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Interactions of ferrate(VI) and aquatic humic substances in water treatment

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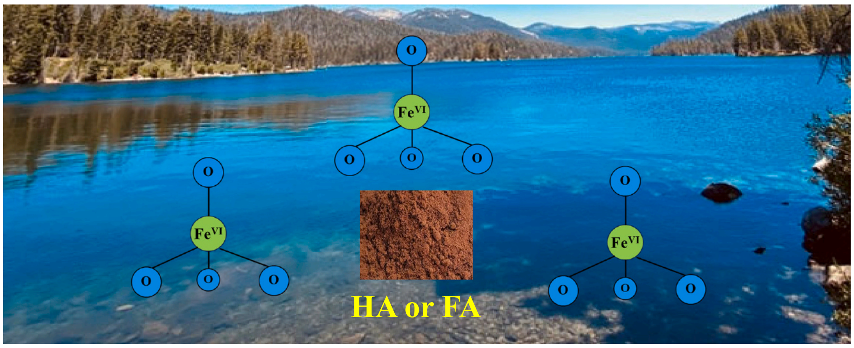
HIGHLIGHTS

- Interplay of Fe(VI) and humic substances in water is investigated.
- Fe(VI) decomposition exhibits a biphasic kinetic pattern in the presence of HA or FA.
- DOC_{50}% is introduced to assess relative dominance of Fe(VI) self-decay and consumption by humic substances.
- Fe(VI) degrades HA and FA across different MW ranges, advantages over ozone.
- Fe(VI) preferentially attacks high MW, hydrophobic HA and FA molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

Aquatic humic substances, encompassing humic acid (HA) and fulvic acid (FA), can influence the treatment of ferrate(VI), an emerging water treatment agent, by scavenging Fe(VI) to accelerate its decomposition and hinder the elimination of target micro-pollutants. Meanwhile, HA and FA degrade the water quality through the transformation to disinfection byproducts over disinfection, contribution to water color, and enhanced mobility of toxic metals. However, the interplay with ferrate(VI) and humic substances is not well understood. This study aims to elucidate the interactions of ferrate(VI) with HA and FA for harnessing ferrate(VI) in water treatment. Laboratory investigations revealed distinctive biphasic kinetic profiles of ferrate(VI) decomposition in the presence of HA or FA, involving a 2^{nd} order kinetic reaction followed by a 1^{st}-order kinetic reaction. Both self-decay and reactions with the humic substances governed the ferrate(VI) decomposition in the initial phase. With increasing dissolved organic carbon (DOC), the contribution of self-decomposition to ferrate(VI) decay declined, while humic substance-induced ferrate(VI) consumption increased. To assess relative contributions of the two factors, $DOC_{50\%}$ was first introduced to represent the level at which the two factors equally contribute to the ferrate(VI) loss. Notably, $DOC_{50\%}$ (11.90 mg/L for HA and 13.10 mg/L for FA) exceeded typical DOC in raw water, implying that self-decay predominantly governs ferrate(VI) consumption. Meanwhile, ferrate(VI) could degrade and remove HA and FA across different molecular weight (MW) ranges, exhibiting treatment capabilities that are either better or, at least, equivalent to ozone. The ferrate(VI) treatment attacked high MW, hydrophobic organic molecules, accompanied by the production of low MW, more hydrophilic compounds. Particularly, FA was more effectively removed due to its smaller molecular sizes, higher solubility, and lower carbon contents. This study provides valuable insights into the effective utilization of ferrate(VI) in water treatment in presence of humic substances.

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1. Introduction

Ferrate(VI), that is, FeO_4^{2-}, is an anion containing iron in its +6 oxidation states (Delaude and Laszlo, 1996; Sharma, 2002). Different from many other iron species, it possesses a tetrahedral structure characterized by four equivalent Fe═O bonds (Hoppe et al., 1982). As a burgeoning water treatment agent, ferrate(VI) has gained an increasing attention due to multi-function, the production of non-toxic final products (i.e., iron (hydr)oxides), and the minimal formation of known disinfection by-products (DBPs) (Cui et al., 2018; Jiang et al., 2019; Lin et al., 2021; Marbaniang et al., 2023; Spellman Jr and Goodwill, 2023; Zhang et al., 2020; Zheng et al., 2020).

Particularly, the multiple functions of ferrate(VI) promise its potential application to water treatment to concurrently realize different treatment processes, including chemical oxidation, disinfection, coagulation, precipitation, and adsorption, at a single chemical dose within one reactor (Lee et al., 2004; Zhang et al., 2020; Zheng et al., 2020). Specifically, ferrate(VI) is a highly potent chemical oxidant with a reduction potential up to +2.2 V (Sharma, 2002), capable of chemically degrading wide-ranging traditional and emerging aquatic pollutants (Eng et al., 2006; Qu et al., 2003; Sharma, 2013; Shi et al., 2022; Tian et al., 2022; Waite and Gilbert, 1978) and inactivating various waterborne pathogens (Hu et al., 2012; Jiang et al., 2007; Manoli et al., 2019; Wang et al., 2023b). Moreover, the reduction of Fe(VI) in ferrate(VI) can form Fe(III) to initiate *in-situ* coagulation and precipitation in water, effectively destabilizing colloidal particles (Lv et al., 2018; Ma and Liu, 2002) and eliminating unwanted dissolved pollutants (e.g., arsenic and phosphate) (Fan et al., 2002; Fan et al., 2023; Kong et al., 2023; Prucek et al., 2013; Zheng et al., 2023), respectively. Meanwhile, iron (hydr) oxides resulting from the ferrate(VI) treatment exhibit adsorption capabilities toward different dissolved pollutants, such as heavy metals (Cui et al., 2018; Wang et al., 2019; Wu et al., 2022) and organic compounds (Yang et al., 2020). The aforementioned distinct properties distinguish ferrate(VI) from many existing water treatment agents, thus having a potential to revolutionize the paradigm of water treatment. The current knowledge of ferrate(VI) chemistry, though significantly advanced, remains limited. These limitations restrict the practical application of ferrate(VI) to water treatment practices. Among the constraints, one is the poor understanding of interactions between ferrate(VI) and natural organic matter (NOM), which serves as the dominant matrix constituent in water.

NOM encompasses a complex assemblage of organic substances ubiquitously present in natural water sources (Chen et al., 2002; Matilainen et al., 2010). The organic constituents are typically categorized into hydrophobic and hydrophilic fractions (Korshin et al., 2009; Yan et al., 2015). The hydrophobic NOM molecules are characterized by abundant aromatic carbon, phenolic structures and conjugated C═C double bonds (Hua and Reckhow, 2007; Świetlik et al., 2004). In contrast, the hydrophilic NOM compounds are rich in amine, carboxylic, carbonyl, and ester groups (Hua and Reckhow, 2007; Świetlik et al., 2004). Once dosed to water, ferrate(VI) undergoes self-decay and reactions with reductive chemicals in water. Given that NOM has abundant electron-donating moieties, it can serve as a major sink of ferrate (VI) and thus impact the kinetic patterns of ferrate(VI) decomposition in water (Deng et al., 2018; Jiang et al., 2015; Lee et al., 2004). Particularly, ferrate(VI) exhibites a preferential reactivity toward the hydrophobic NOM portion as opposed to its hydrophilic group (Barışçı, 2017; Deng et al., 2018; Graham et al., 2010; Jiang et al., 2016; Song et al., 2016).

Aquatic humic substances, including humic acid (HA) and fulvic acid (FA), are the principal portion of hydrophobic NOM molecules (Świetlik et al., 2004). HA constitutes the fraction of humic substances that are soluble in dilute alkaline solution but precipitate at a low pH (< 2) (Steelink, 1963). In contrast, FA represents the humic substances capable of being dissolved across a wide range of pH (Saar and Weber, 1982; Schnitzer and Kerndorff, 1981). Although the decomposition behaviors of ferrate(VI) in the presence of NOM were investigated in our previous study (Deng et al., 2018), very few efforts were made to evaluate the respective roles of HA and FA on the kinetics of ferrate(VI) decomposition in water. Particularly, the comparison of different quantitative ferrate(VI) decomposition patterns with HA and FA is lacking. Considering that an accurate ferrate(VI) decay profile over time is key to the determination of its oxidant exposure (a critical operating parameter in the degradation of reductive water pollutants and the inactivation of pathogens), there is an urgent need for gaining deeper insights into the impacts of HA and FA on the kinetic patterns of ferrate (VI) decomposition in water.

On the other hand, it is vital to comprehend the transformation of HA and FA over the ferrate(VI) treatment. While aquatic humic substances are not water contaminants themselves, they may greatly impact water quality in different pathways. As the major precursors, HA and FA may transform to harmful DBPs during disinfection to threaten public health (Boucherit et al., 2015; Singer, 1999). Moreover, aquatic humic substances can contribute to the water color and complex with certain toxic metal ions to increase their solubility in water (Oliver et al., 1983; Petrović et al., 1999; Town et al., 2012; Weber and Wilson, 1975). Although ferrate(VI) oxidation of NOM or aquatic humic substances was studied (Graham et al., 2010; Jiang and Wang, 2003; Lim and Kim, 2009, 2010; Qu et al., 2003; Song et al., 2016), there remains a need for a comprehensive assessment of the oxidative capacity of ferrate(VI) in chemical degradation and transformation of HA and FA. Particularly, there is a dearth of assessments to compare ferrate(VI) against established chemical oxidants in terms of the oxidative efficiency and the NOM degradation.

This study aimed to elucidate the interactions of ferrate(VI) with HA and FA for harnessing ferrate(VI) in water treatment. To this end, the kinetic patterns of ferrate(VI) decomposition in the presence of HA and FA were assessed, while the transformation of HA and FA was investigated. To better understand the ferrate(VI) reactions with HA or FA, ferrate(VI) was compared with ozone (O_3) in terms of their kinetic decomposition behaviors and chemical degradation of humic substances in water. In this study, O_3 rather than other chemical oxidants was chosen primarily based on the following three considerations. First, ozonation is a well-established and commercially viable chemical oxidation technology in practical water treatment for decades (Anderson et al., 1985; Imai et al., 2009; Rodríguez et al., 2014, 2016; Wang et al., 2016; Xiong et al., 1992). Second, in contrast to other methods such as chlorination, both ferrate(VI) and O_3 treatments typically have a lower potential to produce harmful DBPs (Jiang et al., 2019; Richardson et al., 2000; Sharma et al., 2005). Third, ferrate(VI) and O_3 are often used for similar treatment purposes in water treatment, including disinfection, chemical oxidation, and the improvement of water aesthetic quality parameters (e.g., taste and color) (Jiang, 2014; Jiang et al., 2019; Liu et al., 2018; Ramseier et al., 2011). Therefore, the comparison of ferrate(VI) against ozone better advances our assessments in the performance of ferrate(VI) technology in water treatment.

2. Materials and methods

2.1. Chemical and reagent

All the reagents used were of analytical grade, unless otherwise specified. Potassium ferrate(VI) (K_2FeO_4) (> 96 %) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All the other chemicals were obtained from Fisher-Scientific (Fair Lawn, NJ, USA). All solutions were prepared using ultrapure water (>18.2 MΩ·cm) generated from a Milli-Q water purification system (Milli-Q Direct 8, France). Suwannee River Humic Acid (SR-HA) (humic acid standard III, 3S101H) and Suwannee River Fulvic Acid (SR-FA) (fulvic acid standard II, 2S101F) were purchased from the International Humic Substances Society (IHSS) (St. Paul, MN, USA). Their stock solutions (DOC = 100.0 mg/L) were prepared by dissolving a certain mass of SR-HA or SR-FA in ultrapure water, followed by the filtration through 0.45 μm nitrocellulose microfiltration membrane (Millipore, Burlington, MA, USA) to remove any particulate matter. To prepare HA or FA solutions with DOC ranging within 0.00–32.40 mg/L, a borate-buffered solution (10 mM) was spiked with an appropriate aliquot of HA or FA stock solutions. Prior to the experiments, the solution pH was adjusted to 7.50 with 0.01 M sodium hydroxide (NaOH) and 0.01 M hydrogen chloride (HCl). The selected pH falls within the typical pH range of fresh surface water and groundwater sources. It should be noted that the added chloride had a limited influence on the ferrate(VI) decomposition and oxidation (Jiang et al., 2015; Kolařík et al., 2018). A concentrated 3.58 mM ferrate(VI) stock solution (i.e., 200 mg/L Fe(VI)) was prepared by dissolving a specific amount of K_2FeO_4 in ultrapure water immediately before use.

2.2. Experimental procedure

2.2.1. Kinetic tests of ferrate(VI) and O_3 decomposition

In all the ferrate(VI) or O_3 decomposition tests, 800 mL of borate-buffered solutions prepared as described in Section 2.1 were added into 1 L beakers. The experiments were conducted at room temperature (20 ± 1 °C). The solution pH was manually controlled at 7.50 using 0.01 M HCl or 0.01 M NaOH. Ferrate(VI) and O_3 were dosed at the same normality (N), that is, 36.0 μM Fe(VI) and 53.6 μM O_3. The selected O_3 dose falls within the typical ozone dosage range in water treatment practices (Crittenden et al., 2012). In the kinetic tests of ferrate(VI) decomposition, the ferrate(VI) decay occurred once an aliquot volume of ferrate(VI) stock solution was added. At designated sampling times, 10 mL solution was collected to immediately measure the residual ferrate (VI) using the ABTS method at a wavelength of 410 nm (Lee et al., 2005). On the other hand, the kinetic tests of O_3 decomposition were carried out in a batch mode by dosing a specific volume of O_3 stock solution (i.e., 6.0 mg/L) to the borate-buffered samples (DOC = 0.00 mg/L) to reach designated dissolved O_3 concentration. O_3 in the stock solution was produced from oxygen (O_2) using a laboratory air-cooled corona discharge O_3 generator (0.0–10.0 g O_3/h, Model LAB2B, Ozonia Triogen, UK). At all the designated sampling times, 10 mL solutions were collected for the measurement of residual O_3 in water. The pH of O_3 stock solution was maintained by introducing 50 μL of 500 mM nitric acid (Jiang et al., 2019; Reckhow et al., 1986; Staehelin and Hoigne, 1982). Meanwhile, light was blocked to mitigate photo-initiated O_3 decomposition (Jiang et al., 2019; Reckhow et al., 1986; Staehelin and Hoigne, 1982). Off-gas was collected into a glass flask with 2 % potassium iodide solution for disposal.

2.2.2. Chemical oxidation of humic substances in water

HA- or FA-containing stock solutions were filtered using 0.45 μm nitrocellulose membrane prior to ultrafiltration using an Amicon ultrafiltration (UF) stirred cell (Amicon 8200, Millipore, Burlington, Massachusetts, USA) driven by pressured N_2 gas. Two ultrafiltration membranes with different MW cut-offs (100 kDa and 10 kDa) (Millipore, Billerica, MA, USA) were used separately for the filtration to obtain three samples with different MW ranges (i.e., < 0.45 μm, < 100 kDa, and < 10 kDa). Following the filtration, the samples were diluted with ultrapure water until DOC was 4.0 mg/L.

Chemical oxidative treatment tests were implemented in 200 mL HA or FA solutions within 250 mL beakers. A magnetic stirrer mixer was used to ensure a completely mixed state. Initial solution pH was adjusted to 7.50 with 0.01 M HCl or 0.01 M NaOH and then spiked with a borate-buffer stock solution to prepare 10 mM borate-buffered samples. Once an appropriate volume of ferrate(VI) and O_3 stock solutions was dosed to HA or FA-containing solutions, the treatment was initiated. The solutions were rapidly mixed at 150 rpm until the residual ferrate(VI) and O_3 was undetectable. Ferrate(VI) and O_3 were dosed at the same normality, that is, 36.0 μM ferrate(VI) and 53.6 μM O_3. If needed, the solution pH was manually maintained at 7.50 using 0.01 M HCl or 0.01 M NaOH.

After the ferrate(VI) or O_3 treatment, the <0.45 μm filtered samples were sequentially filtered with 100 kDa and 10 kDa UF membranes to fractionate dissolved organic matter into >100 kDa, 10–100 kDa, and < 10 kDa. Moreover, the 100 kDa UF filtered samples were filtered with 10 kDa UF membranes to obtain the samples with two MW ranges (i.e., 10–100 kDa and < 10 kDa). Furthermore, 10 kDa UF membrane filtered samples were filtered using 10 kDa UF membranes to obtain the <10 kDa MW samples.

2.3. Analytical methods

Residual O_3 in water was measured using the indigo method (Bader and Hoigné, 1981). The ferrate(VI) concentration in the stock solution was verified using the ABTS method as described in detail elsewhere (Lee et al., 2005). DOC was quantified by measuring total organic carbon (TOC) of 0.45 μm nitrocellulose membrane filtered water samples with a TOC analyzer (TOC-LCPH, Shimazu Corp., Kyoto, Japan). UV_{254} absorbance of water samples was determined at a wavelength of 254 nm using a UV/Vis spectrophotometer (HACH DR 5000). Specific ultraviolet absorbance (SUVA) was computed based on Eq. (1).

$$\mathrm{SUVA}\left(\frac{\mathrm{L}}{\mathrm{mg.m}}\right)=\frac{\mathrm{UV_{254}\ absorbance}\left(\frac{1}{\mathrm{cm}}\right)}{\mathrm{DOC}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right)}\times 100\frac{\mathrm{cm}}{\mathrm{m}} \tag{1}$$

Student's *t*-tests with the confidence level of 95 % (i.e., $p < 0.05$) were conducted to assess statistical significance of the oxidant decomposition or humic substance treatment tests. All the experiments were conducted with three replicates. The reported analytical data represents the mean values obtained from the three replicate samples, with the error bars representing one standard deviation of these measurements.

3. Results

Kinetic data of ferrate(VI) decomposition in the HA- and FA-containing solutions are shown in Fig. 1(a) and (b), respectively (pH = 7.50, $[\mathrm{Fe(VI)}]_0 = 36.0$ μM, and HA or FA = 0.00–32.40 mg/L DOC). Within the first 30 min, a vast majority of ferrate(VI) in the presence of HA or FA decomposed. In the ultrapure water (i.e., HA or FA = 0.00 mg/L), the ferrate(VI) loss was ascribed to the self-decomposition of ferrate (VI). Of note, in the first 5 min, the self-decay well followed a 2nd-order reaction pattern ($R^2 = 0.99$) with a rate constant k_1 of 0.12 $\mathrm{mM^{-1}\cdot s^{-1}}$ (**Fig. SI 1**), as represented by Eq. (2).

$$r_1 = -\frac{d[\mathrm{Fe(VI)}]^1_{\text{ultrapure water}}}{dt} = -k_1[\mathrm{Fe(VI)}]^2 \tag{2}$$

Here, r_1 represents the self-decomposition rate of ferrate(VI) in ultrapure water; $[\mathrm{Fe(VI)}]^1_{\text{ultrapure water}}$ is the Fe(VI) concentration in ultrapure water; and k_1 is the rate constant of ferrate(VI) self-decay in ultrapure water.

Within the same duration, the overall degradation rates of ferrate(VI) in HA- and FA-containing solutions are the sums of rates of its self-decomposition and reactions with HA and FA, as shown in Eq. (3) and Eq. (4), respectively.

$$r_2 = -\frac{d[\mathrm{Fe(VI)}]^1_{\text{HA solution}}}{dt} = r_1 + r_4 \tag{3}$$

$$r_3 = -\frac{d[\mathrm{Fe(VI)}]^1_{\text{FA solution}}}{dt} = r_1 + r_5 \tag{4}$$

Here, r_2 and r_3 represent the overall decomposition rates of ferrate (VI) in HA- and FA- containing solutions, respectively; and, r_4 and r_5 are the rates of ferrate(VI) decomposition due to the reactions with HA and FA, respectively. Based on Eqs. (3)–(4), r_4 and r_5 can be determined as follows.

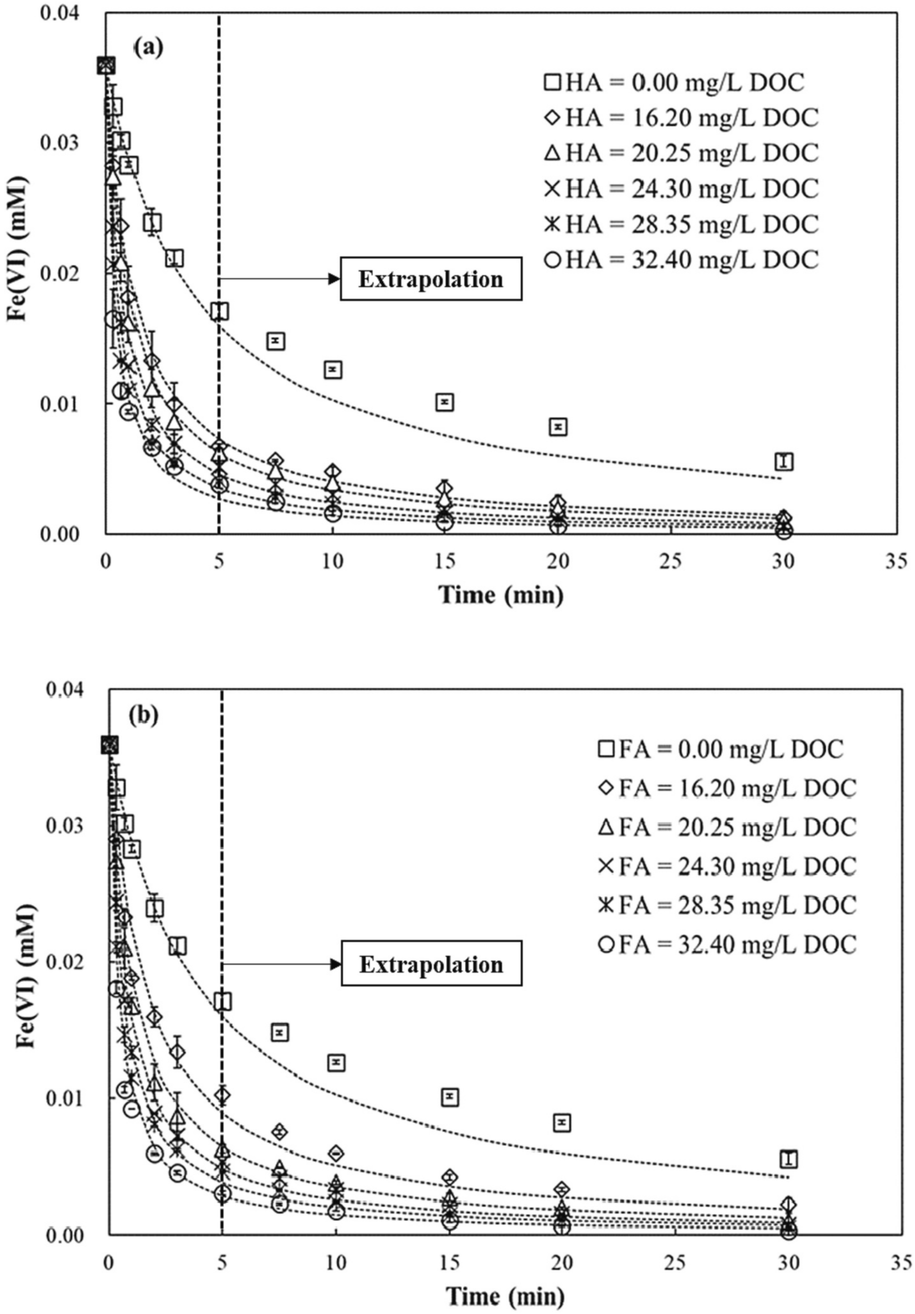

Fig. 1. Ferrate(VI) decomposition in the presence of (a) HA and (b) FA (Experimental conditions: pH = 7.50; $[Fe(VI)]_0$ = 0.036 mM; HA or FA = 0.00–32.40 mg/L DOC). Scattered symbols and dot lines represent the experimentally measured and modelled data, respectively.

$$r_4 = -\frac{d[Fe(VI)]^{HA\ only}_{HA\ solution}}{dt} = r_1 - r_2 \qquad (5)$$

$$r_5 = -\frac{d[Fe(VI)]^{FA\ only}_{FA\ solution}}{dt} = r_1 - r_3 \qquad (6)$$

Here $\frac{d[Fe(VI)]^{HA\ only}_{HA\ solution}}{dt}$ and $\frac{d[Fe(VI)]^{FA\ only}_{FA\ solution}}{dt}$ are the rates of ferrate(VI) decomposition due to the reactions with HA and FA, respectively. It should be noted that the overall Fe(VI) decomposition rates in ultrapure water (r_1), HA solution (r_2), and FA solution (r_3) can be experimentally determined, as shown in Fig. 1(a) and (b). Therefore, r_4 and r_5 can be computed based on Eqs. (5) and (6), respectively.

On the other hand, the rate laws of r_4 and r_5 can be written as below.

$$r_4 = \frac{d[Fe(VI)]^{HA\ only}_{HA\ solution}}{dt} = -k_2[Fe(VI)]^a HA^b \qquad (7)$$

$$r_5 = \frac{d[Fe(VI)]^{FA\ only}_{FA\ solution}}{dt} = -k_3[Fe(VI)]^c FA^d{}_0 \qquad (8)$$

k_2 and k_3 are the intrinsic rate constants of the reactions of ferrate (VI) with HA and FA, respectively; a and b are the reaction orders with respective to ferrate(VI) and HA, respectively; and, c and d are the reaction orders with respect to ferrate(VI) and FA, respectively. Of note, DOC of HA and FA remained nearly constant within the first 5 min. Therefore, Eq. (7) and Eq. (8) can be simplified into Eq. (9) and Eq. (10), respectively.

$$r_4 = -k_{obs1}[Fe(VI)]^a \qquad (9)$$

$$r_5 = -k_{obs2}[\mathrm{Fe(VI)}]^{c} \tag{10}$$

Here, k_{obs1} and k_{obs2} indicate the observed rate constants of ferrate (VI) decomposition due to the reactions with HA and FA, respectively. Based on the plots of $[\mathrm{Fe(VI)}]_{\mathrm{HA\ solution}}^{\mathrm{HA\ only}}$ and $[\mathrm{Fe(VI)}]_{\mathrm{FA\ solution}}^{\mathrm{FA\ only}}$ with time t at any specific DOC, k_{obs1} and k_{obs2} could be determined. Meanwhile, the ferrate(VI) decay was a 2nd order reaction with respective to Fe(VI) in the HA or FA solution (**Fig. SI 1**), suggesting that a and c are both 2.0.

Of interest, the log-log linear relations were observed between the observed rate constants (k_{obs1} or k_{obs2}) and DOC ($\log k_{obs1} = 2.02\log DOC_{HA} - 3.08$ for HA and $\log k_{obs2} = 2.48 \log DOC_{FA} - 3.76$ for HA; $R^2 > 0.99$) (Figs. 2(a) - (b)). This finding reveals that $k_{obs1} = 0.0008\ DOC_{HA}^{2.02}$ and $k_{obs2} = 0.0002\ DOC_{FA}^{2.48}$. Therefore, the overall rates of ferrate(VI) decomposition within the first 5 min in the HA and FA solutions are obtained as shown in Eq. (11) and Eq. (12), respectively.

$$r_2 = -\left(0.12 + 0.0008DOC_{HA}^{2.02}\right)[\mathrm{Fe(VI)}]_0^2 \tag{11}$$

$$r_3 = -\left(0.12 + 0.0002DOC_{FA}^{2.48}\right)[\mathrm{Fe(VI)}]_0^2 \tag{12}$$

To reveal the transformation of HA or FA over the ferrate(VI) treatment, ferrate(VI) was separately dosed to <10 kDa, < 100 kDa, and < 0.45 μm solutions. To facilitate the comparison of the transformation results, each of the solutions had its DOC at 4.00 mg/L DOC. In order to gain deeper insights into the ferrate(VI) treatment performance, another set of treatment tests with O_3 at the same normality were performed at the identical treatment conditions. Ozonation is an established chemical oxidation process in water treatment with well-documented information on the reactions with aquatic humic substances (Cho et al., 2003; Siddiqui et al., 1997; Świetlik et al., 2004; Świetlik and Sikorska, 2004; Westerhoff et al., 1999). Therefore, comparing the data from ferrate(VI) and ozonation treatments would advance the understanding on the degradation of humic substances by ferrate(VI).

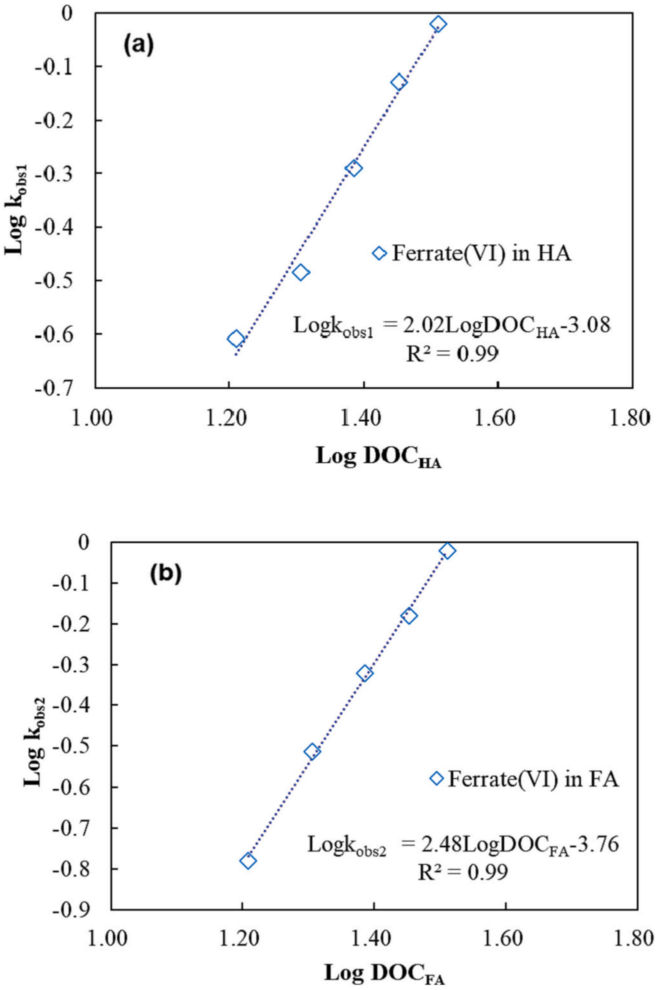

Fig. 2. Log-log linear dependence of ferrate(VI) decay rate constants of k_{obs} on (a) DOC_{HA} and (b) DOC_{FA}. Scattered symbols and dote lines represent the experimentally measured and modelled data, respectively.

DOC variation and its MW distribution before and after ferrate(VI) and O_3 treatment of <10 kDa, < 100 kDa, and < 0.45 μm HA and FA solutions are shown in Figs. 3(a) and (b), respectively. Of note, HA or FA solutions were filtered into <10 kDa, < 100 kDa, or < 0.45 μm before ferrate(VI) treatment or ozonation. Thereafter, the <10 kDa, 10–100 kDa, and > 100 kDa DOC represent the measures of low, medium, and high MW groups, respectively, in this study. In the case of <10 kDa HA solution, low MW HA molecules were degraded with the decrease of its DOC from 4.00 to 2.51 and 2.72 mg/L after ferrate(VI) and O_3 treatments, respectively. The higher DOC removal in the ferrate(VI) treatment (5 %) indicates that ferrate(VI) was slightly advantageous over O_3 in the removal of low HA molecules. For the <100 kDa HA solution (4.00 mg/L DOC), ferrate(VI) treatment and ozonation decreased the overall DOC to 2.84 and 2.98 mg/L, respectively. Specifically, the medium MW HA compounds (2.73 mg/L) declined to 1.52 and 1.67 mg/L DOC over the ferrate(VI) and ozonation treatments, respectively, while 1.25 mg/L low MW DOC marginally increased to 1.31–1.32 mg/L, regardless of either treatment. Besides the better capability of ferrate(VI) in terms of the DOC removal, these findings indicate that ferrate(VI) and O_3 can degrade the medium MW HA molecules into low MW ones, as evidenced by the slight increase of DOC in the low MW groups after the treatments. In the case of <0.45 μm HA solution (4.00 mg/L DOC), DOC due to medium MW HA compounds decreased from 2.80 to 1.80 and 1.93 mg/L after ferrate(VI) treatment and ozonation, respectively. In contrast, DOC contributed from low MW compounds remained nearly constant (1.09–1.14 mg/L) after the ferrate(VI) and O_3 treatments, while DOC contributed from high MW molecules slightly dropped from 0.12 mg/L to 0.09 mg/L after the ferrate(VI) or O_3 treatments.

Overall, two lines of important collective information can be concluded from Fig. 3(a). First, ferrate(VI) can effectively remove DOC of the medium and high MW groups. During the ferrate(VI) treatment of <0.45 μm HA solution containing composite MW fractions, the mitigation of DOC from low MW molecules was not remarkable, primarily because of an increase in their actual concentrations, resulting from the degradation of high and medium MW HA compounds into low MW molecules during the ferrate(VI) treatment. Second, ferrate(VI) exhibited better, at least equivalent, capacities than O_3 in the removal of DOC within different MW ranges. Similar findings were observed during the ferrate(VI) and O_3 treatment of FA solutions (Fig. 3(b)), except that ferrate(VI) treatment or ozonation could better alleviate FA than HA in terms of the DOC removal. For example, the residual DOC was 2.62 mg/L after ferrate(VI) treatment of FA (4.00 mg/L DOC), with a 10 % greater removal than the DOC removal observed in the HA solution (the residual DOC = 3.00 mg/L).

Meanwhile, UV_{254} absorbance was measured as shown in Fig. 4(a) and (b). For the <10 kDa HA solution, the initial UV_{254} absorbance of 0.114 cm^{-1} dramatically decreased to 0.047 and 0.052 cm^{-1} after the ferrate(VI) and O_3 treatment, respectively, corresponding to the removal efficiencies of 59 % and 54 %. In the case of <100 kDa HA solution, the UV_{254} absorbance of low (0.036 cm^{-1}) and medium (0.096 cm^{-1}) MW compounds both declined to 0.009 and 0.047 cm^{-1} after the ferrate(VI) treatment and to 0.012 and 0.056 cm^{-1} after ozonation, respectively. For <0.45 μm HA solution, ferrate(VI) treatment and ozonation decreased the UV_{254} absorbance of low (0.038 cm^{-1}), medium (0.096 cm^{-1}), and high (0.013 cm^{-1}) MW groups to 0.023, 0.058, and 0.001 cm^{-1} after ferrate(VI) treatment and to 0.027, 0.058, and 0.001 cm^{-1} after ozonation, respectively. These findings show that the removal of UV absorption exhibited similar patterns with the mitigation of DOC, except that the UV_{254} absorbance of all the MW groups consistently

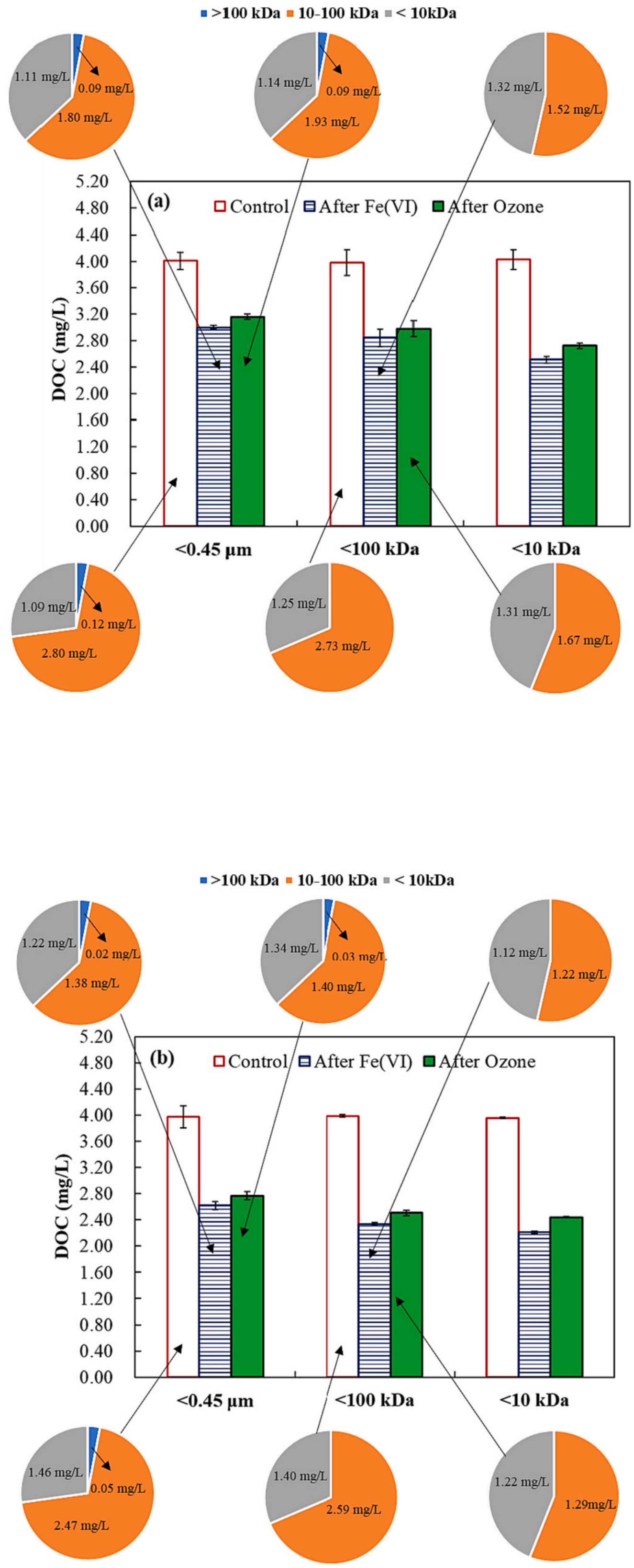

Fig. 3. Residual DOC after ferrate(VI) and O_3 treatment in HA- or FA-containing solutions at different MW groups; (a) overall <0.45 μm, <100 kDa, and < 10 kDa HA-containing solutions; (b) overall <0.45 μm, <100 kDa, and < 10 kDa FA-containing solutions; (Experimental condition: pH = 7.50; initial [Fe(VI)] = 0.036 mM; initial [O_3] = 0.054 mM; initial HA or FA = 4.00 mg/L DOC).

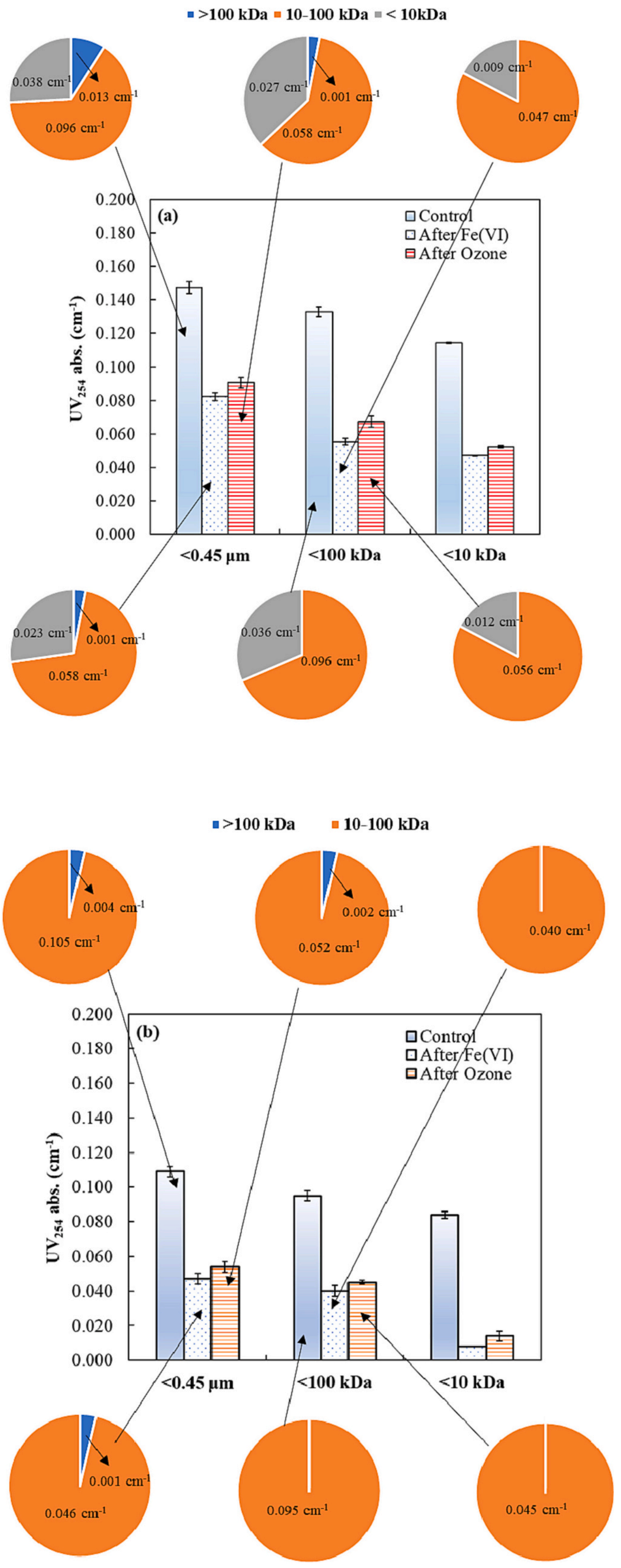

Fig. 4. Residual UV_{254} absorbance after ferrate(VI) and O_3 treatment in HA- or FA-containing solutions at different MW groups; (a) overall <0.45 μm, <100 kDa, and < 10 kDa HA-containing solutions; (b) overall <0.45 μm, <100 kDa, and < 10 kDa FA-containing solutions (Experimental condition: pH = 7.50; initial [Fe(VI)] = 0.036 mM; initial [O_3] = 0.054 mM).

declined, but DOC in low MW group might increase due to the degradation of high MW compounds into low MW ones, after the ferrate(VI) or O_3 treatment.

On the other hand, though the mitigation patterns of the UV absorptions were similar between the FA and HA solutions, attention needs to be paid to two aspects. First, ferrate(VI) or O_3 more readily alleviated the UV_{254} absorbance of FA than that of HA. For example, ferrate(VI) removed the UV_{254} absorbance of <10 kDa FA by 90 %, much >59 % reduction in the UV_{254} absorbance due to <10 kDa HA. Second, for HA molecules, a majority of UV_{254} absorbance was contributed from the medium MW fraction, while high and low MW molecules little contributed to UV absorption.

4. Discussion

4.1. Patterns of ferrate(VI) decomposition in the presence of aquatic humic substances

Once dosed to water, ferrate(VI) undergoes decomposition through three pathways: self-decay, consumption by water matrix constituents, and reactions with specific target contaminants (Deng and Guan, 2024). To enhance the efficiency of ferrate(VI) for addressing the target pollutants in water treatment, understanding the kinetics governing ferrate (VI) self-decay and its interactions with water matrix constituents is of paramount importance. Moreover, the advances on the kinetics of ferrate(VI) chemistry enable more precise sizing of its reactor for water treatment. This is of particular significance for a ferrate(VI) treatment system, because an undersized reactor may result in the inadequate treatment of target water pollutants and a high concentration of residual ferrate(VI) entering downstream water treatment units, causing water discoloration due to excess ferrate(VI), while an oversizing may result in the inefficiency in energy and resource consumption, long detention time, wasted spaces, and high associated capital and operational costs.

The overall reaction of the ferrate(VI) self-decay in water is shown in Eq. (13) (Goff and Murmann, 1971; Wood, 1958). The self-decay comprises two sequential steps (Rush et al., 1996), that is, the formation of di-ferrate ($Fe_2O_7^{2-}$) intermediate through the dimerization of two ferrate (VI) species, and the reduction of Fe(VI) in $Fe_2O_7^{2-}$ to Fe(III), accompanied by the production of dioxygen.

$$2FeO_4{}^{2-} + 5H_2O \rightarrow 2Fe^{3+} + 10OH^- + 1.5O_2\uparrow \tag{13}$$

Meanwhile, it should be noted that humic substances abundantly present in source water as the principal matrix component represents a major sink for ferrate(VI). Both HA and FA are rich in electron-donating moieties (e.g., phenolic functional groups), which serve as the sites where ferrate(VI) potentially attacks. For example, the organic discharge densities of phenolic functional groups in the Suwannee River Standard HA and FA were reported to be 3.79 and 2.47 meq/g C, respectively (Driver and Perdue, 2014).

In this study, the initial kinetic behaviors of ferrate(VI) decomposition (0–5 min), due to the collective effects of self-decomposition and reactions with humic substances, was observed to follow a 2nd-order reaction order, in consistence with findings from previous studies (Deng et al., 2018; Jiang et al., 2015; Lee et al., 2004; Rush et al., 1996; Song et al., 2016). Our earlier study reveals that ferrate(VI) in the presence of NOM undergoes a three-phase decay kinetic pattern, sequentially including instant loss because of the reactions with NOM, a 2nd order decomposition in a homogeneous or near-homogeneous solution in the initial stage, and a following 1st order decay in a heterogenous solution due to the formation of iron oxide particles (Deng et al., 2018). While the instant ferrate(VI) loss was not measured at the onset, this study reveals that ferrate(VI) decay obeyed a 2nd order decomposition pattern in the initial phase. As shown in Fig. 1, as the 2nd kinetic models were extrapolated beyond the first 5 min, the deviations between the experimental and modelled data became more pronounced, because the overall decomposition gradually transited to a 1st-order decomposition pattern with the accumulation of iron (hydr)oxide particles likely capable of surface-catalyzing Fe(VI) decay (Deng et al., 2018; Jiang et al., 2015).

Specifically, the kinetic data obtained enables a quantitative assessment of relative dominance of ferrate(VI) decomposition due to self-decay and its reactions with humic substances in the absence of targeted pollutants. In the HA solution, the proportion of ferrate(VI) loss due to self-decay in the overall decomposition process can be determined.

$$\text{Percentage of Fe(VI) self}-\text{decay} = \frac{0.12}{0.12 + 0.0008\text{DOC}_{\text{HA}}^{2.02}} \times 100\% \tag{14}$$

Consequently, the fraction of ferrate(VI) consumption due to the reactions with HA can be obtained as follows (Eq. (15)).

$$\begin{aligned}&\text{Percentage of Fe(VI) decay due to HA}\\&\quad = 100\% - \text{Percentage of Fe(VI)self}-\text{decay}\end{aligned} \tag{15}$$

Clearly, the portions are a function of DOC only, regardless of [Fe (VI)].

The ferrate(VI) fractions due to self-decay and HA degradation over 0–20 mg/L DOC within the first 5 min are presented in Fig. 5(a). The broad DOC range was selected because NOM in surface water sources can reach up to 20.00 mg/L. As HA increased from 0.00 to 4.00 mg/L DOC, the fraction of self-decay slightly declined from 100 % to 90 %, while the percentage of ferrate(VI) loss due to HA increased to 10 %. While DOC further increased to 20.00 mg/L, the portion for self-decay decreased to 26 %, accompanied by the significant increase of the ferrate(VI) consumption by HA from 10 % to 74 %. To facilitate understanding the effect of aquatic humic substances on the ferrate(VI) decay through different mechanisms, a new indicator, that is, $DOC_{50\%}$, is introduced. Here $DOC_{50\%}$ is defined as the level of DOC, at which the contributions of ferrate(VI) self-decomposition and interactions with dissolved organic matter to the overall ferrate(VI) loss are equal, that is, 50 % in the study conditions. In this study, $DOC_{50}\% = 11.90$ mg/L for HA.

In a similar manner, the proportions of ferrate(VI) self-decay and reactions with FA in the overall decomposition process can be estimated in Eq. (16) and (17), respectively.

$$\text{Percentage of Fe(VI) self}-\text{decay} = \frac{0.12}{0.12 + 0.0002\text{DOC}_{\text{FA}}^{2.48}} \times 100\% \tag{16}$$

$$\begin{aligned}&\text{Percentage of ferrate(VI) decay due to FA}\\&\quad = 100\% - \text{Percentage of Fe(VI) self}-\text{decay}\end{aligned} \tag{17}$$

The fractions of Fe(VI) self-decay and loss due to FA exhibited similar patterns with DOC. Of interest, $DOC_{50\%}$ for FA is 13.10 mg/L, which is 10 % greater than $DOC_{50\%}$ for HA, suggesting that ferrate(VI) more preferentially reacts with FA than HA.

It should be noted that DOC in source water, though broadly varied, is typically <5 mg/L in surface freshwater and <2 mg/L in groundwater (Edzwald, 2011). Therefore, self-decay predominantly governs the initial ferrate(VI) decomposition, highlighting its pivotal role in the fate of ferrate(VI) across most treatment scenarios. Alternatively, the water sources such as bogs, marshes, and swamps, or eutrophic water bodies could have DOC exceeding 20 mg/L. At such conditions, the reactions with NOM would prevail over self-decomposition in the ferrate(VI) loss. Consequently, the interactions of ferrate(VI) with NOM become a crucial factor influencing the fate of ferrate(VI) in the Fe(VI)-water system.

4.2. Impacts of ferrate(VI) on aquatic humic substances

4.2.1. Ferrate(VI) vs. ozonation

While prior studies delved into ferrate(VI) decomposition and removals of humic substances in water, the comparative information

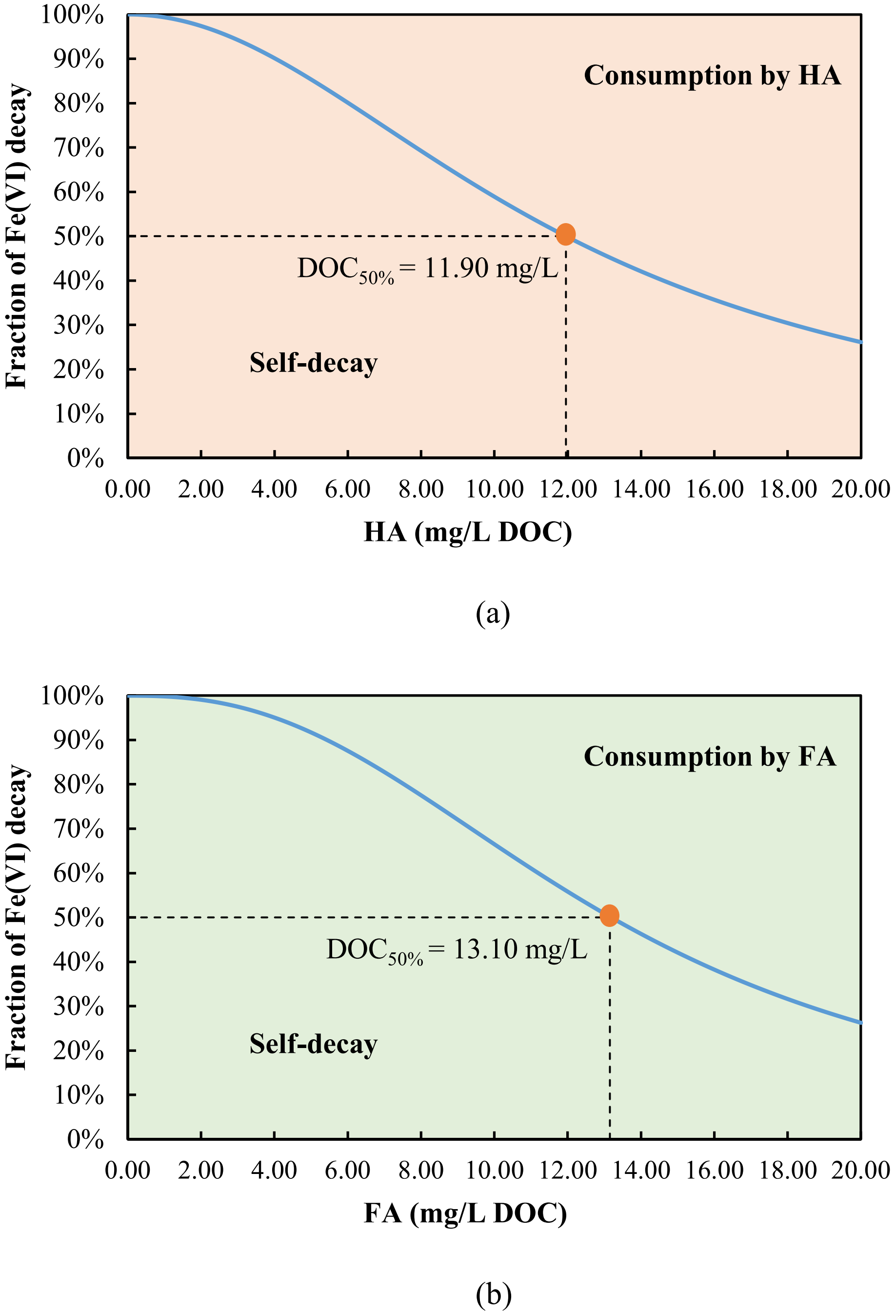

Fig. 5. Fractions of ferrate(VI) decomposition due to self-decay and reactions with humic substances at different DOC: a) HA solution; and b) FA solution (Experimental condition: pH = 7.50; initial [Fe(VI)] = 0.036 mM; *t* = 5 min).

between ferrate(VI) treatment and established chemical oxidation processes remains highly limited. To address this gap, a comparative analysis of ferrate(VI) treatment and ozonation concerning their reactions with HA and FA was conducted.

As demonstrated in Figs. 3 and 4, ferrate(VI) consistently exhibits slightly better, or at least equivalent, removals in terms of the mitigation of DOC and UV_{254} absorbance. It is of interest to observe the different treatment performance between the two oxidative processes that both degrade organics principally through electron transfer (Sharma, 2013). At the study pH (7.5), the dominant ferrate(VI) species are $HFeO_4^-$ and FeO_4^{2-} ($pK_a = 7.3$ V) (Carr et al., 1985; Rush et al., 1996). The reported reduction potentials (E^o) of $HFeO_4^-/Fe^{3+}$ and FeO_4^{2-}/Fe^{3+} in acidic conditions are 2.07 and 2.20 V (Lide, 2004), but acutely decline to 0.70 V as pH increased to an alkaline environment (Sharma, 2002). Therefore, the true E^o of ferrate(VI) at the pH in this study is below E^o (2.08 V) of O_3 (Lide, 2004). Consequently, the improved treatment performance of ferrate(VI) cannot be interpreted based on the difference in the reduction potential.

Instead, the observation is likely ascribed to an greater oxidant exposure of ferrate(VI) and the role of ferrate(VI) resultant particles. Under the identical conditions, the self-decomposition of O_3 at the same normality, that is, 0.11 meq/L, with ferrate(VI) in Fig. 1, followed a 1st-order reaction pattern with the rate constant of 0.0042 s^{-1} (**Fig. SI 2**). Consequently, the ferrate(VI) exposure (i.e., $\int_0^t Cdt$) is 211 % of the O_3 exposure within the first 30 min. The greater longevity of ferrate(VI) can lead to a higher oxidant exposure and thus favors the removal of humic substances.

On the other hand, accompanied by the reduction of Fe(VI) in ferrate (VI), Fe(III) *in-situ* forms to generate iron (hydr)oxide solids at a nearly neutral condition. The ferrate(VI) resultant particles are reported to have crystalline or amorphous structures and may exist in nanosized particles or in the state of flocs (Cui et al., 2018; Goodwill et al., 2015; Lv et al., 2018; Prucek et al., 2013).The inconsistent observations in their structures and sizes appear to rely heavily on the reaction conditions (e.g., pH and ferrate(VI) dose). Regardless, the formed solid phase exhibits the potential to adsorb various dissolved organic compounds through complexation, hydrogen bonding, or other chemical and physical adsorption mechanisms (Wang et al., 2022; Yang et al., 2020; Yang et al., 2018). Therefore, the ferrate(VI) system likely behaves as the Fenton process in terms of the adsorption capability. In the Fenton treatment, Fe(II) and hydrogen peroxide generate highly active hydroxyl radicals with the formation of Fe(III) oxide particles (Deng and Englehardt, 2006). In the Fenton removal of dissolved organic matter, the adsorption mechanism may even outweigh chemical oxidation (Deng, 2007). While accurately discerning the specific contributions of ferrate (VI) oxidation and adsorption of humic substances is technically challenged (Song et al., 2016), part of humic substances was plausibly captured by the formed ferrate(VI) resultant solids in this study.

The results (Fig. 3) obtained from the significant reduction of DOC in HA- or FA-containing solutions after ferrate(VI) or O_3 treatment demonstrate that ferrate(VI) or O_3 possesses the capacity to mineralize a portion of HA or FA molecules. This capability arises from the oxidizing nature of ferrate(VI) or O_3, allowing for the oxidation of electron rich organic moieties, such as phenol, olefin, amine, aniline moieties that are commonly present in HA and FA molecules (Kasprzyk-Hordern et al., 2003; Song et al., 2016; Yang et al., 2012). The observed decrease of SUVA (Fig. 6) is typically accompanied by an increased proportion of hydrophilic fractions (Edzwald, 2011). These findings align with previous studies reported in the literature (Barışçı, 2017; Graham et al., 2010; Song et al., 2016; Wang et al., 2023a; Yang et al., 2012; Zhang et al., 2020). However, a complete degradation of HA or FA molecules was not achieved in the experimental conditions because the reactivity of ferrate(VI) or O_3 with electron withdrawing moieties found in HA or FA was relatively limited (Chen et al., 2003; Lee et al., 2009; Önnby et al., 2018). The presence of recalcitrant functional groups within these compounds can impart persistence to the oxidative attack by ferrate(VI) or O_3, challenging the organic mineralization.

UV light can primarily be adsorbed by aromatic structures or conjugated $C=C$ double bonds in the HA or FA molecules. Hence, UV_{254} absorbance and SUVA values are the indicators of the aromatic content and organic matter quality in water (Lavonen et al., 2015). As shown in Figs. 4 and 6, HA exhibits higher aromatic content and phenolic group concentrations compared to FA, as indicated by the corresponding UV_{254} absorbance and SUVA values. It has been well known that higher aromatic contents, higher phenolic group concentrations, and higher SUVA values are associated with a greater consumption of ferrate(VI) or O_3 (Huang et al., 2007; Świetlik et al., 2004). This can be attributed to the preferential reactivity of ferrate(VI) or O_3 toward electron-donating groups rather than electron-withdrawing ones (Lee et al., 2009; Önnby et al., 2018). In this study, UV_{254} absorbance values within individual MW ranges were dramatically reduced after ferrate(VI) or O_3 treatment (Fig. 4), reflecting that ferrate(VI) or O_3 has a tendency to react with electron-rich, UV-blocking organic functional groups present in HA or FA molecules, which are responsible for absorbing UV light. Consequently, the presence of electron-donating groups in organic compounds, such as those found in HA or FA (e.g., phenolic groups and alkenyl groups) (Aeschbacher et al., 2012), enhances their reactivity toward ferrate(VI) or O_3, resulting in more rapid decomposition of the two oxidants.

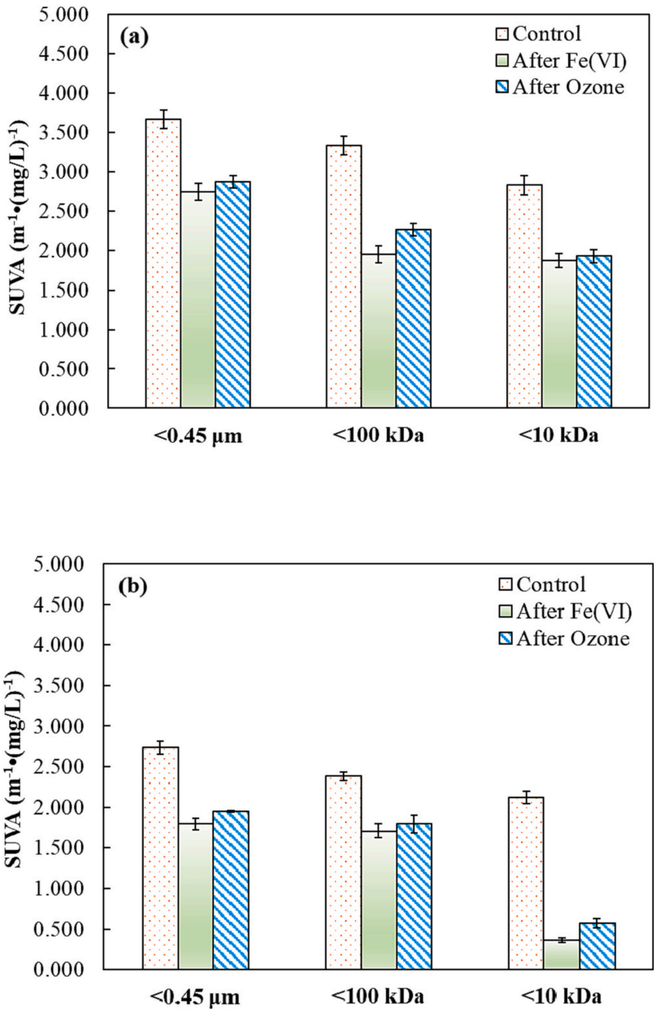

Fig. 6. Residual SUVA after ferrate(VI) and O_3 treatment in HA- or FA-containing solutions at different MW groups; (a) overall <0.45 μm, <100 kDa, and < 10 kDa HA-containing solutions; (b) overall <0.45 μm, <100 kDa, and < 10 kDa FA-containing solutions (Experimental condition: pH = 7.50; initial [Fe(VI)] = 0.036 mM; initial $[O_3]$ = 0.054 mM).

This study also indicates that ferrate(VI) more effectively removes FA than HA. Typically, FA is more water-soluble and possesses smaller molecular sizes than HA (Schellekens et al., 2017; Weng et al., 2006). The inherent attributes allow ferrate(VI) to more effectively penetrate the molecular structure of FA and attack its electron-donating moieties. Moreover, FA (40.7 % - 50.6 %) exhibits a lower carbon content than HA (53.8 % - 58.7 %) (Stevenson, 1994). The lower carbon fraction disfavors chemical stability of carbon bonds within FA molecules.

Although the ferrate(VI) mineralization of HA or FA remains challenging, the ferrate(VI) reactions with aquatic humic substances may bring about three positive impacts on water treatment, as demonstrated in prior studies. First, ferrate(VI) oxidation can degrade humic substance coated on iron flocs forming from the ferrate(VI)-induced coagulation, tend to promote its hydrophilicity and the floc aggregation, and improve the coagulation performance (Lv et al., 2018). Second, ferrate(VI) oxidation can effectively remove humic substance-related color in water to improve the aesthetic effect (Barışçı, 2017; Talaiekhozani et al., 2017). Third, ferrate(VI) treatment reduces SUVA and hydrophobicity of aquatic humic substances, thus alleviating the formation potential of DBPs (Jiang et al., 2019).

5. Conclusion

This study provides insights into the interactions between ferrate(VI) and aquatic humic substances in water. The knowledge gained advances ferrate(VI) chemistry in the presence of humic substances and builds a basis for harnessing ferrate(VI) for practical water treatment. Ferrate

(VI) decomposition is primarily governed by its self-decay and consumption due to the reactions with humic substances, when target micro-pollutants are absent. Consequently, the decomposition exhibits a unique biphasic kinetic pattern. More specifically, self-decay dominates the ferrate(VI) loss at a low DOC level. However, the fraction of ferrate (VI) decay due to humic substances gradually becomes pronounced with the increase of DOC. Here a new parameter, that is, DOC$_{50\%}$, is proposed to assess how self-decay and DOC competes for the oxidant consumption. The specific level of DOC$_{50\%}$ may depend heavily on the nature of the oxidant and NOM as well as the solution chemistry conditions. In this study, DOC$_{50\%}$ of Suwannee River HA and FA in the ferrate(VI) treatment was 11.90 and 13.10 mg/L, respectively, at pH 7.50. Given that the levels are typically greater than raw water DOC, self-decay plays a pivotal role in the ferrate(VI) consumption in the most water treatment scenarios. It should be noted that the concept of DOC$_{50}$% can be extended to the investigations of many other chemical oxidants, besides ferrate(VI), when self-decomposition and reactions with specific matrix constituents simultaneously occur.

Meanwhile, aquatic humic substances undergo transformation and removal over the ferrate(VI) treatment, thus impacting water quality. Generally, ferrate(VI) can remove dissolved organic matter within different MW ranges, to different degrees. Between HA and FA, ferrate (VI) oxidation is more reactive toward the latter one due to its smaller molecular sizes, higher solubility, and lower carbon contents. Furthermore, ferrate(VI) is slightly advantageous over, or equivalent to, ozone in the mitigation of DOC and UV$_{254}$ absorbance. The enhanced performance is likely ascribed to greater oxidant exposures and/or additional removal due to ferrate(VI) resultant iron oxide-induced adsorption.

Insights gained in this study have significant implications for water treatment practices. Understanding the intricate kinetic profiles of ferrate(VI) decomposition in water allows for precisely sizing ferrate(VI) reactors and determining its oxidant exposure, a key parameter for the treatment performance. Furthermore, though humic substances are not water contaminants themselves, their reactivity toward ferrate(VI) implies the potential of ferrate(VI) technology to address water quality challenges related to humic substances, such as water color, the formation of organic DBPs in downstream disinfection, and the enhanced mobility of toxic metals. Additionally, the ferrate(VI) treatment consistently demonstrates superior treatment capabilities in mitigating HA and FA compared to ozonation, underscoring the promise of ferrate(VI) technology as an effective water treatment process.

CRediT authorship contribution statement

Junkui Cui: Conceptualization, Investigation, Methodology, Writing – original draft. **Zepei Tang:** Formal analysis. **Qiufeng Lin:** Formal analysis. **Lisitai Yang:** Formal analysis. **Yang Deng:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.170919.

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