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

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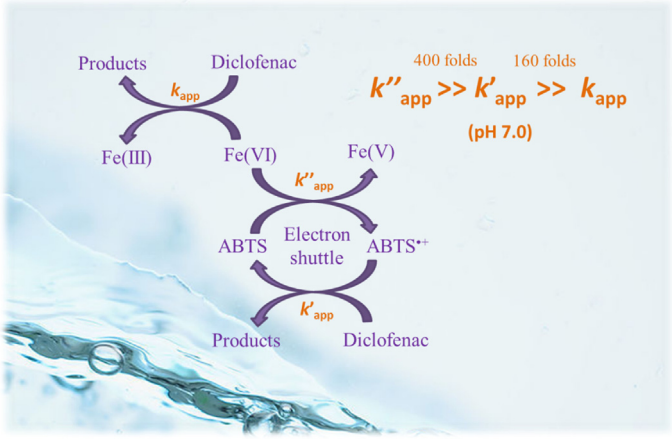
HIGHLIGHTS

- Addition of ABTS could accelerate the DCF degradation by Fe(VI).
- Formation of $ABTS^{\bullet+}$ 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 $ABTS^{\bullet+}$ 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 μM ABTS was found to be 36.2 folds of that without ABTS, with values of 3.08 and 0.085 min^{-1}, respectively. It was partly attributed to the formation of $ABTS^{\bullet+}$. The apparent second-order rate constant (k_{app}) for the oxidation of ABTS by Fe(VI) at pH 7.0 was determined to be $1.1 \times 10^6\ M^{-1}\ s^{-1}$, which was 3–5 orders of magnitude higher than those for the reactions of $ABTS^{\bullet+}$ with DCF ($k_{app,ABTS^{\bullet+}\text{-}DCF} = 2.8 \times 10^3\ M^{-1}\ s^{-1}$) and Fe(VI) with DCF ($k_{app,Fe(VI)\text{-}DCF} = 17.7\ M^{-1}\ s^{-1}$). Both the $k_{app,Fe(VI)\text{-}ABTS}$ and $k_{app,Fe(VI)\text{-}DCF}$ decreased obviously with increasing pH, while the $k_{app,ABTS^{\bullet+}\text{-}DCF}$ 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).

$$H_3FeO_4^+ \rightarrow H_2FeO_4 + H^+ \; pK_1 = 1.5 \quad (1)$$

$$H_2FeO_4 \rightarrow HFeO_4^- + H^+ \; pK_2 = 3.5 \quad (2)$$

$$HFeO_4^- \rightarrow FeO_4^{2-} + H^+ \; pK_3 = 7.2 \quad (3)$$

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 $ABTS^{\bullet+}$ formation. Various inorganic radicals (e.g., $HO^{\bullet}$, $Br_2^{\bullet-}$), 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 $ABTS^{\bullet+}$ [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)

$$Fe(VI) + ABTS \rightarrow Fe(V) + ABTS^{\circ+} \quad (4)$$

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 $ABTS^{\bullet+}$ 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, K_2FeO_4 (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 ($Na_2S_2O_3$, $K_2S_2O_8$, NaOH, H_2SO_4, $Na_2B_4O_7$ and Na_2HPO_4) 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 Na_2HPO_4/1 mM borate). The concentration of Fe(VI) stock solution was determined by measuring Fe(VI) absorbance at 510 nm (ε_{510nm} = 1150 M^{-1} 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 $Na_2S_2O_3$ 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 datas 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 $ABTS^{\bullet+}$) solutions were simultaneously injected into the optical cell of the SFS. The two automatic syringes of SFS were driven by compressed N_2. 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 $ABTS^{\bullet+}$ with DCF, $ABTS^{\bullet+}$ stock solution was prepared by incubating 2 mL $K_2S_2O_8$ (10 mM) with 2 mL ABTS (20 mM) at 25 °C for 12 h as described by Re et al. [28]. The formed $ABTS^{\bullet+}$ was quantitatively determined at 415 nm (ε_{415nm} = 34000 M^{-1} cm^{-1}). The apparent second-order rate con-