



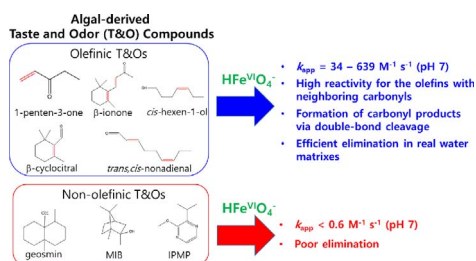
Oxidation kinetics of algal-derived taste and odor compounds during water treatment with ferrate(VI)

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GRAPHICAL ABSTRACT



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ABSTRACT

The potential of ferrate(VI) to oxidize algal-derived taste and odor (T & O) compounds during water treatment was assessed by investigating the reaction kinetics of ferrate(VI) with selected T & O compounds. Apparent second-order rate constants (k_{app}) were determined in phosphate buffered waters in the pH range of 6–9. The olefinic T & O compounds show an appreciable reactivity to ferrate(VI); $k_{app} = 34\text{--}639 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7. The non-olefinic T & O compounds such as geosmin and 2-methylisoborneol show negligible reactivity to ferrate(VI) ($k_{app} < 0.6 \text{ M}^{-1} \text{ s}^{-1}$). The reactivity of olefinic T & O compounds toward ferrate(VI) is poorly correlated with the Taft sigma constant as a descriptor of the olefin's substituents while the high reactivity is found for the carbon double bond of α,β -unsaturated carbonyl groups. The elimination rate of the olefinic T & O compounds during ferrate(VI) treatment was significantly enhanced with increasing ferrate(VI) dose, in which the enhancement was more than the model prediction that considers the ferrate(VI) reaction alone. Aldehydes were formed from the ferrate(VI) oxidation of olefinic T & O compounds indicating the double bond cleavage as one of the major oxidation pathways. Oxidation experiments in lake and river water matrices spiked with selected T & O compounds confirmed the efficient elimination of olefinic T & O compounds.

1. Introduction

Algal and cyanobacterial blooms in fresh and coastal waters are a global environmental issue and are expected to increase due to climate change and/or increasing nutrient discharge [1–3]. Algal blooms have also been a serious concern for drinking water production due to their negative impacts on the drinking water treatment processes, such as

clogging of filters by algal cells, or on the water quality due to the release of taste and odor (T & O) compounds, algal toxins, or precursors of disinfection by-products [4–6]. Among the drinking water quality problems associated with algal blooms, T & O compounds have been one of the most important issues as they can impair the public's perception of the safety of drinking water despite their negligible toxicological effects on the water's consumers [7,8].

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Many T & O compounds have been identified as being produced by different cyanobacteria or algae species [9,10]. Geosmin and 2-methylisoborneol (MIB) are the two most prominent T & O compounds of concern in the drinking water industry based on their frequent detection, low threshold odor values (i.e., 4 ng/L for geosmin and 15 ng/L for MIB [11]), and persistency during conventional drinking water treatment processes such as coagulation, flocculation, sedimentation, filtration, and chlorine disinfection [12,13]. Other T & O compounds such as β -ionone, 2-isopropyl-3-methoxy-pyrazine (IPMP), or *trans,cis*-2,6-nonadienal have also been detected in algal-impacted water resources with very low threshold odor values (0.2–20 ng/L, respectively [8,11]) and thus have been a concern for the drinking water industry.

Preoxidation by chlorine, ozone, or permanganate before the particle removal processes (e.g., coagulation) has been reported to be effective for treating algal-impacted waters as it can promote the coagulation of algal cells by changing their surface properties or by excreting polymeric substances as a coagulation aiding agent [14]. However, recent studies have shown that preoxidation with strong oxidants such as ozone or chlorine can induce lysis of algal cells and release intracellular T & O compounds and algal toxins [15–18]. In addition, formation of toxic chlorinated byproducts can limit the application of high chlorine doses [6,19]. Accordingly, the preoxidation processes should be carefully chosen and optimized for treating algal-impacted waters. Previous studies have shown that preoxidation with permanganate as a mild oxidant has a potential to increase the coagulation efficiency of algal cells while achieving a minimized release of intracellular organic matter [20–23].

Ferrate(VI), an iron in +6 oxidation state, has been proposed for use in drinking water or wastewater treatment as an oxidant and a coagulant [24,25]. Ferrate(VI) shares common characteristics with permanganate as a water treatment oxidant: both are transition metal-based oxidants and the products after their oxidation reactions can be used as *in-situ* coagulants in the form of iron oxides and manganese oxides, respectively. In addition, the two oxidants show a mild, selective reactivity to organic compounds containing electron-rich moieties such as phenols, anilines, olefins, and amines, although the reactivity patterns and magnitudes differ depending on the type of moieties [26–30]. The preoxidation with ferrate(VI) has also been demonstrated to enhance the coagulation efficiency of algal cells [31]. The kinetic information for the oxidation of T & O compounds by ferrate(VI) can be useful to optimize the ferrate(VI) preoxidation process for treating algal-impacted waters by ensuring an optimal elimination of dissolved T & O compounds while minimizing the release of intracellular organic matter from algal cell lysis. Currently, such kinetic information is not available.

Good correlations have been found for water treatment oxidants between the second-order rate constants for an oxidation reaction of closely related compounds having a common moiety and substituent descriptor variables such as Hammett or Taft sigma constants [32]. The quantitative structure-activity relationships (QSARs) approach has been demonstrated to be quite useful in assessing or predicting the elimination efficiency of organic micropollutants during oxidative water treatment [33,34]. The olefinic moiety is a substructure of many organic micropollutants including algal-derived T & O compounds. Currently, a limited number of second-order rate constants are available for the reaction of ferrate(VI) with olefinic compounds [24,27], which makes it difficult to derive any QSAR relationships.

The objective of this study was to assess the potential of ferrate(VI) oxidation to eliminate algal-derived T & O compounds during treatment of algal-impacted waters. For this, second-order rate constants were determined in synthetic buffer solutions in the pH range of 6–9 for the reaction of ferrate(VI) with selected T & O compounds: olefin-containing compounds such as β -ionone, β -cyclocitral, *cis*-3-hexen-1-ol, *trans,cis*-2,6-nonadienal, and 1-penten-3-one, and non-olefinic compounds such as geosmin, IPMP, and MIB (see Table 1 for their chemical structures). The determined second-order rate constants were used to

inspect the structure-reactivity relationship for the reaction of ferrate (VI) with olefinic compounds. The elimination kinetics of selected T & O compounds was then investigated in phosphate buffered solutions and compared with the model predictions using the determined second-order rate constants. Finally, oxidation experiments of the selected T & O compounds were performed in natural waters with various concentrations of dissolved organic matter (DOM).

2. Materials and methods

2.1. Standards and reagents

All chemicals and solvents (mostly the highest purity available) were purchased from various commercial suppliers and used as supplied. Potassium ferrate was purchased from Sigma-Aldrich (K_2FeO_4 , 723835). Stock solutions of Fe(VI) (0.2–1 mM) were freshly prepared by dissolving solid samples of potassium ferrate in pure water (pH \approx 9.2), followed by rapid filtration through a 0.45 μ m PVDF syringe filter (Whatman, USA), and then standardized spectrophotometrically at 510 nm using ϵ of 1150 $M^{-1} cm^{-1}$ [35]. The details of chemical sources are provided in SI-Text-1 of the Supplementary Information (SI).

2.2. Kinetic and stoichiometric experiments in phosphate buffered solutions

Kinetic studies were performed in a batch reactor (200 mL) in the pH range of 6–9 at room temperature (22 ± 1 °C). Phosphate (5 mM) was used as a buffer as well as a complexing agent for Fe(III) from ferrate(VI) decay for all pH conditions [36]. Borate (2 mM) was used as a buffer for pH 9 together with the phosphate buffer. Kinetic experiments were conducted in two different reactant conditions: (1) under a pseudo first-order condition for ferrate(VI) by employing an excess of T & O compound relative to ferrate(VI) (i.e., $[T \& O]_0 \geq 10 \times [Fe(VI)]_0$ and $[Fe(VI)]_0 = 1\text{--}3 \mu M$); and (2) under a pseudo first-order condition for the T & O compound by employing an excess of ferrate(VI) relative to the T & O compound ($[Fe(VI)]_0 \geq 10 \times [T \& O]_0 = 2 \mu M$). The reaction was initiated by adding a small volume (< 2 mL) of an aliquot of ferrate(VI) stock solution (0.2–1 mM) to the solution (100 mL) containing a T & O compound and buffered at the desired pH under rapid mixing for the initial 10 s. The reaction solutions were sampled as a function of reaction time and mixed with a 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) to measure the residual ferrate (VI) following the ABTS method [37] or a thiosulfate solution (1 mM) to measure the residual T & O compound concentrations, respectively. Reaction products and stoichiometry were investigated for β -ionone and 1-penten-3-one. For this, 5 μM or 10 μM of β -ionone or 1-penten-3-one was treated for more than 30 min with a range of ferrate(VI) doses (0–30 μM) at pH 7 (phosphate buffer). The treated samples were analyzed within a few hours for the parent T & O compound and oxidation products. Care was taken to minimize the exposure of samples to indoor light (e.g., by using amber vials) as some of T & O compounds such as β -ionone are known to be photo-active [38]. Nevertheless, the degradation of T & O compounds in our control experiments (i.e., without ferrate(VI) addition) was found to be negligible. All experiments were conducted in duplicate or triplicate and the average values with standard deviations were reported.

2.3. Taste and odor elimination experiments in real water matrixes

Water from a lake (Dongbok lake: 2.3 mg/L of dissolved organic carbon (DOC) and 59 mg/L of $CaCO_3$ alkalinity) and water from a river (Nakdong river: 5.8 mg/L of DOC, 123 mg/L of $CaCO_3$ alkalinity) were used as the real water matrixes for the T & O compound elimination experiments. Dongbok lake and Nakdong river are the drinking water sources for the cities of Gwangju and Busan, respectively, in Korea. The water samples were filtered through 0.45 μ m cellulose acetate filters (Advantec, Japan) upon arrival in the laboratory and stored at 4 °C. The

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