclocitral in a more complex system (Case C2) is similar to that in a pure water system. In addition, it may also be inferred that the degradation rate of chemical β-cyclocitral is different from that of β-carotene-associated β-cyclocitral.

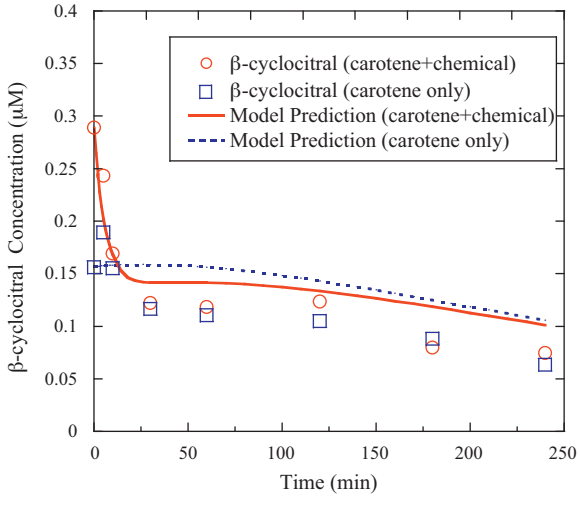


**Fig. 6.** Concentration change of β-cyclocitral during oxidation of β-carotene and of both β-carotene and β-cyclocitral.

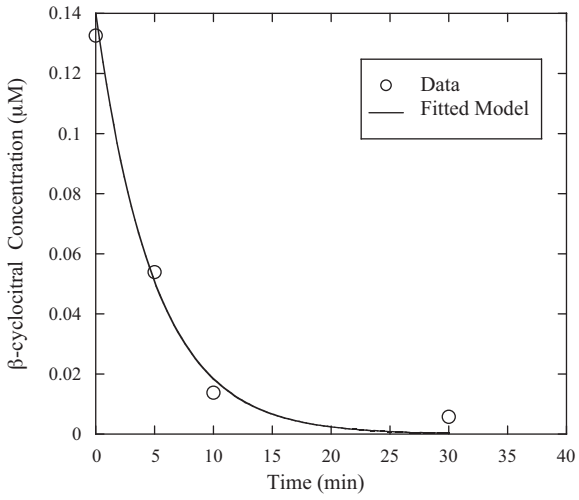


**Fig. 7.** Data and simulation results for the degradation of β-cyclocitral.

To account for the effect of the slower degradation rate for the β-carotene-associated β-cyclocitral during oxidation, Eq. (5) was modified as expressed in Eq. (6).

$$\frac{d[C_{\beta\text{-cyclocitral}}]}{dt} = k_1[C_{\beta\text{-carotene}}] - k_2[C_{\beta\text{-cyclocitral,C}}] - k_{CM}[C_{\beta\text{-cyclocitral}}][C_{KMnO_4}]_0 \quad (6)$$

In the equation, $k_1$, $k_2$, and $k_{CM}$ are the same as those shown in Eqs. (3) and (5), and may be obtained from experiments as indicated in previous sections. Therefore, the three extracted $k$ values ($k_1 = 0.00070\ min^{-1}$, $k_2 = 0.0057\ min^{-1}$, and $k_{CM} = 69\ M^{-1}\,s^{-1}$) may be used to predict the β-cyclocitral concentration change in experiments. Although not perfectly matched, the predictions capture the experimental data and trend fairly well for both cases, suggesting that the model reasonably describes the formation and degradation of β-cyclocitral in the system.

### 3.3. Oxidation of β-cyclocitral extracted from M. aeruginosa

The cyanobacterium *Microcystis* is known to be a β-cyclocitral producer [5]. When the cells are broken, β-carotene in the cells is cleaved by β-carotene oxygenase, forming β-cyclocitral quickly. It is of interest to know whether the oxidation kinetics

**Table 2**
Kinetic rate constants for permanganate oxidation of β-cyclocitral from two sources.*

| Source of β-cyclocitral | pH | $[KMnO_4]_0$ (μM) | $[KMnO_4]$ (mg $L^{-1}$) | $k_{CM}$ ($s^{-1}$ $M^{-1}$) | $R^2$ |
|---|---|---|---|---|---|
| Chemicals | 7.4 | 50.4 | $C \approx C_o$ | 86 | 0.991 |
| | 7.4 | 100.8 | | 94 | 0.995 |
| *M. aeruginosa* | 7.4 | 50.4 | $C = 1.7 \times \exp(-0.077t) + 6.4$ | 34 | 0.972 |
| | 7.4 | 100.8 | $C = 2.5 \times \exp(-0.075t) + 14.0$ | | |

* Temperature was controlled at 25 °C.

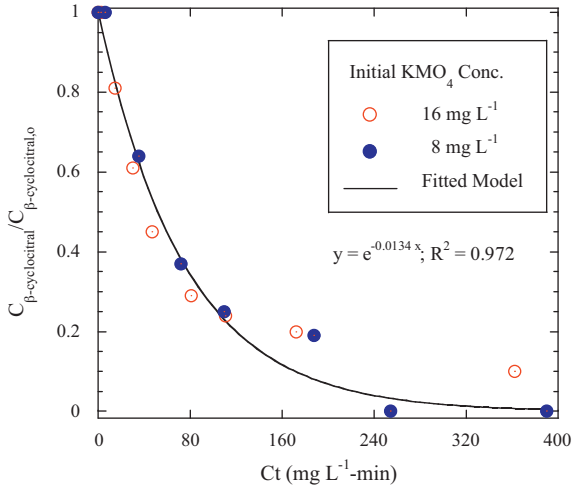


**Fig. 8.** Experimental data and model fits for β-cyclocitral extracted from *M. aeruginosa*.

of β-cyclocitral extracted from *Microsystis* is similar to that of β-cyclocitral obtained from pure chemical. Similar to Section 3.1 for β-cyclocitral oxidation, the reaction was found to follow second-order kinetics (first order with respect to each reactant). During the experiments, permanganate continued to decay due to reactions. Therefore, in obtaining the rate constant for the reaction ($k_{CM}$), the concentration change of permanganate was taken into account. The permanganate decay kinetics was fitted with a first-order decay model, as shown in Eq. (7).

$$[C_{KMnO_4}] = [C_{KMnO_4}]_1 \times e^{-k_{KMnO_4} t} + [C_{KMnO_4}]_2 \quad (7)$$

where $C_{KMnO_4,1}$ is the permanganate demand of the sample (mg $L^{-1}$), $k_{KMnO_4}$ is the rate constant for permanganate decay ($min^{-1}$), and $C_{KMnO_4,2}$ is the amount of permanganate not reacted with the sample (mg $L^{-1}$). The three-parameter model has been successfully employed by Daly et al. [24] and Lin et al. [7] to describe chlorine decay during oxidation of cyanobacteria-laden water. In the present study, the model also fits permanganate decay data very well, with correlation coefficients ($R^2$) exceeding 0.90 for both cases (data not shown).

When permanganate is decaying, Eq. (7) may be substituted into Eq. (3) to describe the degradation kinetics of β-cyclocitral. After integration with time, β-cyclocitral concentration may be expressed as:

$$C_{KMnO_4} t = \frac{[C_{KMnO_4}]_1}{k_{KMnO_4}} \times (e^{-k_{KMnO_4} t} - 1) + [C_{KMnO_4}]_2 t \quad (8)$$

where $[C_{\beta\text{-cyclocitral}}]_0$ is the initial concentration of β-cyclocitral and $[C_{KMnO_4} t]$ is the permanganate exposure (mg $L^{-1}$ min) that can be estimated from an integration of Eq. (7) with time.

$$[C_{\beta\text{-cyclocitral}}] = [C_{\beta\text{-cyclocitral}}]_0 \times \exp\{-k_{CM}[C_{KMnO_4} t]\} \quad (9)$$

Eqs. (8) and (9) were used to simulate the change of β-cyclocitral concentration. Fig. 8 shows the relative concentration of β-cyclocitral $[C/C_0]$ versus $Ct$ for two permanganate doses. The model describes the data very well, with $R^2 = 0.972$. Although higher permanganate dosages gave slightly faster kinetics for β-cyclocitral degradation, the difference was slight. Table 2 lists the best fitted $k_{CM}$ from Fig. 8 for the β-cyclocitral extracted from *M. aeruginosa* and that from the oxidation of chemical β-cyclocitral. As shown in table, the degradation rate of natural β-cyclocitral is about 40% lower than that of chemical β-cyclocitral. The lower reaction rates may be due to the matrix effect and the attachment of β-cyclocitral with β-carotene. Although the water used in the experiment was filtrated, it is very likely that β-cyclocitral may bind to some small β-carotene particles. The reaction rate would become slower due to a mass transfer limitation. The DOC concentration was extremely high in the solution. Therefore, it is expected that permanganate may also react with other organics, causing slower rates for the oxidation of β-cyclocitral.

## 4. Conclusion

During permanganate oxidation, the degradation of β-cyclocitral prepared from pure chemicals was well fitted by second-order kinetics with a rate constant of $91.7 \pm 2.4\ M^{-1}\ s^{-1}$ and that of the β-cyclocitral precursor, β-carotene, followed first-order kinetics with a rate constant of $0.0054 \pm 0.0004\ min^{-1}$. During the oxidation of β-carotene, β-cyclocitral was produced. The formation and degradation can be simulated by first-order kinetics with respect to β-carotene and β-cyclocitral concentrations, respectively. The degradation rate of β-cyclocitral produced from β-carotene was found to be much slower than that of β-cyclocitral obtained from pure chemicals, very likely due to a mass transfer limitation. The kinetic models used and kinetic parameters extracted under different experimental conditions are reasonable. This kind of approach may be applied in the estimation of the formation and degradation of β-cyclocitral and perhaps other compounds relevant to β-carotene, such as β-ionone, in water treatment systems.

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