Impact of humic acid on the degradation of levofloxacin by aqueous permanganate: Kinetics and mechanism

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Abstract

Levofloxacin (LF) is a frequently detected fluoroquinolone in surface water, and permanganate (MnO4−) is a commonly used oxidant in drinking water treatment. This study investigated the impact of humic acid (HA) on LF degradation by aqueous MnO4− from both kinetic and mechanistic aspects. In the absence of HA, the second-order rate constant (k) of LF degradation by MnO4− was determined to be 3.9 M−1 s−1 at pH 7.5, which increased with decreasing pH. In the presence of HA, the pseudo-first-order rate constant (kobs) of LF degradation at pH 7.5 was significantly increased by 3.8- and 2.8-fold at [HAo]:[KMnO4o] (mass ratio) = 0.5 and 1, respectively. Secondary oxidant scavenging and electron paramagnetic resonance tests indicated that HA could form a complex with Mn(III), a strongly oxidative intermediate produced in the reaction of MnO4− with HA, to induce the successive formation of superoxide radicals (O2−·) and hydroxyl radicals (·OH). The resulting ·OH primarily contributed to the accelerated LF degradation, and the complex [HA-Mn(III)] could account for the rest of acceleration. The degradation of LF and its byproducts during MnO4− oxidation was mainly through hydroxylation, dehydrogenation and carboxylation, and the presence of HA led to a stronger destruction of LF. This study helps better understand the degradation of organic micropolllutants by MnO4− in drinking water treatment.

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1. Introduction

Levofloxacin (LF) is an important fluoroquinolone antibiotic for the treatment of bacterial infections (e.g., tuberculosis, acute bacterial sinusitis, pneumonia) of humans and even HIV-affected patients (Goodwin et al., 1994; Mittmann et al., 2002). However, LF is mostly excreted through urine with only 15–20% metabolism in human body (Wong et al., 1997). Moreover, fluoroquinolones are degraded very ineffectively in wastewater treatment plants (Yuan et al., 2015), and thus are eventually released into aquatic environments through effluent discharge and sludge disposal. As a result, LF has been frequently detected in surface waters with concentrations usually at ng L−1 level (Conley et al., 2008; Kim et al., 2009). In particular, its occurrence in drinking water sources has attracted public concerns.

At drinking water treatment plants, permanganate (MnO4−) is a commonly-used oxidant to remove taste and odor, enhance coagulation via producing MnO2(s), and reduce the formation of disinfection byproducts via oxidizing their precursors (Jiang et al., 2009; Sharma et al., 2012). In addition, MnO4− can also oxidize organic micropolllutants present in water and the oxidation reaction is selective depending on the electron density of certain moieties of a micropolllutant. For example, the second-order rate constants (k) for the reactions of MnO4− with salbutamol and sulfamethoxazole were reported to be 283 and 0.11 M−1 s−1 at pH 7, respectively, which show a great difference (Rodríguez-Álvarez et al., 2015; Zhang et al., 2015). As the pH increased, even though the redox potential of Mn(VII) decreased, the reactivity of MnO4− toward phenol, lincomycin and sulfamethoxazole increased (Hu et al., 2010; Du et al., 2012; Gao et al., 2014), but the reactivity toward trimethoprim decreased (Hu et al., 2010). Therefore, the redox potential of Mn(VII) and the pKₐ values of an organic micropolllutant can both affect the reaction rate in an aqueous solution.

As a typical natural organic matter in drinking water sources, humic acid (HA) was found to enhance the degradation of phenol, 17 β-estradiol and triclosan (He et al., 2009; Jiang et al., 2009, 2012), inhibited sulfamethoxazole degradation (Gao et al., 2014), and had little impact on carbamazepine degradation (Hu et al., 2009) during
MnO₄⁻ oxidation. Several mechanisms have been proposed for the accelerated degradation of organic micropollutants by MnO₄⁻ in the presence of HA: (1) HA forms a complex with the reaction intermediate Mn(III) as a ligand, preventing the disproportionation of Mn(III), and the complex continues to oxidize an organic micropollutant at a fast rate (jiang et al., 2010); (2) HA increases the electron density of an organic micropollutant, thus accelerating its degradation by MnO₄⁻ (He et al., 2009); and (3) the in-situ produced MnO₂(s) from the reaction of MnO₄⁻ with HA oxidizes an organic micropollutant faster than the ex-situ MnO₂(s) (Sun et al., 2013). It is seen that HA has different impacts on the degradation of organic micropollutants by MnO₄⁻ in water, and thus the reaction mechanism needs further investigation.

This study was to investigate the impact of HA on LF degradation by aqueous MnO₄⁻ in the following aspects: (1) determine the kinetics of LF degradation by MnO₄⁻ in the absence of HA; (2) determine the kinetics of LF degradation by MnO₄⁻ in the presence of HA; (3) clarify the mechanism for HA accelerating LF degradation through secondary oxidant scavenging and electron paramagnetic resonance (EPR) tests; and (4) propose the degradation pathways of LF in the absence and presence of HA based on identified byproducts. This study helps better understand the degradation of organic micropollutants by MnO₄⁻ in drinking water treatment.

2. Materials and methods

2.1. Chemicals

Milli-Q water (Advantage A10, Millipore, USA) was used in all experiments and analytical determinations. KMnO₄ (99.5%) was purchased from Sinopharm Chemical Reagent (China), LF (98%) from Tokyo Chemical Industry (Japan), HA (technical grade) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%) from Sigma-Aldrich (Germany), and 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide (BMPO, 99%) from Dojindo (Japan). All other chemicals were of analytical grade or higher. As the spin-trapping agents for radicals, DMPO, BMPO and their aqueous stock solutions were stored in a refrigerator at −20 °C. A freshly prepared MnO₂ stock solution (10 mM) was used for no more than 3 days and stored at 4 °C in the dark. HA stock solution was prepared by double filtering an aqueous HA suspension through 0.2-μm membrane filters. Solution pH was buffered with 1 mM phosphate and H₂SO₄ solutions. The phosphate buffer had little effect on LF degradation by MnO₂, and the change of pH was insignificant over the reaction course.

2.2. Analytical methods

LF was quantified with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-QTOF-MS/MS, AcQuity LC, Xevo G2 QTOF MS, Waters, USA) coupled with an Eclipse Plus C18 column (2.1 × 150 mm, 3.5 μm, Agilent, USA). The mobile phases consisted of 0.2% formic acid in water (A) and acetonitrile (B) at a total flow rate of 0.2 mL min⁻¹. The gradient elution program (time in min, % mobile phase B) was set as follows: (0, 10), (20, 90), and (25, 10). The MS system was operated in the ESI⁻ mode with the following settings: capillary voltage 3 kV, cone voltage 30 V, source temperature 100 °C, desolvation temperature 280 °C, desolvation gas flow rate 500 L h⁻¹, and MS/MS collision energy 15–35 eV.

Solution absorbance was measured by a UV–Vis spectrophotometer (DR6000, Hach, USA), and total organic carbon (TOC) was measured by a TOC-VCPH Analyzer (Shimadzu, Japan). The quantification of inorganic ions and low-molecular-weight organic acids is detailed in Text S1.

2.3. Experimental procedures

Under the pseudo-first-order conditions for LF degradation by MnO₄⁻ (i.e., [MnO₄⁻]₀/[LF]₀ > 10:1), the degradation kinetics and mechanism of LF were comparatively investigated in the absence and presence of HA. By using tert-butanol (TBA) and p-benzoquinone (BQ) to respectively scavenge hydroxyl radicals (·OH) and superoxide radicals (O₂⁻·) and sodium pyrophosphate (PP, Na₄P₂O₇) as a ligand to complex Mn(III), the mechanism of HA accelerating LF degradation by MnO₄⁻ was examined. Experiments were conducted in triplicate in 50-mL conical flasks with magnetic stirring at ambient temperature (20 ± 2 °C). After a certain amount of MnO₄⁻ stock solution was added to the reaction solution containing other reactants with pH pre-adjusted, water samples were withdrawn at preselected times, immediately quenched with an excessive Na₂S₂O₃, and filtered by 0.2-μm membrane filters. HA was quantified in terms of TOC concentration, and [HA]₀/[KMnO₄]₀ represented the initial mass ratio of HA/TOC to KMnO₄. By contrast, molar ratio was used for all other reactants with known molecular weights. To identify the degradation byproducts of LF formed during MnO₄ oxidation, higher concentrations of MnO₄ (2800 μM), LF (28 μM) and HA were purposely adopted for more accurate quantifications, but their concentrations were raised proportionally.

MnO₄⁻ solution has a maximum absorbance at 525 nm (A₅₂₅) (Waldemer and Tratnyek, 2006). Under the pseudo-first-order conditions for MnO₄⁻ consumption by LF ([LF]₀/[MnO₄]₀ = 10:1), the reaction rate constant of LF with MnO₄⁻ was also determined by measuring the decay of A₅₂₅. Experiments were conducted in triplicate in a 1-cm quartz cuvette at ambient temperature (20 ± 2 °C). After a certain amount of MnO₄⁻ stock solution was added, the reaction solution (3 mL) was immediately mixed with a clean pipette tip and then the decay of A₅₂₅ was monitored continuously.

3. Results and discussion

3.1. Reaction kinetics of LF with MnO₄⁻

The degradation of LF followed a pseudo-first-order kinetics with MnO₄⁻ in 200-fold excess (Fig. 1a), indicating that the reaction was of first-order with respect to LF. Meanwhile, at a fixed initial LF
concentration, the pseudo-first-order rate constant \(k_{\text{obs}}\) increased linearly with increasing \(\text{MnO}_4^-\) concentration (Fig. 1b), indicating that the reaction was also of first-order with respect to \(\text{MnO}_4^-\). Therefore, the reaction kinetics of LF with \(\text{MnO}_4^-\) can be expressed by Eq. (1):

\[
\frac{d[\text{LF}]}{dt} = k_{\text{obs}}[\text{LF}] = k[\text{MnO}_4^-][\text{LF}]
\]

(1)

where \(k\) is the second-order rate constant, which was determined to be 3.9 M\(^{-1}\) s\(^{-1}\) at pH 7.5.

Under the pseudo-first-order condition for \(\text{MnO}_4^-\) consumption, the decay of \(A_{525}\) in the \(\text{MnO}_4^-/\text{LF}\) system was monitored in the early reaction phase. The consumption of \(\text{MnO}_4^-\) at pH 7.5 followed the pseudo-first-order kinetics with LF in 10-fold excess and a \(k\) value of 2.7 M\(^{-1}\) s\(^{-1}\) was obtained (Fig. 1c). This value is a little lower than that obtained with \(\text{MnO}_4^-\) in excess (\(k = 3.9\) M\(^{-1}\) s\(^{-1}\)), probably because the colloidal \(\text{MnO}_2\) and some organic intermediates produced from the reaction of \(\text{MnO}_4^-\) with LF had a similar contribution to the \(A_{525}\). In addition, a decrease of pH to 6.5 accelerated the \(A_{525}\) consumption, while an increase of pH to 8.5 hindered the \(A_{525}\) consumption (Fig. 1c), indicating that the reactivity of LF with \(\text{MnO}_4^-\) increased as pH decreased. The \(pK_a\) values associated with the \(N_1\) atom, carboxylic group and \(N_4\) atom in the chemical structure of LF (Fig. S1) are 5.2, 6.2 and 8.2, respectively (De Witte et al., 2009). When the pH decreased from 8.5 to 6.5, the \(N_4\) atom was protonated, which enhanced its electron-withdrawing ability from adjacent groups (Hu et al., 2010) including the side -CH\(_3\) and the -C-C- bond in the piperazinyl moiety (Fig. S1). As can be seen from the degradation pathways of LF proposed later (Section 3.5), the side -CH\(_3\) group was hydroxylated and the -C-C- bond was dehydrated to form -C=O (LF\(_{375}(1)\)), thus both were the primary reaction sites. The olefin structure (-C=C-) tended to further react with \(\text{MnO}_4^-\) by forming a 3 + 2 cyclic diester intermediate (Hu et al., 2010), and then the two carbon atoms in the olefin structure could be eliminated to form LF\(_{335}(2)\), or one was eliminated and the other hydroxylated to form LF\(_{385}\). Thus, as the pH decreased, the \(N_4\) atom facilitated the degradation of LF and some byproducts as well by enhancing the electrophilicity of structural groups adjacent to \(N_4\).

### 3.2. Impact of HA on LF degradation by \(\text{MnO}_4^-\)

At pH 7.5, the \(k_{\text{obs}}\) values of LF degradation were significantly enhanced by 3.8- and 2.8-fold at [HA]\(_o\):[K MnO\(_4\)]\(_o\) = 0.5 and 1, respectively, as compared to that in the absence of HA (Fig. 2a). The mass ratios of [HA]\(_o\):[K MnO\(_4\)]\(_o\) of 0.5 and 1 were purposely selected because both the TOC concentration of raw water and the KMnO\(_4\)
dose are usually in the same range (i.e., 1–3 mg L\(^{-1}\)) in drinking water treatment. It was reported that at \([\text{HA}]_0/[\text{KMnO}_4]_0 < 1\), HA also enhanced the degradation of phenol, 17 β-estradiol and triclosan by MnO\(_4\) (He et al., 2009; Jiang et al., 2009, 2012). However, when the \([\text{HA}]_0/[\text{KMnO}_4]_0\) ratio increased to 2–5, HA inhibited the degradation of sulfamethoxazole by MnO\(_4\) (Gao et al., 2014), most probably because an excessive HA could not only consume more MnO\(_4\) but also strongly compete for secondary oxidants produced from the reaction between HA and MnO\(_4\).

Results further show that at \([\text{HA}]_0/[\text{KMnO}_4]_0 = 0.5\), the addition of TBA inhibited about 75% of the acceleration of LF degradation (Fig. 2a), but TBA itself had little impact on LF degradation (Fig. S2), and the intensity of BMPO-OOH was totally shielded. In addition, this result also implies that Mn(III) should have induced the production of \(\cdot\text{OH}\) in the presence of HA.

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3.3. Evidence for \(\text{O}_2^-\) formation in the reaction of MnO\(_4\) with HA

EPR spectroscopy is commonly utilized to test radical formation by using either a nitrone (e.g., DMPO, BMPO) or a nitroso to trap the radical as a longer-lived nitroxide (Finkelnstein et al., 1980). Compared to the common spin trapping agent DMPO, BMPO is more suitable to trap \(\text{O}_2^-\) due to the longer half-life of the resulting BMPO-OOH (Zhang et al., 2000; Tsai et al., 2003). In this test, a large amount of methanol (\(\text{CH}_3\text{OH}\), 14 M) should be applied to prevent the complete disproportionation of \(\text{O}_2^-\) so that a certain amount of \(\text{O}_2^-\) can be trapped by BMPO. In the absence of HA, both BMPO-OOH and BMPO-OH were identified in the MnO\(_4\)/BMPO/\(\text{CH}_3\text{OH}\) system, implying the production of \(\text{O}_2^-\) and \(\cdot\text{OH}\) (Fig. 3). BMPO-OOH could only be produced through the genuine spin trapping of \(\text{O}_2^-\) by BMPO (Fig. S3a). Because water also existed in the reaction system, a part of \(\text{O}_2^-\) could disproportionate to form \(\cdot\text{OH}\) (Eqs. (3)–(4)), which was then trapped by BMPO to form BMPO-OH (Fig. S3b). In addition, BMPO-OH may also be produced from the direct oxidation of BMPO by MnO\(_4\) without radical formation (Fig. S3b). As the \([\text{HA}]_0/[\text{KMnO}_4]_0\) ratio increased from 0 to 1, 1.5 and 2, the intensity of BMPO-OH increased quickly until exceeding that of BMPO-OOH at \([\text{HA}]_0/[\text{KMnO}_4]_0 = 2\) (Fig. 3), demonstrating an increasing production of \(\text{O}_2^-\) in the reaction of MnO\(_4\) with HA.

![Fig. 3. EPR evidence for \(\text{O}_2^-\) production in the reaction of MnO\(_4\) with HA at different \([\text{HA}]_0/[\text{KMnO}_4]_0\) ratios. Experimental conditions: [MnO\(_4\)]\(_0\) = 200 μM, [BMPO]\(_0\) = 6.6 mM, [methanol]\(_0\) = 14 M.](image-url)
3.4. Evidence for \( ^{\cdot}\text{OH} \) formation in the reaction of MnO\(_4\) with HA

In the MnO\(_4\)/DMPO system ([DMPO]_o/[MnO\(_4\)]_o = 8.2), DMPOX was identified (Fig. 4a), which has the characteristic hyperfine splitting constants of \( a_N = 7.2 \) G and \( a_H = 4.1 \) G (Lawrence et al., 2003). Potential pathways for DMPOX formation included: (1) \(^{\cdot}\text{OH} \) production in the reaction of MnO\(_4\) with an excessive DMPO, and subsequent DMPO-OH formation (through the genuine spin trapping of \(^{\cdot}\text{OH} \) by DMPO) and its dehydrogenation by MnO\(_4\) to DMPOX (Fig. S4a); and (2) direct oxidation of DMPO by MnO\(_4\) to DMPO-OH and its subsequent dehydrogenation to DMPOX without radical formation (Fig. S4b).

At \([\text{HA}]_0:[\text{KMnO}_4]_0 = 0.5, 1 \) and \( 3 \), the intensity of DMPOX formed was enhanced by 2-, 2.8- and 1.4-fold, respectively, as compared to that in the absence of HA (Fig. 4a). At \([\text{HA}]_0:[\text{KMnO}_4]_0 = 5 \), the formation of DMPOX was inhibited notably. This result indicates again the production of \(^{\cdot}\text{OH} \) in the reaction of MnO\(_4\) with HA. At \([\text{HA}]_0:[\text{KMnO}_4]_0 = 3 \) and \( 5 \), the produced \(^{\cdot}\text{OH} \) could be consumed by HA with a higher concentration more significantly. After DMPOX was produced in the absence of HA, it could be further oxidized by MnO\(_4\) (Fig. 4b). In the presence of HA, the oxidation rate of DMPOX was enhanced by 2.3- and 3.0-fold at \([\text{HA}]_0:[\text{KMnO}_4]_0 = 0.5 \) and \( 1 \), respectively. This enhancement provides an additional evidence for the production of \(^{\cdot}\text{OH} \) in the reaction of MnO\(_4\) with HA. The produced \(^{\cdot}\text{OH} \) could not only oxidize DMPO to DMPOX (Fig. S4a) resulting in an increased initial intensity of DMPOX (Fig. 4b), but also further oxidize DMPOX resulting in its accelerated degradation (Fig. 4b).

Trapping \(^{\cdot}\text{OH} \) by DMPO first produces DMPO-OH. An excessive DMPO can prevent all DMPO-OH produced from being dehydrogenated to DMPOX by MnO\(_4\). This is verified by the identification of DMPO-OH, which has the characteristic hyperfine splitting constants of \( a_N = a_H = 14.9 \) G (Finkelstein et al., 1980), when the [DMPO]_o/[MnO\(_4\)]_o ratio was increased to 500 in the absence of HA (Fig. 4c). In the presence of HA, the intensity of DMPO-OH was enhanced by 1.2-fold at \([\text{HA}]_0:[\text{KMnO}_4]_0 = 0.5 \), indicating once more that \(^{\cdot}\text{OH} \) was produced in the reaction of MnO\(_4\) with HA. At \([\text{HA}]_0:[\text{KMnO}_4]_0 = 1 \), the intensity of DMPO-OH decreased to some extent, because an increasing HA could consume more MnO\(_4\) and \(^{\cdot}\text{OH} \).

As the \([\text{HA}]_0:[\text{KMnO}_4]_0 \) ratio increased from 0 to 0.5, the enhanced LF degradation (Fig. 2) and the enhanced formation of DMPOX and DMPO-OH (Fig. 4) all indicate an increasing \(^{\cdot}\text{OH} \) yield. As the \([\text{HA}]_0:[\text{KMnO}_4]_0 \) ratio further increased to 1, the formation of DMPOX was enhanced significantly (Fig. 4a), while the enhancement of LF degradation and DMPO-OH formation were both weakened. At \([\text{HA}]_0:[\text{KMnO}_4]_0 = 0.5 \) and \( 1 \), the different trends of DMPOX and DMPO-OH could be attributed to the different extents of DMPO oxidation by MnO\(_4\) and \(^{\cdot}\text{OH} \). The weakened acceleration of LF degradation at \([\text{HA}]_0:[\text{KMnO}_4]_0 = 1 \) denotes a stronger consumption of MnO\(_4\) and \(^{\cdot}\text{OH} \) by HA.

3.5. Degradation pathways of LF in the absence and presence of HA

Based on the total ion chromatograms of LF solution treated by MnO\(_4\) (Fig. S5) and the evolution of the relative abundances of identified byproducts (Fig. S6) within the first 30 min, the degradation pathways of LF in the absence of HA were proposed (Fig. 5). The mass measurements of protonated LF and byproducts as well as the MS\(^2\) spectra and proposed fragmentation patterns are detailed in Table 1 and Fig. S7, respectively. In addition, the evolution of TOC, inorganic ions and low-molecular-weight organic acids formed during LF degradation by MnO\(_4\) was determined (Fig. S8).

Fig. S6 shows that as one of the initial degradation byproducts, LF375 (i.e., LF375(1) + LF375(2)) reached a peak of relative abundance at a reaction time of 2 min. As mentioned above, the \( N_4 \) atom in the chemical structure of LF could facilitate the formation of LF375(1) through hydroxylation of the side –CH\(_3\) group and dehydrogenation of the –C\(_{\text{H}}\) –C\(_{\text{H}}\) bond. If the –CH\(_3\) group at the C\(_7\) site was hydroxylated, LF375(2) could be formed. LF377(1) and LF377(2) were formed through hydroxylation of the –CH\(_3\) groups at the C\(_{\text{F}}\) and C\(_{\text{F}}\) sites, respectively. MnO\(_4\) might also attack LF through dehydrogenation to produce LF359(1) and LF359(2), LF335(1) could originate from the removal of –C\(_{\text{H}}\) –C\(_{\text{H}}\) from LF377(2), and LF335(2) from the removal of –C\(_{\text{H}}\) –C\(_{\text{H}}\) from LF359(2), which both induced the formation of oxalate. The simultaneous removal of C\(_{\text{B}}\) and C\(_{\text{G}}\) was also reported during
chlorination of LF, but dehydrogenation was not observed in this reaction system (El Najjar et al., 2013). During the degradation of LF377(2) to LF335(1), LF359(1) might be produced by removing one H2O from the C1−C2 bond of LF377(2) (i.e., forming the C1−C2 bond). As shown in Fig. S6, LF335 was vulnerable to MnO4− oxidation, whose relative abundance declined quickly after a reaction time of 5 min; in contrast, the relative abundance of LF377 increased quickly within the first 5 min, and then kept increasing slowly until it started to decline after 20 min.

In the chemical structure of LF377(1), the N4−CH2OH group and the N1 atom both withdrew electrons from −C4−C5− and −C7−C8−, which may lead to the simultaneous cleavage of the two bonds upon MnO4− attack, and then a triple bond (i.e., −C4=−C8−) was formed to produce LF300. Fig. S8 shows that after reaction for 30 min, NO2− and NO3− occupied 1.9% and 1.5% of the total N in LF, which probably arose from the removal of N4 from LF377(1). The degradation of LF375(1) could produce LF128 and LF385. The removal of C4 from LF375(1) (to form LF385) could induce the formation of formate. The loss of one carbon atom from LF was also observed during ozone treatment (De Witte et al., 2009). In addition, the degradation of LF375(1) to LF385 released F−, which occupied 49.2% of the total F in LF after reaction for 30 min (Fig. S8). LF389 (LF389(1)+LF389(2)) was formed through carboxylation of LF375 (LF375(1)+LF375(2)). Similarly, LF391 (LF391(1)+LF391(2)) was formed through carboxylation of LF377 (LF377(1)+LF377(2)). LF391(3) was either formed through hydroxylation of LF375(2) or both hydroxylation and dehydrogenation of LF377(2). The dehydrogenation of −C1=−C2− or −C7=−C8− of LF391(1) induced the formation of LF389 (LF389(3)+LF389(4)).

It can be concluded that the degradation of LF and its byproducts during MnO4− oxidation was mainly through hydroxylation, dehydrogenation and carboxylation, which occurred at the CH3, −C=C− and −CH2OH groups, respectively. In comparison, for LF degradation by other oxidation processes, free chlorine tended to substitute the COOH group with a chlorine atom, and ozone tended to add an O atom to the N4 (De Witte et al., 2009; El Najjar et al., 2013). As shown in Fig. S8, TOC was only removed by 5.4% after reaction for 30 min, which agrees with the low removal of

Table 1

| Name       | Elemental composition         | Retention time (min) | Nominal ion mass (m/z) | Measured ion mass (m/z) | Calculated ion mass (m/z) | Mass error (ppm) | DBE a |
|------------|-------------------------------|----------------------|------------------------|-------------------------|--------------------------|------------------|-------|
| LF         | C18H20N3O4F                   | 5.00−5.03            | 362                    | 362.1513                | 362.1511                 | +0.6             | 9.5   |
| LF375      | C18H19N3O4F                   | 3.89−3.92            | 376                    | 376.1299                | 376.1303                 | −1.0             | 10.5  |
| LF377      | C18H20N3O4F                   | 4.39−4.46            | 378                    | 378.1447                | 378.1460                 | −3.4             | 9.5   |
| LF335      | C18H19N3O4F                   | 4.79−4.80            | 336                    | 336.1359                | 336.1354                 | +1.5             | 8.5   |
| LF300      | C17H19N3O4F                   | 8.10−8.13            | 301                    | 301.0615                | 301.0619                 | −1.3             | 11.5  |
| LF128      | C18H18N3O5F                   | 2.25−2.26            | 129                    | 129.0656                | 129.0659                 | −2.3             | 2.5   |
| LF385      | C18H18N3O4F                   | 2.25−2.26            | 386                    | 386.1184                | 386.1194                 | −2.6             | 7.5   |
| LF389      | C18H18N3O4F                   | 6.14−6.15            | 390                    | 390.1065                | 390.1096                 | −7.9             | 11.5  |
| LF391      | C18H17N3O4F                   | 7.08−7.10            | 392                    | 392.1270                | 392.1252                 | +4.6             | 10.5  |
| LF306      | C18H16N3O4F                   | 6.52−6.70            | 390                    | 390.1090                | 390.1096                 | −1.5             | 11.5  |
| LF363      | C18H16N3O4F                   | 6.52−6.76            | 364                    | 364.1301                | 364.1303                 | −0.5             | 9.5   |
| LF363’     | C18H16N3O4F                   | 6.77−6.97            | 364                    | 364.1293                | 364.1303                 | −2.7             | 9.5   |

a Double-bond equivalent.
carbon from LF and its byproducts.

Fig. 6 compares the degradation byproducts of LF in the absence and presence of HA during the reaction period of 45–125 min. In the absence of HA, LF389, LF389′ and LF391 could still be detected but with much lower intensities than those within the first 30 min, and three new byproducts including LF306, LF363 and LF363′ were identified (Fig. 6a and S9). In the presence of HA ([HA]o:[KMnO4]o = 0.5), LF363 and LF391 were also detected, but a new byproduct (LF263, Fig. S9) emerged with a high peak (Fig. 6b). LF263 has the simplest structure among the high-molecular-weight organic byproducts formed during LF degradation by MnO4−, which denotes a stronger destruction of LF in the presence of HA (i.e., additional oxidation by [HA-Mn(III)] and *OH).

4. Conclusions

This study investigated the impact of HA on LF degradation by MnO4− in water from both kinetic and mechanistic aspects. Based on the experimental results obtained, the following conclusions can be drawn:

- In the absence of HA, LF reacted toward MnO4− with a second-order rate constant (k) of 3.9 M−1 s−1 at pH 7.5. As the pH decreased from 8.5 to 6.5, the protonation of the N4 atom facilitated the degradation of LF by enhancing the electrophilicity of structural groups adjacent to N4.
- At [HA]o/[KMnO4]o (mass ratio) = 0.5 and 1, the pseudo-first-order rate constant (kobs) of LF degradation was significantly increased by 3.8- and 2.8-fold at pH 7.5, respectively. Secondary oxidant scavenging tests indicated that oxygen-centered radicals could be produced in the reaction of MnO4− with HA.
- HA could form a complex with Mn(III) to successively produce O2*− and -OH. The -OH primarily contributed to the accelerated LF degradation, and the complex [HA-Mn(III)] could account for the rest of acceleration.
- The degradation of LF and its byproducts during MnO4− oxidation was mainly through hydroxylation, dehydrogenation and carboxylation reactions occurring at the –CH3, –C–C– and –CH2OH groups, respectively. The presence of HA caused a stronger destruction of LF.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2017.06.037.

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