Promoted oxidation of diclofenac with ferrate (Fe(VI)): Role of ABTS as the electron shuttle

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HIGHLIGHTS

- Addition of ABTS could accelerate the DCF degradation by Fe(VI).
- Formation of $\text{ABTS}^{\bullet+}$ accelerated DCF degradation.
- Oxidation kinetics of ABTS and DCF by Fe(VI) were governed by pH.
- ABTS could enhance the DCF degradation over wide water quality ranges.

GRAPHICAL ABSTRACT

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ABSTRACT

Reaction of Fe(VI) with 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS) is widely adopted to determine aqueous ferrate (Fe(VI)) concentration based on $\text{ABTS}^{\bullet+}$ formation. Interestingly, this study found that the addition of ABTS could accelerate the oxidation of diclofenac (DCF) by Fe(VI) significantly. Observed first-order rate constant of DCF in the presence of $30\ \mu\text{M}$ ABTS was found to be 36.2 folds of that without ABTS, with values of 3.08 and $0.085\ \text{min}^{-1}$, respectively. It was partly attributed to the formation of $\text{ABTS}^{\bullet+}$. The apparent second-order rate constant (k_{app}) for the oxidation of ABTS by Fe(VI) at pH 7.0 was determined to be $1.1 \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$, which was 3–5 orders of magnitude higher than those for the reactions of $\text{ABTS}^{\bullet+}$ with DCF ($k_{\text{app,ABTS}^{\bullet+}\text{-DCF}} = 2.8 \times 10^3\ \text{M}^{-1}\ \text{s}^{-1}$) and Fe(VI) with DCF ($k_{\text{app,Fe(VI)-DCF}} = 17.7\ \text{M}^{-1}\ \text{s}^{-1}$). Both the $k_{\text{app,Fe(VI)-ABTS}}$ and $k_{\text{app,Fe(VI)-DCF}}$ decreased obviously with increasing pH, while the $k_{\text{app,ABTS}^{\bullet+}\text{-DCF}}$ exhibited little pH dependency. By acting as the electron shuttle, ABTS could enhance the removal efficiency of DCF over wide pH and natural organic matter concentration ranges. This study provides new insights to reconsider the role of organic matter during Fe(VI) oxidation and highlights the potential for increasing the reactivity of Fe(VI).

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1. Introduction

Because of its multiple functions including oxidation, disinfection, and subsequent coagulation, ferrate (Fe(VI)) has received increased attention in water treatment [1,2]. Fe(VI) could react with various (in)organic compounds, preferring to electron-rich organic moieties (e.g., olefins, amines, phenols, and anilines) via one-electron or two-electron transfer mechanisms [3,4]. Meanwhile, Fe(VI) is also one of the few oxidants which seldom form halogenated hazardous byproducts. Moreover, Fe(VI) is generally reduced to Fe(III) after the oxidation, which is non-toxic and could serve as an in-situ coagulant [5]. Fe(VI) is regarded as a novel oxidant with environmental benign for water treatment [6–8].

There are four protonation species for Fe(VI) in water (Eqs. (1)–(3)), which induce the reactivity of Fe(VI) varies obviously depending on its speciation. Generally, Fe(VI) has higher redox potentials under lower pHs. For example, the redox potentials of monoprotonated Fe(VI) vary significantly (with +2.20 and +0.72 V in acidic and alkaline circumstances, respectively) [9–12]. Under acidic and neutral circumstances, Fe(VI) spontaneously decomposes with the formations of ferric hydroxide, hydrogen peroxide, and oxygen, while maintains relatively stable under alkaline circumstance [13,14]. The half-life of Fe(VI) solution is around 3 min at neutral circumstance, increasing to about 2.0 h when pH is >9.0. Both the instability and the pH-dependent reactivity limit the wide application of Fe(VI).

Continued efforts have been made to improve the removal efficiency of oxidation process, especially for the mild oxidants [15,16]. Redox mediators are organic compounds that can be oxidized by oxidant to free radicals. Once the mediator is oxidized to radicals, it may be reduced back to their parent compound during the oxidation, which is recognized as an electron shuttle [17]. These formed radicals, which are usually non-preference during the reaction, can accelerate the degradation of pollutant. This ideal catalytic cycle shows the potential to increase the reactivity of oxidant. The catalytic effects of various redox mediators, including humic acid (HA), fulvic acid, syringaldehyde and acetosyringone on the oxidation of pollutants have been reported [18,19]. For example, both syringaldehyde and acetosyringone could promote the degradation of sulfamethoxazole within a few hours in laccase-mediator system.

Reaction of 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS, chemical information in Table S1) with Fe(VI) is widely adopted to measure aqueous Fe(VI) concentration via determining ABTS^{•+} formation. Various inorganic radicals (e.g., HO[•], Br₂^{•-}), organic radicals (e.g., alkoxylperoxyl or alkoxyl radicals) and non-radical oxidants (e.g., Fe(VI), bromine and chlorine species) are ready to react with ABTS to stoichiometrically produce ABTS^{•+}. As shown in Eq. (4), ABTS was oxidized by Fe(VI) through an one-electron transfer step with the formation of Fe(V) and ABTS^{•+} [20]. Previous study showed that ABTS could promote the degradation of substituted phenols by permanganate (Mn(VII)) obviously at pH 5.0–9.0 [21]. As a similar mild oxidant like Mn(VII), the reactivity of Fe(VI) may also be promoted after the addition of ABTS. However, the kinetics and intrinsic mechanism of the promoted oxidation of Fe(VI) with ABTS are rarely reported. To our limited knowledge, this is the first study which investigates the promoted effect of ABTS on the micropollutant oxidation by Fe(VI)

Diclofenac (DCF) is one of the widely administrated non-steroidal anti-inflammatory pharmaceuticals in the world [22,23]. Due to metabolite excretions by human and animals and incomplete removal in wastewater treatment plants (WWTPs), DCF has been detected in surface water. The average influent and effluent concentrations of DCF in WWTPs were reported as 0.23 and 0.22 µg L⁻¹, respectively [24]. Even with concentration <1.0 µg L⁻¹, adverse effects of DCF on humans, fishes and birds have been reported [25,26]. This study selected DCF as a model compound to examine whether ABTS could act as a redox mediator to promote the oxidation of DCF by Fe(VI). The kinetics for the reactions of Fe(VI) with ABTS, Fe(VI) with DCF and ABTS^{•+} with DCF were compared at pH 6.0–10.0 to investigate the promoted mechanism. Moreover, the effect of ABTS on the oxidation of DCF by Fe(VI) was also examined under various water qualities. It is expected to provide new insights to reconsider the role of organic matter during Fe(VI) oxidation and highlight the potential for increasing the reactivity of Fe(VI) via the addition of redox mediator.

2. Materials and methods

2.1. Standards and materials

All chemicals and solvents were used as received from various commercial suppliers. Chemical DCF (99%), ABTS (98%), HA, K₂FeO₄ (97%) were purchased from Sigma-Aldrich. Methanol (high performance liquid chromatography (HPLC) grade) and formic acid (≥99.0%) were obtained from Thermo Fisher Scientific and Dikma Technologies, respectively. The other reagents (Na₂S₂O₃, K₂S₂O₈, NaOH, H₂SO₄, Na₂B₄O₇ and Na₂HPO₄) were purchased from Beijing Chemical Reagents Company. All stock solutions were prepared with ultrapure water (>18.2 MΩ cm) obtained from a Millipore Milli-Q system. The stock solutions of Fe(VI) (1–5 mM) were freshly prepared by dissolving solid potassium ferrate in pH 9.1 buffer (5 mM Na₂HPO₄/1 mM borate). The concentration of Fe(VI) stock solution was determined by measuring Fe(VI) absorbance at 510 nm ($\epsilon_{510\text{nm}} = 1150 \text{ M}^{-1} \text{ cm}^{-1}$ for pH 9.1) [27].

2.2. Experimental procedures and kinetics

The oxidation experiment of DCF by Fe(VI) was conducted in 100 mL brown glass bottle with magnetic stirrer. Appropriate volumes of DCF and Fe(VI) stock solutions were added to achieve a 50 mL reaction solution with predetermined molar ratios of DCF and Fe(VI). In a typical experiment, 0.15 mM Fe(VI) and 0.03 mM DCF were employed. At predetermined time intervals, 1.0 mL of the reaction liquid was transferred and quenched with 100 µL Na₂S₂O₃ solution (0.20 M) to terminate the reaction immediately. After filtration with a 0.22 µm filter, the sample was analyzed by HPLC as soon as possible.

As the oxidation of ABTS^{•+} takes place so quickly that a stopped-flow spectrophotometer (SFS) (Model SX20) was used to conduct kinetics experiments of ABTS^{•+}. A computer was used to control the SFS and the kinetic data were analyzed by the Pro-Data software of Applied Photophysics Ltd. Typically, an equal volume of reductant (DCF or ABTS) and oxidant (Fe(VI) or ABTS^{•+}) solutions were simultaneously injected into the optical cell of the SFS. The two automatic syringes of SFS were driven by compressed N₂. The concentration of one injection was kept in at least 5-fold excess of another to simulate the pseudo-first-order reaction conditions. To investigate the reaction kinetics between ABTS^{•+} with DCF, ABTS^{•+} stock solution was prepared by incubating 2 mL K₂S₂O₈ (10 mM) with 2 mL ABTS (20 mM) at 25 °C for 12 h as described by Re et al. [28]. The formed ABTS^{•+} was quantitatively determined at 415 nm ($\epsilon_{415\text{nm}} = 34000 \text{ M}^{-1} \text{ cm}^{-1}$). The apparent second-order rate con-

Fig. 1. Effect of initial ABTS concentration on the promoted oxidation of DCF with Fe(VI). Experimental conditions: $[\text{Fe(VI)}]_0 = 0.15 \text{ mM}$, $[\text{DCF}]_0 = 30 \text{ }\mu\text{M}$, $[\text{ABTS}]_0 = 0.30 \text{ }\mu\text{M}$, $\text{pH} = 8.0$, $T = 25^\circ\text{C}$. ABTS: 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonate); DCF: diclofenac; Fe(VI): ferrate.

stants (k_{app}) of DCF with Fe(VI), DCF with $\text{ABTS}^{\bullet+}$ and ABTS with Fe(VI) were determined at $\text{pH} 6.0\text{--}10.0$. 10 mM phosphate solution was used as the buffer at $\text{pH} 6.0\text{--}8.0$ and 5 mM $\text{Na}_2\text{HPO}_4/1 \text{ mM}$ borate was used as the buffer at $\text{pH} 9.0\text{--}10.0$. As HA is the predominant species of natural organic matter (NOM), the HA stock solution was prepared and used to investigate the effect of water quality on the degradation of DCF by Fe(VI) in the presence and absence of ABTS. Unless otherwise stated, all kinetics experiments were carried out in triplicate at 25°C .

2.3. Analytical methods

The DCF concentration was determined with an Agilent 1200 HPLC at 275 nm coupled with a diode array detector. Separation was performed by a Waters Atlantis column ($3 \text{ }\mu\text{m}$, $150 \times 2.1 \text{ mm}$) with elution at 0.5 mL min^{-1} . The mobile phase consisted of purified water (containing 0.1% formic acid, 25%) and methanol (75%). The sample injection volume was $20 \text{ }\mu\text{L}$ and analytical column temperature was controlled at 25°C . The spectrophotometric measurements were conducted with a Hach DR 6000 UV–vis. spectrophotometry.

3. Results and discussion

3.1. Effect of initial ABTS concentration

The effect of ABTS addition on the DCF degradation was firstly investigated and the change of the normalized DCF concentration (C/C_0) with reaction time is illustrated in Fig. 1. An insignificant removal (about 30%) of DCF was observed after 10 min by Fe(VI) alone. With the addition of ABTS, the degradation of DCF was promoted to different extents which could be fit well with pseudo-first-order kinetics ($R^2 > 0.98$). The degradation of DCF was promoted obviously with the increase of ABTS concentration. The observed pseudo-first-order degradation rate (k_{obs}) of DCF in the presence of $30 \text{ }\mu\text{M}$ ABTS was found to be 36.2 folds of that without ABTS, with values of 3.08 and 0.085 min^{-1} , respectively. Meanwhile, the decay of Fe(VI) was also promoted after the addition of ABTS, indicating that the reaction between Fe(VI) and ABTS took place firstly (Fig. S1). It was reported that $\text{ABTS}^{\bullet+}$ could oxidize a wide variety of refractory compounds, including aromatic dyes and polyphenolic compounds with high degradation rates [29,30]. Song et al. [21] proposed a catalytic role between $\text{ABTS}^{\bullet+}$ and ABTS pair during the oxidation of phenol by Mn(VII). Thus, the addition of ABTS to the oxidation of DCF by Fe(VI) may play similar catalytic

Fig. 2. Effect of initial ABTS (A) and DCF (B) concentrations on the formation of $\text{ABTS}^{\bullet+}$. The inset shows the k_{obs} values of $\text{ABTS}^{\bullet+}$ formation at various ABTS concentrations. Experimental conditions: $[\text{Fe(VI)}]_0 = 2.0 \text{ }\mu\text{M}$, $\text{pH} 8.0$, $T = 25^\circ\text{C}$; $[\text{ABTS}]_0 = 0.01\text{--}0.5 \text{ mM}$ for (A); $[\text{ABTS}]_0 = 15 \text{ }\mu\text{M}$, $[\text{DCF}]_0 = 0.01\text{--}0.5 \text{ mM}$ for (B).

role via $\text{ABTS}^{\bullet+}$ and ABTS pair cycling to promote the DCF degradation. As the formation of $\text{ABTS}^{\bullet+}$ via the oxidation of ABTS by Fe(VI) is the prerequisite for the catalytic reaction to occur, it is necessary to investigate the kinetic parameters for the reaction of Fe(VI) with ABTS in detail.

3.2. $\text{ABTS}^{\bullet+}$ formation in the reaction of Fe(VI) with ABTS

As the formation of $\text{ABTS}^{\bullet+}$ during the reaction of ABTS with Fe(VI) is usually completed within 1.0 s, SFS was adopted to analyze the kinetics of $\text{ABTS}^{\bullet+}$ formation. Under the simulated pseudo-first-order reaction conditions, the kinetic trace of $\text{ABTS}^{\bullet+}$ formation acquired at 415 nm could be fitted well to a single-exponential curve (Fig. 2A), indicating that the reaction was of first-order with respect to Fe(VI). If plotting the k_{obs} values as a function of initial ABTS concentration, a linear correlation with a zero intercept was observed (Fig. 2A, inset), indicating that the reaction was also of first-order with respect to ABTS. Thus, the formation rate of $\text{ABTS}^{\bullet+}$ can be expressed as Eq. (5). Interestingly, with the increase of initial DCF concentration, the concentration of $\text{ABTS}^{\bullet+}$ exhibited a firstly increasing and then decreasing trend after it reached the plateau (Fig. 2B). This trend was more obvious when the initial DCF concentration reached 0.5 mM. The concentration profiles of $\text{ABTS}^{\bullet+}$ with the presence of DCF indicated that Fe(VI) and ABTS take reaction firstly when the Fe(VI), ABTS and DCF coexisted. Then the formed $\text{ABTS}^{\bullet+}$ may oxidize the DCF, which promoted the degradation of DCF. Based on the results in Fig. 2B, the k_{app} values order between Fe(VI) and ABTS, $\text{ABTS}^{\bullet+}$ and DCF and Fe(VI) and DCF should follow: $k_{\text{app,Fe(VI)-ABTS}} > k_{\text{app,ABTS}^{\bullet+}\text{-DCF}} > k_{\text{app,Fe(VI)-DCF}}$, which needed a further verification.

$$\frac{d[\text{ABTS}^{\bullet+}]}{dt} = k_{\text{app,Fe(VI)-ABTS}}[\text{Fe(VI)}]_{\text{tot}}[\text{ABTS}]_{\text{tot}} \quad (5)$$

Fig. 3. Model fitting of the second-order reaction rate constant of ABTS with Fe(VI) as a function of solution pH. Experimental conditions: T = 25 °C.

where $k_{app,Fe(VI)-ABTS}$ is the apparent second-order rate constant for the reaction of ABTS with Fe(VI), $[Fe(VI)]_{tot}$ is the total concentration of four Fe(VI) species, and $[ABTS]_{tot}$ is the total concentration of two ABTS species.

Fig. S2 shows the measured k_{obs} of ABTS with Fe(VI) at pH 6.0–10.0 as a function of initial ABTS concentration. It was found that the formation rate of $ABTS^{*+}$ during the oxidation of ABTS by Fe(VI) exhibited an obvious pH dependence, which can be attributed to the species-specific reactivity between Fe(VI) and ABTS. The reactions between the two ABTS species and four Fe(VI) species (eight in total) can be summarized with Eq. (6).

$$\begin{aligned} d[ABTS^{*+}]_{tot}/dt &= k_{app,Fe(VI)-ABTS}[Fe(VI)]_{tot}[ABTS]_{tot} \\ &= \sum_{\substack{i=1,2,3,4 \\ j=1,2}} k_{ij}\alpha_i\beta_j[Fe(VI)]_{tot}[ABTS]_{tot} \end{aligned} \quad (6)$$

where $[Fe(VI)]_{tot} = [H_3FeO_4^+] + [H_2FeO_4] + [HFeO_4^-] + [FeO_4^{2-}]$, $[ABTS]_{tot} = [HABTS^+] + [ABTS]$, α_i and β_j are the molar fraction of Fe(VI) and ABTS, i and j are each of the four Fe(VI) species and two ABTS species, respectively, and k_{ij} is the species-specific second-order rate constant for the reaction between the Fe(VI) species i with the ABTS species j .

The kinetic model (Eq. (6)) could be further simplified based on the following facts: (1) the reaction related to FeO_4^{2-} could be neglected due to a much lower reactivity of FeO_4^{2-} than those of $HFeO_4^-$ and H_2FeO_4 [2]; and (2) only ABTS ($pK_{ABTS} = 1.5$), H_2FeO_4 and $HFeO_4^-$ species was considered which dominated the ABTS and Fe(VI) species at pH 6.0–10.0 [14]. Therefore, the reaction of ABTS with Fe(VI) occurred predominantly between the neutral (i.e., unprotonated) species of ABTS and $HFeO_4^-$ and H_2FeO_4 .

Fig. 3 shows the measured and model fitting of the k_{app} of ABTS with Fe(VI) as a function of solution pH. It was found that the modeled $k_{app,Fe(VI)-ABTS}$ could match the measured $k_{app,Fe(VI)-ABTS}$ value well. At pH 7.0, the $k_{app,Fe(VI)-ABTS}$ was determined to be $1.1 \times 10^6 M^{-1} s^{-1}$. Meanwhile, the $k_{app,Fe(VI)-ABTS}$ of Fe(VI) and ABTS decreased with increasing pH, which could be well explained by species-specific reactions between Fe(VI) species and ABTS. The species-specific k_{app} values of the reaction of H_2FeO_4 and $HFeO_4^-$ with ABTS were determined to be 1.75×10^6 and $1.67 \times 10^6 M^{-1} s^{-1}$, respectively via least-squares nonlinear regressions ($R^2 > 0.98$). The contribution of main species to the overall reaction rate at pH 6.0–10.0 could be modeled with these species-specific k_{app} values. Overall, the contribution of $HFeO_4^-$ outweighed H_2FeO_4 and FeO_4^{2-} during the oxidation of DCF by Fe(VI) at pH 6.0–10.0. Lee et al. [14] reported that the reaction

Fig. 4. Model fitting of the second-order reaction rate constants of DCF with Fe(VI) and DCF with $ABTS^{*+}$ as a function of solution pH. Experimental conditions: T = 25 °C.

of Fe(VI) with ABTS varied significantly with the increase of pH, consistent with the k_{app} values obtained in this study.

3.3. Kinetics comparison of $ABTS^{*+}$ and Fe(VI) during the oxidation of DCF

To compare the k_{app} differences between the oxidation of DCF by $ABTS^{*+}$ and Fe(VI), respectively, the degradation kinetics of DCF with $ABTS^{*+}$ and Fe(VI) were investigated individually. Both the concentration profiles of DCF in the oxidation of DCF by Fe(VI) and $ABTS^{*+}$, respectively followed pseudo-first-order kinetics at a given oxidant concentration and the value of k_{obs} increased linearly ($R^2 > 0.99$) with oxidant concentrations increased, indicating that both the reactions between DCF with Fe(VI), and DCF with $ABTS^{*+}$ were first-order with respect to each reactant. As anion DCF is the main species of DCF and H_2FeO_4 and $HFeO_4^-$ are the two main species of Fe(VI) at pH 6.0–10.0 [31,32], the k_{app} modeling of the oxidation of DCF by Fe(VI) could be simplified similar with the oxidation of ABTS by Fe(VI).

The measured and modeled values of k_{app} values for the reactions of Fe(VI) with DCF, and $ABTS^{*+}$ with DCF as a function of pH are presented in Fig. 4. At pH 7.0, the $k_{app,ABTS^{*+}-DCF}$ value was determined to be $2.8 \times 10^3 M^{-1} s^{-1}$, while the $k_{app,Fe(VI)-DCF}$ value was just $17.7 M^{-1} s^{-1}$. More importantly, the $k_{app,Fe(VI)-DCF}$ of the reaction also decreased significantly with increasing pH. The k_{app} values for the reaction of DCF with H_2FeO_4 and $HFeO_4^-$ were determined to be 19.0 and $5.7 M^{-1} s^{-1}$, respectively via least-squares nonlinear regressions ($R^2 > 0.99$). A similar pH-dependence of the k_{app} was reported during the chlorination of DCF, which was induced by the acid-catalyzed reaction between HOCl and DCF [33]. With the increase of pH, the decreased molar fractions of H_2FeO_4 and $HFeO_4^-$ and increased molar fraction of unreactive FeO_4^{2-} induced the significant decrease of $k_{app,Fe(VI)-DCF}$. The k_{app} values for the reaction of $ABTS^{*+}$ with DCF were calculated with the SFS results (e.g. pH 7.0 in Fig. S3). As the molar fractions of $ABTS^{*+}$ anion DCF kept almost unchanged at pH 6.0–10.0, the measured $k_{app,ABTS^{*+}-DCF}$ values kept stable (2809 – $2856 M^{-1} s^{-1}$) and the k_{app} value between $ABTS^{*+}$ and DCF^- was determined to be $2850 M^{-1} s^{-1}$. Thus, after the addition of ABTS during the oxidation of DCF by Fe(VI), $ABTS^{*+}$ was firstly formed due to the high $k_{app,Fe(VI)-ABTS}$ value. Then, DCF could be quickly oxidized by $ABTS^{*+}$ and Fe(V) with much higher rates than that for the reaction of Fe(VI) with DCF, which was followed by the regeneration of ABTS. Thus, ABTS promoted the oxidation of DCF by Fe(VI) via acting as an electron shuttle, which lost one electron firstly during the oxidation by Fe(VI), then got one electron from the DCF. Note that the formation of Fe(V) during the oxidation of ABTS may also contribute to the promoted degradation of DCF, which

Fig. 5. Effect of initial pH on the removal of DCF by Fe(VI) in the absence and presence of ABTS after 10 min. Experimental conditions: $[\text{Fe(VI)}]_0 = 0.15 \text{ mM}$, $[\text{DCF}]_0 = 0.03 \text{ mM}$, $[\text{ABTS}]_0 = 5 \mu\text{M}$ for with ABTS, $T = 25^\circ\text{C}$. Error bars represent the 95% confidence interval.

Fig. 6. Effect of natural organic matter (NOM) on the removal of DCF by Fe(VI) in the absence and presence of ABTS after 10 min. Experimental conditions: $[\text{Fe(VI)}]_0 = 0.15 \text{ mM}$, $[\text{DCF}]_0 = 0.03 \text{ mM}$, $[\text{ABTS}]_0 = 5 \mu\text{M}$ for with ABTS, pH 8.0, $T = 25^\circ\text{C}$. Error bars represent the 95% confidence interval.

is usually a more powerful oxidant than Fe(VI) [16]. However, as the instability of this intermediate Fe(V), the contribution of Fe(V) in the oxidation of DCF was not investigated in this study, which needed a further research in future.

3.4. Effect of water quality

The effect of water quality on the removal of DCF by Fe(VI) was investigated in the presence and absence of ABTS. Figs. 5 and 6 show the removal efficiencies of DCF at different pH (6.0–10.0) and different concentration of NOM (0–20 mg TOC L⁻¹). As shown in Fig. 5, the removal efficiency of DCF by Fe(VI) exhibited an obviously decreasing trend with the increase of pH. The removal efficiency of DCF at pH 7.0 after 10 min was 51.2%, which decreased to 22.2% at pH 9.0. This is reasonable as the $k_{\text{app,Fe(VI)-DCF}}$ decreased significantly with the increase of pH (Fig. 4). However, the removal efficiency of DCF kept stable (88.6–98.0%) with the addition of 5 μM ABTS under the tested pH range. As mentioned above, the effect of pH on $k_{\text{app,ABTS}^{*+}\text{-DCF}}$ was limited. Although the $k_{\text{app,Fe(VI)-ABTS}}$ value is pH-dependent (Fig. 3), the $k_{\text{app,Fe(VI)-ABTS}}$ could reach $2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9.0, which is 3 orders of magnitude higher than that of $k_{\text{app,Fe(VI)-DCF}}$. Therefore, with the addition of ABTS the high removal

Fig. 7. Effect of initial molar ratio of $[\text{ABTS}]_0/[\text{ABTS}^{*+}]_0$ on the ABTS^{*+} decay in the presence of DCF. Experimental conditions: $[\text{DCF}]_0 = 0.03 \text{ mM}$, $[\text{ABTS}^{*+}]_0 = 5 \mu\text{M}$, pH 8.0, $T = 25^\circ\text{C}$.

efficiency of DCF by Fe(VI) could be maintained even under alkaline circumstance.

Fig. 6 shows the effect of NOM concentration on the removal of DCF by Fe(VI). It was found that the presence of NOM decreased the removal efficiency of DCF by Fe(VI). When the NOM concentration reached 20 mg TOC L⁻¹, the removal efficiency of DCF at pH 8.0 decreased from 34.5% to 21.3% after 10 min. Yang and Ying [2] reported similar decreasing removal efficiencies of benzophenone-3 from 60% to 31% by Fe(VI) when the NOM concentration was 15 mg TOC L⁻¹, which was attributed to the competition and consumption for oxidant between DCF and NOM. Lee and von Gunten [34] proposed that the main competitor for the target pollutant during the oxidation of Fe(VI) derived from the electron-rich organic moieties present in NOM. With the addition of 5 μM ABTS, the removal efficiency of DCF could keep around 90% even when the NOM concentration reached 20 mg TOC L⁻¹. Overall, ABTS could enhance the oxidation of DCF by Fe(VI) over wide pH and NOM concentration ranges, indicating that the addition of ABTS could broaden the applicable water quality range of Fe(VI).

3.5. Environmental implications

As mentioned before, Lee et al. [35] proposed the use the oxidation of ABTS by Fe(VI) as a quantitative method to determine aqueous Fe(VI) concentration. This study found that the addition of ABTS to Fe(VI) could accelerate the oxidation of DCF by Fe(VI) at pH 6.0–10.0. Is it inappropriate to use this ABTS^{*+} -based method for the quantitative analysis of Fe(VI) concentration again? Scott et al. reported the electron-exchange rate constant of inner-electron-exchange process between ABTS^{*+} and ABTS was around $4.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in neutral water [20]. Hence, the presence of excessive ABTS may inhibit the reaction of ABTS^{*+} with DCF. To verify this assumption, the effect of initial molar ratio of $[\text{ABTS}]_0/[\text{ABTS}^{*+}]_0$ on the decay of ABTS^{*+} was investigated by SFS with different molar ratios (i.e., 0, 1, 5 and 10). As shown in Fig. 7, the decay rate of ABTS^{*+} was effectively inhibited with the increase of $[\text{ABTS}]_0/[\text{ABTS}^{*+}]_0$. When the initial $[\text{ABTS}]_0/[\text{ABTS}^{*+}]_0$ reached 10, no obvious decay of ABTS^{*+} with the presence of DCF was observed. This result indicated that the ABTS^{*+} -based quantitative method proposed by Lee et al. [6] still could be used to analyze the aqueous Fe(VI) concentration. However, an excessive initial dose of ABTS ($[\text{ABTS}]/[\text{Fe(VI)}] > 10$) is necessary to prevent the potential reactions of formed ABTS^{*+} with compounds in the solution. On the other hand, NOM ubiquitously exists in soils and waters, which can act as redox mediators involved in various chem-

ical and biochemical processes. Manoli et al. [16] reported that the low-molecular-weight organic acid could accelerate the oxidation of micropollutant by Fe(VI) oxidation, which was mainly ascribed to its roles as the reductant and complexing simultaneously. The oxygen-containing functional groups in NOM may also promote Fe(VI) oxidation of micropollutant via a catalytic mechanism involving pair (NOM and NOM_{oxi}) analogous to the pairing of ABTS and $\text{ABTS}^{\bullet+}$. This study provides new insights to reconsider the role of NOM during the Fe(VI) oxidation and highlights the potential for increasing the reactivity of Fe(VI).

4. Conclusions

This study investigated the promoted effect of ABTS on DCF degradation by Fe(VI). Based on the experimental results, the following conclusions can be drawn:

- The addition of ABTS to Fe(VI) could accelerate the oxidation of DCF by Fe(VI) at pH 6.0–10.0. The $k_{\text{app,Fe(VI)-ABTS}}$ for oxidation of ABTS by Fe(VI) at pH 7.0 was determined to be $1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, which were 3–5 orders of magnitude higher than those for the reactions of $\text{ABTS}^{\bullet+}$ with DCF ($k_{\text{app,ABTS}^{\bullet+}\text{-DCF}} = 2.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) and Fe(VI) with DCF ($k_{\text{app,Fe(VI)-DCF}} = 17.7 \text{ M}^{-1} \text{ s}^{-1}$).
- The $k_{\text{app,Fe(VI)-DCF}}$ decreased significantly with increasing pH, while the $k_{\text{app,ABTS}^{\bullet+}\text{-DCF}}$ exhibited little pH dependency.
- ABTS could enhance the removal of DCF by Fe(VI) over wide pH and NOM concentration ranges.
- The reaction of $\text{ABTS}^{\bullet+}$ with DCF could be inhibited with initial $[\text{ABTS}]_0/[\text{ABTS}^{\bullet+}]_0 \geq 10$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2017.04.056>.

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