Oxidative treatment of diclofenac via ferrate(VI) in aqueous media: effect of surfactant additives

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ABSTRACT

The potential reaction of diclofenac (DCF) with ferrate(VI) and influences of coexisting surfactants have not been investigated in depth, and are the focus of this study. The results demonstrated that DCF reacted effectively and rapidly with Fe(VI) and approximately 75% of DCF (0.03 mM) was removed by excess Fe(VI) (0.45 mM) within 10 min. All of the reactions followed pseudo first-order kinetics with respect to DCF and Fe(VI), where the apparent second-order rate constant ($k_{app}$) was 5.07 M$^{-1}$·s$^{-1}$ at pH 9.0. Furthermore, the degradation efficiencies of DCF were clearly dependent on the concentrations of dissolved organic matter additives in the substrate solution. Primarily, inhibitory effects were observed with the samples that contained anionic (sodium dodecyl-benzene sulfonate, SDBS) or non-ionic (Tween-80) surfactants, which have been attributed to the side reactions between Fe(VI) and surfactants, which led to a reduction in the available oxidant for DCF destruction. Furthermore, the addition of a cationic surfactant (cetyltrimethyl ammonium bromide, CTAB) and humic acid (HA) conveyed significantly promotional effects on the DCF-Fe(VI) reaction. The rate enhancement effect for CTAB might be due to micellar surface catalysis, through the Coulomb attraction between the reactants and positively charged surfactants, while the catalytic action for HA resulted from the additional oxidation of Fe(V)/Fe(IV) in the presence of HA. The results provided the basic knowledge required to understand the environmental relevance of DCF oxidation via Fe(VI) in the presence of surfactant additives.

Key words | diclofenac, ferrate(VI), humic acid, kinetics, surfactants

INTRODUCTION

Ferrate(VI) (FeO$_4^{2-}$) exhibits powerful oxidizing properties that may be seen from the redox potential of 0.57 V under basic conditions, and 2.20 V under acidic conditions (Hu et al. 2009; Yang et al. 2011a), which is greater than O$_3$ and is the most potent disinfectant used in pulp and water treatment systems. Fe(VI) is a promising triple-functional chemical that typically undergoes oxidation, disinfection and subsequent coagulation to form non-toxic Fe$_3^{5+}$ or Fe(OH)$_3$ (Yang et al. 2011b), which has been successfully applied into green technology for organic syntheses, high energy density rechargeable batteries, and multi-purpose water remediation processes (Sharma 2013; Jiang 2014). Due to its selective oxidizing properties and environmental compatibility, Fe(VI) is garnering increased attention for the elimination of several pharmaceuticals and other emerging micropollutants such as antibiotics, anti-inflammatory drugs, endocrine disrupters and cyanides (Yngard et al. 2007; Anquandah et al. 2013; Jiang 2014). Fe(VI) has the capacity to remove more than 85% of various organic substrates that contain electron-rich moieties (Lee et al. 2009). Meanwhile, the kinetic profiles of Fe(VI) with several pharmaceuticals, along with the formation of intermediates, have been under study (Sharma 2008; Lee & von Gunten 2010; Zhou & Jiang 2015). Further, previous reports have confirmed that cyanides may be removed by Fe(VI) within seconds to generate relatively non-toxic end-products (Yngard et al. 2007). The pH dependence and instability of Fe(VI) salts have limited its use in the water industry. However, recent efforts for preparation technologies of on-site Fe(VI) using...
an electrochemical method makes it an alternative oxidant for the treatment of effluents from waste-water treatment plants (WWTPs) (Alsheyab et al. 2009; Macova et al. 2009; Yang et al. 2011b). Concerning the advantages of the application of Fe(VI) as an environmentally compatible agent, many pharmaceuticals and their metabolites of concern have become targets of great interest for the investigation of their response to Fe(VI) mediated oxidation.

The current study has its focus on diclofenac (DCF), 2-[2,6-dichlorophenyl] amino] phenylacetic acid, which is extensively consumed as a non-steroidal anti-inflammatory drug, prescribed particularly in antirheumatic, antiarthritic, antiphlogistic, analgesic and antipyretic treatments (Khalaf et al. 2009; Zheng et al. 2011). According to earlier studies (Yu et al. 2013; Michael et al. 2014), hundreds of tons of DCF are produced annually throughout the world, a portion of which is discharged as effluents, excreted through urine and faeces in its original form, or as biodegraded metabolites from patients. In recent years, rather high concentrations of DCF in municipal WWTPs and ambient surface water have been frequently detected, ranging from ng L$^{-1}$ to μg L$^{-1}$ in Germany, the United States, France and Pakistan (Bae et al. 2013; Huguet et al. 2015). Toxicities after exposure to DCF have been investigated in aquatic systems (Achilleos et al. 2010; Marco-Urrea et al. 2010), there are potential hazards for human health, as some metabolites may be more harmful than their parent compounds. For example, DCF may cause physiological alterations in the livers, kidneys and gills of rainbow trout, with the lowest observed effect under a concentration of 1 μg L$^{-1}$ (Triebkorn et al. 2004; Taggart et al. 2007). DCF has also been considered as very toxic to bacteria (EC$^{50} < 1$ mg L$^{-1}$), invertebrates and algae (EC$^{50} = 1-10$ ng L$^{-1}$) based on the EC$^{50}$ values reported in the literature (Hernando et al. 2006). As a result, it was felt that the degradation of DCF via ferrate(VI) should be carried out, providing a fundamental understanding of the fate and behavior of DCF during water purification treatment.

Dissolved organic matter (DOM), principally in the forms of hydrophilic surfactants and humic substances, is typically present in ambient surface waters, groundwater and drinking water. Surfactants are generally surface-active agents that reduce interfacial tension in aqueous media. Surfactants contain both hydrophilic groups (heads) and hydrophobic groups (tails). Contingent on the nature of the hydrophilic group, surfactants are classified as the following four types: anionic, cationic, nonionic and amphoteric surfactants. The annual worldwide production of surfactants is estimated to be 15 million tons, about half of which constitute soaps (Ceresana Research 2013). Surfactants have been found to contaminate a wide range of aquatic environments due to their comparatively complex behaviors and widespread applications in industrial, biological, technological, and domestic fields (Seng et al. 2000; Mandal et al. 2011). Therefore, the effects of coexisting surfactants on the elimination of water contaminants have been intensively investigated (Oliveira et al. 2011; Exall et al. 2013; Yang et al. 2014).

Humic acid (HA) is a key constituent of humic substances, which is another primary component of DOM. Since numerous and diverse biomacromolecules are combined in natural environments by variable physical associations, the HA concentration is typically estimated to be 90% of the total organic carbon (Ji et al. 2012). The presence of HA in water may have a significant impact on the extent of contaminant removal, and react with the oxidants to form disinfection by-products, which are harmful to human health. Thus, the action of HA during water treatment can not be neglected.

Considering the paucity of reports that are involved with the influences of various DOM species on the degradation of pharmaceuticals, potential environmental behaviors are seldom focused on when organic contaminants exist together with surfactants or HA in natural waters. In this study, an optimized reaction condition will be found to explore the effects of DOM additives on the oxidation of DCF via ferrate(VI), based on the reaction kinetics in our previous work (Wang et al. 2015). Furthermore, the influences of the addition of DOM species, such as different concentrations of surfactants or HA to the synthetic wastewater, might be illustrated by a systematic experiment when initial concentration of DCF and Fe(VI) are fixed at a constant temperature and pH. The results provide the first investigation on common water quality parameters that influence the removal of contaminants from water and wastewater by comparing the presence and absence of DOM additive in spiked samples. It is strategically significant to establish the importance of environmental factors.

**MATERIALS AND METHODS**

**Chemicals and reagents**

Analytical grade DCF sodium salt (DCF-Na, ≥98% purity) was purchased from J&K Chemical Co. Ltd (Beijing, China). Solid K$_2$FeO$_4$ of ~86% purity was synthesized according to Guan et al. (Guan et al. 2014). Fe(VI) stock...
solutions were prepared freshly in a 5 mM K₂HPO₄/1 mM Na₂B₄O₇ buffer at pH 9.0, which was reported to stabilize Fe(VI) and minimize autodecomposition (Hu et al. 2009). Stock solutions were immediately filtered using a 0.22 μm hydrophilic nylon syringe filter (Shanghai, China) and utilized within 3 h of preparation. The Fe(VI) concentrations in the solution were determined using the molar adsorption coefficient of 1,150 M⁻¹ cm⁻¹ at 510 nm (Jiang et al. 2012; Anquandah et al. 2015). DCF stock solutions for calibration were prepared by dissolving the solid compound in ultrapure Milli-Q water at a concentration of 3.0 mM. Analytical grade surfactants, cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl-benzene sulfonate (SDBS), and Tween-80 were supplied by Shanghai Chemical Company (Shanghai, China). Fluka HA was obtained from Saint-Quentin Fallavier Co. Ltd (France). High performance liquid chromatography (HPLC) grade methanol was purchased from Tedia Company Inc. (USA). All other reagents (Na₂S₂O₃, phosphate, acetic acid, etc.) were of analytical grade. 18.2 MΩ ultrapure water, obtained from Milli-Q Water filtration system (Millipore, USA), was used throughout the experimental procedures and chromatographic analyses.

Kinetic experiments

To evaluate the performance of ferrate(VI) for DCF oxidation, a series of kinetic experiments were conducted in 60 mL circulating jacket beakers connected to a thermostatic bath at 25 °C and pH 9.0 unless stated otherwise. All reactions were initiated by spiking excess Fe(VI) stock solution into the substrate solutions containing 0.03 mM DCF, 5 mM K₂HPO₄/1 mM Na₂B₄O₇ buffer, and surfactant additives of interest under rapid stirring. At fixed time intervals, 2 mL of the reaction liquid was rapidly transferred with a pipette to a small beaker, which contained 50 μL of pre-loaded Na₂S₂O₃ (0.10 M) to quench the reaction immediately. The resulting solutions were then filtered through 0.22 μm membrane filters into HPLC vials. The concentration of residual DCF was measured directly using HPLC to determine the degradation efficiency (η) by the following Equation (1):

\[ \eta = \frac{[DCF]_0 - [DCF]}{[DCF]_0} \times 100\% \]  

(1)

where [DCF]₀ (mM) is the initial concentration of DCF, and [DCF] (mM) is the concentration of residual DCF. Changes in the pH value of the reaction solution were negligible, since a phosphate buffer (pH 9.0) was applied as a reaction medium throughout the entire process. Meanwhile, the reaction temperature (25 °C) was controlled simultaneously with a WX-08 water cryostat (Shanghai Bilon Instruments Co. Ltd, China). It is worth noting that the initial concentrations of Fe(VI) and DCF were controlled at 0.45 mM and 0.03 mM, respectively, which enabled the data to remain consistent with the pilot experiments in order to verify the influences of coexisting organic matter on the oxidation of DCF by Fe(VI). Initial concentrations of the additives SDBS, Tween-80 and CTAB were in a range from 0.015 mM to 0.15 mM, while the initial concentration of added HA varied between 1.00 ppm and 10.00 ppm. All trials were performed in triplicate and the mean of three separate measurements are quoted in the figures. The corresponding error limits of the means were never higher than 20%.

Analytical procedures

The DCF concentration was analyzed using a Waters HPLC system consisting of a 1525 pump and 2998 photodiode array detector (Waters Corporation, Massachusetts, USA). HPLC conditions were as follows: a C₁₈ reverse phase column (150 mm × 4.6 mm, 5 μm) with a guard column (C₁₈, 20 mm × 4.6 mm, 5 μm); the mobile phase was 75% methanol and 25% water (containing 1% acetic acid), and the flow rate was controlled at 1.0 mL min⁻¹. The injection volume was 20 μL, and the detection wavelength was set at 276 nm.

RESULTS AND DISCUSSION

Kinetics of the Fe(VI)-DCF reaction

The oxidation of DCF (0.03 mM) via ferrate(VI) was investigated under varied conditions using excess concentrations of Fe(VI) (0.30–0.90 mM). All of the experiments were carried out at pH 9.0 and 25 °C. Figure 1 depicts a typical curve with [Fe(VI)]₀ = 0.45 mM and [DCF]₀ = 0.03 mM. Perusal of Figure 1 shows that the depletion of DCF followed exponential decay, where 75.23% of the DCF was oxidized by Fe(VI) within 10 min, suggesting that the reaction was rather rapid. Employing the Kinetic fit software and using the first-order integral Equation (2):  

\[ \ln \left( \frac{[DCF]}{[DCF]_0} \right) = -k_{\text{obs}}t + A \]  

(2)

Batch experimental data showed that the curve-fitting result was in fair agreement with DCF residues, indicating
that the reaction was first-order with respect to DCF. Table 1 summarizes the kinetic parameters, including the observed rate constants ($k_{obs}$), dynamic equation and correction coefficient ($R^2$) of DCF oxidized by various initial concentrations of Fe(VI) at pH 9.0. The plot of $\ln([\text{Fe(VI)}])_0$ vs. $\ln k_{obs}$ gave a linear curve with a slope of 1.06 and correction coefficient of 0.9970, confirming that the reaction rate had a first-order dependence on $[\text{Fe(VI)}]_0$. Given that the reaction not only had a higher reaction rate but also met the needs of a subsequent toxicity test (Marco-Urrea et al. 2010), the optimal concentrations of DCF and Fe(VI) were determined as 0.03 mM and 0.45 mM, respectively.

Second-order rate constants were calculated ($k_{app}$, M$^{-1}$ s$^{-1}$) by considering Equation (3):

$$k_{app} = \frac{k_{obs}}{[\text{Fe(VI)}]_0}$$

This is supplemented in Table 1. As can be seen, the mean of $k_{app}$ was determined to be $5.07$ M$^{-1}$ s$^{-1}$, which is very close to that of the oxidation of atenolol ($k_{app}$, $7.0$ M$^{-1}$ s$^{-1}$) by Fe(VI) at pH 8.0 (Lee & vonGunten 2010). The reaction kinetics of Fe(VI) with other pharmaceuticals including propranolol (Anquandah et al. 2013), sulfonamide antimicrobials (Sharma et al. 2006), trimethoprim (TMP) (Anquandah et al. 2011) and tetracycline (Ma et al. 2012) have been studied in order to evaluate their possible removal from water. Comparatively, sulfonamide antibiotics ($k_{app}$, $10^2$–$10^3$ M$^{-1}$ s$^{-1}$) (Sharma et al. 2006), ciprofloxacin ($k_{app}$, $4.7 \times 10^2$ M$^{-1}$ s$^{-1}$) (Jiang et al. 2012) and carbamazepine ($k_{app}$, $70 \pm 3$ M$^{-1}$ s$^{-1}$) (Hu et al. 2009) showed generally higher rates than those of enrofloxacin ($k_{app}$, $4.6$ M$^{-1}$ s$^{-1}$) (Jiang 2014), ibuprofen ($k_{app}$, $0.09$ M$^{-1}$ s$^{-1}$) (Zhou & Jiang 2015) and tramadol ($k_{app}$, $7.4$ M$^{-1}$ s$^{-1}$) (Zimmermann et al. 2012). This may be explained by the former having a strong electron-donating effect of substituents located at the aromatic rings; however, the carboxylic group in ibuprofen, DCF and enrofloxacin had an electron withdrawing group, which exhibited negligible reactivity to Fe(VI) (Jiang et al. 2012; Jiang & Zhou 2015).

**Effects of coexisting SDBS on DCF degradation**

Surfactants routinely accumulate in soils by varied means, and into waste systems, whether as part of an intended process or as domestic and industrial waste (Seng et al. 2000; Mandal et al. 2011). The widespread application of cleaners

<table>
<thead>
<tr>
<th>[Fe(VI)]$_0$ (mM)</th>
<th>Dynamic equation</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>Correlation coefficient ($R^2$)</th>
<th>$k_{app}$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>$\ln([\text{DCF}]/[\text{DCF}]_0) = -0.0858t+0.0018$</td>
<td>$1.43 \times 10^{-3}$</td>
<td>0.9957</td>
<td>4.77</td>
</tr>
<tr>
<td>0.45</td>
<td>$\ln([\text{DCF}]/[\text{DCF}]_0) = -0.1396t+0.0713$</td>
<td>$2.26 \times 10^{-3}$</td>
<td>0.9910</td>
<td>5.17</td>
</tr>
<tr>
<td>0.60</td>
<td>$\ln([\text{DCF}]/[\text{DCF}]_0) = -0.1841t+0.0568$</td>
<td>$3.06 \times 10^{-3}$</td>
<td>0.9964</td>
<td>5.11</td>
</tr>
<tr>
<td>0.75</td>
<td>$\ln([\text{DCF}]/[\text{DCF}]_0) = -0.2307t+0.0077$</td>
<td>$3.84 \times 10^{-3}$</td>
<td>0.9988</td>
<td>5.13</td>
</tr>
<tr>
<td>0.90</td>
<td>$\ln([\text{DCF}]/[\text{DCF}]_0) = -0.2773t+0.0001$</td>
<td>$4.62 \times 10^{-3}$</td>
<td>0.9998</td>
<td>5.14</td>
</tr>
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and detergents has resulted in vast quantities of surfactants being released directly into the environment and their wide dispersal in natural water bodies, with concentrations at levels of ng L\(^{-1}\) to μg L\(^{-1}\) (Ceresana Research 2015). Some of these compounds are known to be toxic to human health and ecosystems, and may act to increase the diffusion of other environmental contaminants (Emmanuel et al. 2005; Murphy et al. 2005). To investigate the influences of coexisting surfactants in aqueous media on the oxidation of DCF by Fe(VI), SDBS, CTAB and Tween-80 were selected as reactive anionic, cationic and non-ionic surfactant additives, respectively.

The effects of different SDBS concentrations on the oxidation of DCF are shown in Figure 2. The inhibition rate was introduced to express the effects of surfactant additives on the oxidation of DCF according to the following Equation (4):

\[
\text{Inhibition rate} = \frac{k_{0,\text{obs}} - k_{i,\text{obs}}}{k_{0,\text{obs}}} \times 100\%
\]  

where \(k_{0,\text{obs}}\) (s\(^{-1}\)) is the observed rate constant of DCF oxidation by Fe(VI) in the absence of DOM, and \(k_{i,\text{obs}}\) (s\(^{-1}\)) is the rate constant in the presence of SDBS or Tween-80 additives. Linear plots of ln ([DCF]/[DCF]\(_0\)) vs. treatment time, obtained at SDBS concentrations of 0.00, 0.015, 0.03, 0.06, 0.15, 0.30 mM, produced a \(k_{\text{app}}\) of 4.87, 4.12, 3.96, 3.84, 3.50 and 3.13 M\(^{-1}\) s\(^{-1}\), respectively, which accounted for a decline in the degradation efficiency of DCF from 72.83% to 57.32% determined by Equations (1)–(3). Similar correlation coefficients (R\(^2\) ≥ 0.99) were obtained for all parallel tests.

It may thus be inferred that SDBS inhibited DCF oxidation across the entire concentration range. When the SDBS concentration was increased from 0.015 mM to 0.30 mM, the inhibition rate was elevated from 15.40% to 35.73%, as calculated by Equation (4). This has been caused by opposite coulomb repulsion between the negatively charged reactants and SDBS, which might lead to the weakening of the solubilizing action of the surfactants. Furthermore, the molecular structure of SDBS contains aromatic moieties with unsaturated C-C bonds, which is likely vulnerable to attack by oxidizing agents such as Fe(VI). The reactant DCF was simultaneously solubilized in aqueous media due to the presence of a considerable population of H-bonds with lyophilic sulfonic acid groups of SDBS (Mandal et al. 2011). These complex interactions had the results of reducing the amount of Fe(VI) required to react with DCF, while doing so at higher energy levels.

**Effects of coexisting Tween-80 on DCF degradation**

Figure 3 presents the effects of various Tween-80 concentrations on the degradation kinetics of DCF. As observed, experiments that were employed at Tween-80 concentrations of 0.00, 0.015, 0.03, 0.06, 0.15 and 0.30 mM generated the corresponding \(k_{\text{app}}\) of 4.87, 4.29, 3.98, 3.58, 3.02 and 2.12 M\(^{-1}\) s\(^{-1}\), respectively, whereas the rates of degradation inhibition were determined to be 11.91% and 56.47%, respectively. The rate constants and removal efficiency of DCF was synchronously reduced with elevated concentrations of Tween-80, showing an adverse trend for nonionic surfactants. Likewise, the results may also be attributed to the competitive reaction of Fe(VI) with Tween-80 and DCF.

It is recognized that the hydrophilic groups in Tween-80 molecules are polyoxyethylene chain, which are ethylene oxide polymers, hence Tween-80 is very susceptible to oxidation by Fe(VI). Moreover, similarly to SDBS, the formation of hydrogen bonds between the lyophilic

![Figure 2](https://iwaponline.com/wst/article-pdf/75/6/1342/454567/wst075061342.pdf)

**Figure 2** | Effects of SDBS concentrations on DCF degradation kinetics.
polyether groups of Tween-80 and –COOH of DCF might affect the stability and decomposition of the micelles, which might initiate a significant decrease in the DCF-Fe(VI) reactions on micellar surfaces (Oliveira et al. 2011). Tween-80 appeared to exhibit a greater inhibitory effect than SDBS due to the stronger reducibility of the hydroxyl-terminated aliphatic polysorbates and the relatively larger dimensions of the head groups in the nonionic surfactant structure (Mandal et al. 2011).

**Effects of coexisting CTAB on DCF degradation**

The influences of different CTAB concentrations on the degradation of DCF by Fe(VI) are illustrated in Figure 4. As may be clearly seen from the presence of CTAB with concentrations of 0.00, 0.015, 0.03, 0.06, 0.15 and 0.50 mM, the $k_{app}$ of DCF-Fe(VI) reactions were calculated to be 4.87, 5.15, 9.17, 17.4, 25.6 and 52.9 M$^{-1}$ s$^{-1}$, respectively. The experimental degradation efficiency was determined by Equation (1) as corresponding to 72.83%, 75.02%, 90.28%, 98.94% at 10 min, 85.941% and 96.43% at 2 min. It may be concluded that CTAB served to enhance and optimize the oxidation of DCF by Fe(VI) at any concentration of CTAB.

The surface promotion effects of CTAB on DCF-Fe(VI) reactivity might possibly be explained by micellar surface catalysis action (Mandal et al. 2011; Exall et al. 2015). Electro-weak interactions between the cationic surface active agent and the oppositely charged DCF$^-$ were occupied by wide-range coulomb attractions. With the presence of CTAB in the matrix solution, the negative reactants (DCF$^-$, FeO$_4^{2-}$) may attract positively charged head groups of CTAB through weak coulombic interactions. Thus, the cationic surfactant may facilitate bringing the two reactants into closer proximity, thereby dramatically accelerating the DCF-Fe(VI) reaction process.

**Effects of coexisting HA on DCF degradation**

The effects of different concentrations of HA on the degradation of DCF by Fe(VI) are shown in Figure 5. At pH 9.0 and 25 °C, the removal of DCF appeared to be linearly increased with elevating HA concentrations. When the
HA concentration was raised from 1.00 to 10.00 ppm, the \( k_{\text{app}} \) increased from 4.87 to 6.50 \( \text{M}^{-1} \text{s}^{-1} \), which accounted for 72.83\% and 83.44\% of the degraded DCF. As obtained from Figure 5, HA had an obvious enhancing effect on the oxidation of DCF by Fe(VI), and the degradation rates were elevated in response to increased HA concentrations. The experimental results might be explained by considering two effective interactions, including single-electron transfer steps (Equations (5)–(7)) and \( \pi-\pi \) interaction (Sharma 2013, 2010).

\[
\text{HA} + \text{Fe(VI)} \rightarrow \text{HA} \cdot \text{Fe(V)} \quad (5)
\]

\[
\text{HA} + \text{Fe(V)} \rightarrow \text{HA} \cdot \text{Fe(IV)} \quad (6)
\]

\[
\text{DCF} + \text{Fe(VI)} \rightarrow \text{products} + \text{Fe(III)} \quad (7)
\]

\[
\text{DCF} + \text{Fe(V)} \rightarrow \text{products} + \text{Fe(III)} \quad (8)
\]

\[
\text{DCF} + \text{Fe(IV)} \rightarrow \text{products} + \text{Fe(III)} \quad (9)
\]

Since Fe(V) and Fe(IV) react 2–3 orders of magnitude faster than Fe(VI) in aqueous solutions (Huang et al. 2001), reactions (8) and (9) must occur very rapidly, hence reaction (7) is the rate-determining step. As reported by Smekkalova et al. (Smekkalova et al. 2009) and Zhang et al. (Zhang et al. 2013), the non-covalent binding of HA with phenyl compounds was related to the formation of \( \pi-\pi \) interactions between the aromatic constituents of HA and the benzene rings of pharmaceuticals. The \( \pi-\pi \) interaction with HA might enhance the electron cloud density of carbon atoms in the phenyl acetic acid moiety, which could lead to the improvement in the oxidation of DCF by ferrate.

The functional mechanisms of HA, although with a few similarities, differ from other previous literature. As to the oxidation of TMP (Anquandah et al. 2011), the presence of HA in the water increased the demand for Fe(VI) since it would be in higher concentration compared to the TMP. With the degradation of flumequine (FLU) (Feng et al. 2016) and benzophenone-3 (BP-3) (Yang & Ying 2015) at pH 8.0, the addition of HA reduced the removal efficiency of FLU and BP-3, which should be attributed to the significant consumption of Fe(VI) and the competition with FLU and BP-3 by HA. In our work, DCF is an electron-rich organic matter, which is susceptible to selective oxidation by excess Fe(VI). Considering that Fe(VI) suffered autocomposition and the solubility of HA was decreased at below pH 8.0, the selected pH (9.0) for combined degradation was in a weak alkaline medium, with the result that the percentage of DCF removal was enhanced. Nevertheless, it may be concluded that additive HA plays different roles during the Fe(VI) treatment process depending on the properties of the pollutants and pH value of water matrices.

**CONCLUSIONS**

This study investigated the reaction kinetics and influences of common DOM additives on the oxidation of DCF by ferrate(VI) during the water purification process. Important elucidations were as follows:

1. DCF might be effectively oxidized by excess Fe(VI). The loss of each reactant could be modeled by pseudo first-order kinetics. The appropriate concentrations of reactants and pH value were deduced for the investigation of the effects of DOM.

2. The addition of SDBS and Tween-80 exhibited obvious inhibitory effects on the removal of DCF. The results suggested that SDBS and Tween-80 competed with...
DCF to react with Fe(VI), so that a lesser quantity of Fe(VI) was available for the destruction of DCF.

(3) However, CTAB enhanced the efficiency of DCF removal. The promotional effect might be due to the adsorption of reaction species on micellar surfaces.

(4) As well, HA potentially increased the degradation efficiency of DCF, which could be explained by the additional oxidation of DCF via Fe(V)/Fe(IV) in the presence of HA.

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