

Removal of Personal Care Products Through Ferrate(VI) Oxidation Treatment

Bin Yang and Guang-Guo Ying

Abstract Personal care products (PCPs) have been widely used in daily life and continually introduced to the aquatic environment, posing potential risks to the aquatic ecosystem and human health. Due to incomplete removal of PCPs in traditional wastewater and water treatment systems, advanced oxidation technologies can be applied to increase the removal efficiency of those PCPs. As a powerful oxidant, ferrate(VI) (Fe(VI)) has a great potential for removal of PCPs during water treatment. In this chapter, we firstly introduced the aqueous chemistry of Fe(VI); then critically reviewed the reaction mechanisms of Fe(VI) with typical PCPs by using removal rates, reaction kinetics, linear free-energy relationships, products identification, and toxicity evaluation; and finally discussed the removal of PCPs during water treatment by Fe(VI). Published phenolic and nitrogen-containing PCPs can be completely removed by Fe(VI) oxidation treatment except triclocarban. The reactions between the PCPs and Fe(VI) follows second-order reaction kinetics with the apparent second-order rate constants (k_{app}) ranging from 7 to 1,111 $M^{-1} s^{-1}$ at pH 7.0. The reactivity of Fe(VI) species with the PCPs has the following decreasing order of $H_2FeO_4 > HFeO_4^- > FeO_4^{2-}$, through the electrophilic oxidation mechanism. The phenolic PCPs can be transformed by Fe(VI) oxidation based on phenoxyl radical reaction, degradation, and coupling reaction. More importantly, the oxidation of each phenolic PCPs by Fe(VI) leads to the loss of its corresponding toxicity. The coexisting constituents present in source water have significant effects on PCP removal during Fe(VI) oxidation treatment. In practical applications, in situ production of Fe(VI) solution appears to be a promising technology for removal of PCPs during pilot and full-scale water treatment.

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Abbreviations

5CBT	5-Chloro-1H-benzotriazole
5MBT	5-Methyl-1H-benzotriazole
ABTS	2,2'-Azinobis-(3-ethylbenzothiazoline-6-sulfonate)
AHTN	7-Acetyl-1,1,3,4,4,6-hexamethyl-tetralin
BP-3	Benzophenone-3
BT	1H-benzotriazole
BTs	Benzotriazoles
DMBT	5,6-Dimethyl-1H-benzotriazole hydrate
DOC	Dissolved organic carbon
Fe(III)	Ferric hydroxide
Fe(V)	Ferrate(V)
Fe(VI)	Ferrate(VI)
GC-MS	Gas chromatography-mass spectrometry
HA	Humic acid
HBT	1-Hydroxybenzotriazole
HHCB	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- γ -2-benzopyrane
I ⁻	Iodide
k_{app}	Apparent second-order rate constants
PCPs	Personal care products
pK_a	Acid dissociation constants
RRLC-MS/MS	Rapid resolution liquid chromatography-tandem mass spectrometry
$t_{1/2}$	Half-life
TCC	Triclocarban
TCS	Triclosan

1 Introduction

Personal care products (PCPs), including moisturizers, lipsticks, and fragrances to sunscreens, soaps, and anticavity toothpastes, make billions of people around the world to live a better and healthier lifestyle. These products are commonly used in large quantities, and after use, they are discharged directly or indirectly into receiving aquatic environments. Due to limited capacity for removal of these chemicals, environmental contamination by these chemicals has been reported [1–3]. Some of them were found to be environmentally persistent, bioactive, and bioaccumulative [4]. Moreover, some chemicals exhibited endocrine disruptive effects *in vitro* and *in vivo* and they have the potential to interfere with natural hormones, causing problems in the nervous and reproductive systems [5]. PCPs have received an increasing attention in recent years and they have been regarded as emerging contaminants. Therefore, it is necessary to remove PCPs from traditional water treatment effluents by using advanced oxidation technology.

Ferrate(VI) (Fe(VI)) is a powerful oxidant and its decomposition product is nontoxic ferric hydroxide (Fe(III)). Thus, Fe(VI) is regarded as an environmentally friendly oxidant in water treatment process [6–8]. Fe(VI) has been widely used to remove emerging organic contaminants [9–12], heavy metals [13, 14], and pathogens [15–18] during water treatment processes. Fe(VI) selectively reacts with electron-rich organic moieties of emerging organic contaminants, such as phenols, anilines, amines, and olefins through electrophilic oxidation mechanism [9, 10, 12, 19, 20]. The corresponding apparent second-order reaction rate constants range from >1 to $10^5 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solution [9, 12]. Besides, the coexisting constituents present in source water are also responsible for a rapid Fe(VI) consumption, which determine its ability to remove emerging organic contaminants.

This chapter aims to firstly introduce the aqueous chemistry of Fe(VI), then assess the potential for removal of typical PCPs during Fe(VI) treatment by chemical reaction kinetics, propose the reaction pathway of phenolic PCPs by Fe(VI) oxidation based on products identification, evaluate the safety of above treatment processes by toxicity tests, and finally clarify the impact of coexisting constituents in the source water on the removal processes. This chapter will provide a scientific basis for the removal of PCPs through ferrate(VI) oxidation treatment.

2 Aqueous Chemistry of Fe(VI)

Ferrate(VI) (K_2FeO_4 , Fe(VI)) is a black-purple crystalline compound in which iron is in the +6 oxidation state. There are three main approaches for preparation of Fe(VI): wet oxidation, dry thermal, and electrochemical synthesis [6–8]. The concentration of Fe(VI) in aqueous solution can be determined by volumetric (chromite and arsenite), electrochemical (cyclic voltammetry and potentiometry), as well as

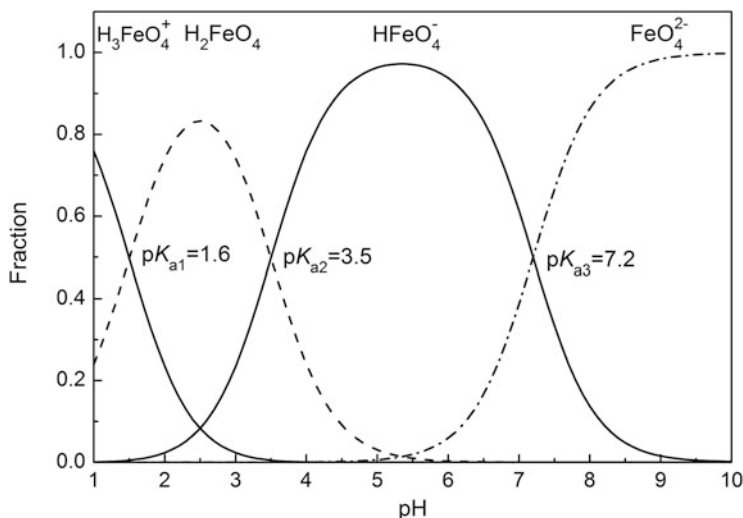


Fig. 1 Speciation of Fe(VI) in aqueous solution

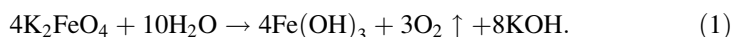
spectrophotometric methods (FTIR, Mössbauer, UV-vis (direct 510 nm, iodide (I^-); 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS)), and fluorescence) [21]. For water treatment research, direct 510 nm ($\epsilon_{510\text{nm}} = 1,150 \text{ M}^{-1} \text{ cm}^{-1}$) and ABTS methods ($\epsilon_{415\text{nm}} = 34,000 \text{ M}^{-1} \text{ cm}^{-1}$) are the most suitable techniques for studying the reaction kinetics of Fe(VI) in aqueous solution [22–25]. Besides, phosphate buffer has been widely used as the reaction solution since not only it reacts very slowly with Fe(VI) but also it can prevent the precipitation of generated ferric ion from Fe(VI) decomposition which causes interference for optical monitoring of Fe(VI) concentration [8].

The rates of decay and changes in spectral features of Fe(VI) solution as a function of pH can be utilized to estimate the values of the acid dissociation constants (pK_a) [26]. Three pK_a values of Fe(VI) in aqueous solution of 1.6, 3.5, and 7.2 suggest the presence of four Fe(VI) species in the entire pH range, such as $H_3FeO_4^+$, H_2FeO_4 , $HFeO_4^-$, and FeO_4^{2-} (Fig. 1). Therefore, $HFeO_4^-$ and FeO_4^{2-} are the predominant species in neutral and alkaline pH solution. Fe(VI) ion (FeO_4^{2-}) has tetrahedral structure, with four equivalent oxygen atoms covalently bonded to central iron atom [27].

Fe(VI) is the most powerful oxidant at acidic pH condition with the redox potential of 2.20 V (Table 1), but it becomes a relatively mild oxidant (0.57 V) at alkaline pH condition [6, 8, 20]. Due to its strong oxidizing property, Fe(VI) undergoes a rapid decomposition according to Eq. (1) in the presence of water, leading to the formation of molecular oxygen and a nontoxic by-product ferric hydroxide (Fe(III)), which makes Fe(VI) an environmentally friendly oxidant for water treatment. Additionally, the generated Fe(III) can act as an effective coagulant/precipitant during water treatment:

Table 1 Redox potential for the oxidants used in water treatment

Disinfectant/oxidant	Reaction	E ⁰ (V)
Ferrate(VI)	$\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O}$	2.20
	$\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_3 + 5\text{OH}^-$	0.70
Chlorine	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	1.36
	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{OH}^-$	0.84
Hypochlorite	$\text{HClO} + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}^- + \text{H}_2\text{O}$	1.48
	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{OH}^-$	0.84
Chlorine dioxide	$\text{ClO}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{ClO}_2^-$	0.95
Perchlorate	$\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons \text{Cl}^- + 4\text{H}_2\text{O}$	1.39
Ozone	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$	2.08
	$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{O}_2 + 2\text{OH}^-$	1.24
Hydrogen peroxide	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1.78
	$\text{H}_2\text{O}_2 + 2\text{e}^- \rightleftharpoons 2\text{OH}^-$	0.88
Dissolved oxygen	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1.23
Permanganate	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	0.59



The decomposition of Fe(VI) in Eq. (1) is strongly dependent on the pH values of reaction solution, initial Fe(VI) concentration, temperature, and coexisting ions. The decomposition of Fe(VI) in solution follows the second-order kinetics with respect to its concentration. The decomposition rate of Fe(VI) dramatically decreases with the increasing pH, ranging from $10^5 \text{ M}^{-1} \text{ s}^{-1}$ (pH 1) to $<1 \text{ M}^{-1} \text{ s}^{-1}$ (pH 8.2), indicating Fe(VI) has higher oxidation power at acidic pH conditions [8, 13]. The lowest rate of Fe(VI) decomposition occurs at pH 9.4–9.7. Besides, diluted Fe(VI) solutions are reported to be more stable than the concentrated ones. Increasing temperature would decrease the concentration of Fe(VI) in solution. The addition of KCl or KNO_3 as an impurity in solution accelerated the initial decomposition of the Fe(VI) but had the effect of stabilizing a small quantity of Fe(VI). NaCl and FeOOH as impurities caused complete decomposition of Fe(VI) in solution at a rapid rate [28].

3 Oxidation of Personal Care Products by Ferrate(VI)

3.1 Removal Rates

Removal of some PCPs by Fe(VI) has been investigated in the laboratory [29–31]. Figure 2 demonstrates the removal of eight typical PCPs by Fe(VI) oxidation individually under different molar ratios in buffered Milli-Q water at pH 7.0 or

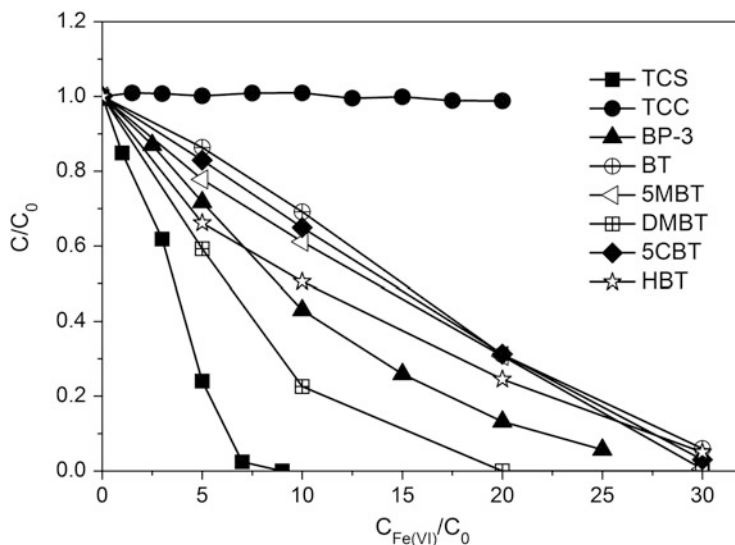


Fig. 2 Removal of typical PCPs by Fe(VI) oxidation in 10 mM phosphate buffer solution. Experimental conditions: $[TCS/TCC]_0 = 2 \mu\text{M}$, $[BP-3]_0 = 1 \mu\text{M}$, $[BTs]_0 = 10 \mu\text{M}$, $V = 25 \text{ mL}$, $T = 24 \pm 1^\circ\text{C}$, and contact time 3 h. The reaction of TCS and TCC was performed in pH 7.0 solution, and BP-3 and BTs in pH 8.0 solution

8.0 and $24 \pm 1^\circ\text{C}$. The eight studied PCPs include antimicrobial triclosan (TCS) and triclocarban (TCC), UV filter benzophenone-3 (BP-3), and anticorrosion agents benzotriazoles (BTs; BT, 1H-benzotriazole; 5MBT, 5-methyl-1H-benzotriazole; DMBT, 5,6-dimethyl-1H-benzotriazole hydrate; 5CBT, 5-chloro-1H-benzotriazole; HBT, 1-hydroxybenzotriazole). With the dosage of Fe(VI) increasing, the concentration of each PCPs gradually decreased. However, TCC did not react with Fe(VI) at pH 7.0. When the molar ratio of Fe(VI) with PCPs increasing up to 30:1, the removal rate of each PCPs reached about >95% except TCC. Besides, the dosed amounts of Fe(VI) for complete removal of PCPs had the following increasing order: $TCS < BP-3 < BTs \ll TCC$, which illustrates the easier oxidation of TCS and BP-3 molecules than BTs and TCC by Fe(VI). Thus, the selected phenolic PCPs have higher reactivity with Fe(VI) than those nitrogen-containing PCPs.

Since Fe(VI) has been known to react with electron-rich organic moieties, such as phenols, anilines, amines, olefins, and organosulfur [9, 10, 12, 20], the reactivity of other categories of PCPs with Fe(VI) can be tentatively deduced as follows. Preservatives p-hydroxybenzoic esters (parabens) with the phenol moieties may be easily removed by Fe(VI) oxidation, but synthetic polycyclic musks (AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-tetralin) and HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- γ -2-benzopyrane)) may not react with Fe(VI). The detailed removal of above PCPs by Fe(VI) oxidation still needs to be further confirmed.

3.2 Reaction Kinetics

Second-order reaction rate equation (Eq. (2)) is commonly used to describe the Fe (VI) oxidation of PCPs in phosphate buffer solutions. Kinetic experiments are conducted under pseudo-first-order conditions with either Fe(VI) or the PCPs in excess. For those with Fe(VI) in excess to PCPs, the decrease in concentrations for Fe(VI) and PCPs is measured as a function of the reaction time. The apparent second-order rate constants (k_{app}) are calculated by plotting the natural logarithm of the PCP concentrations with the Fe(VI) exposure (Fe(VI) concentration integrated over time, $\int_0^t [\text{Fe(VI)}] dt$), as shown in Eq. (3). For those with PCPs in excess to Fe (VI), Eq. (2) can be rewritten as Eq. (4). The values of k_{app} are then determined from the variation in k' as a function of PCP concentrations. The obtained values of rate constants k_{app} for the reaction of Fe(VI) with PCPs as a function of pH (6.0–10.0) are presented in Fig. 3 and Table 2 [29–31]. The determined k_{app} values range from $7 \text{ M}^{-1} \text{ s}^{-1}$ (5CBT) to $1,111 \text{ M}^{-1} \text{ s}^{-1}$ (TCS) at pH 7.0 and $24 \pm 1^\circ \text{C}$ with the half-life ($t_{1/2}$) ranging from 1,917 s to 12 s at a Fe(VI) concentration of 10 mg L^{-1} . The k_{app} values of TCS and BP-3 reaction with Fe(VI) are greater than those of BTs, which is consistent with the results of removal rates. Besides, the k_{app} of the reaction decreased with increasing pH values (Fig. 3). These pH-dependent variations in k_{app} could be explained by species-specific reactions between Fe (VI) species ($\text{HFeO}_4^- \Leftrightarrow \text{H}^+ + \text{FeO}_4^{2-}$, $\text{p}K_{a,\text{HFeO}_4} = 7.23$ [26]), and acid–base species of an ionizable PCP species ($\text{PCPs} \Leftrightarrow \text{H}^+ + \text{PCPs}^-$, $\text{p}K_{a,\text{PCPs}}$) by Eqs. (5)–(11):

$$-d[\text{PCPs}]/dt = k_{app}[\text{Fe(VI)}][\text{PCPs}], \quad (2)$$

$$\ln([\text{PCPs}]/[\text{PCPs}]_0) = -k_{app} \int_0^t [\text{Fe(VI)}] dt, \quad (3)$$

$$-d[\text{Fe(VI)}]/dt = k'[\text{Fe(VI)}] \quad \text{where} \quad k' = k_{app}[\text{PCPs}], \quad (4)$$

$$k_{app}[\text{Fe(VI)}]_{\text{tot}}[\text{PCPs}]_{\text{tot}} = \sum_{\substack{i=1,2,3 \\ j=1,2}} k_{ij} \alpha_i \beta_j [\text{Fe(VI)}]_{\text{tot}} [\text{PCPs}]_{\text{tot}}, \quad (5)$$

$$\alpha_1 = [\text{H}_2\text{FeO}_4]/[\text{Fe(VI)}]_{\text{tot}} = [\text{H}^+]^2/T, \quad (6)$$

$$\alpha_2 = [\text{HFeO}_4^-]/[\text{Fe(VI)}]_{\text{tot}} = [\text{H}^+]K_{a,\text{H}_2\text{FeO}_4}/T, \quad (7)$$

$$\alpha_3 = [\text{FeO}_4^{2-}]/[\text{Fe(VI)}]_{\text{tot}} = K_{a,\text{H}_2\text{FeO}_4}K_{a,\text{HFeO}_4^-}/T, \quad (8)$$

$$T = [\text{H}^+]^2 + [\text{H}^+]K_{a,\text{H}_2\text{FeO}_4} + K_{a,\text{H}_2\text{FeO}_4}K_{a,\text{HFeO}_4^-}, \quad (9)$$

$$\beta_1 = [\text{PCPs}]/[\text{PCPs}]_{\text{tot}} = [\text{H}^+]/([\text{H}^+] + K_{a,\text{PCPs}}), \quad (10)$$

$$\beta_2 = [\text{PCPs}^-]/[\text{PCPs}]_{\text{tot}} = K_{a,\text{PCPs}}/([\text{H}^+] + K_{a,\text{PCPs}}), \quad (11)$$

where $[\text{Fe(VI)}]_{\text{tot}} = [\text{H}_2\text{FeO}_4] + [\text{HFeO}_4^-] + [\text{FeO}_4^{2-}]$, $[\text{PCPs}]_{\text{tot}} = [\text{PCPs}] + [\text{PCPs}^-]$. α_i and β_j represent the respective species distribution coefficients for

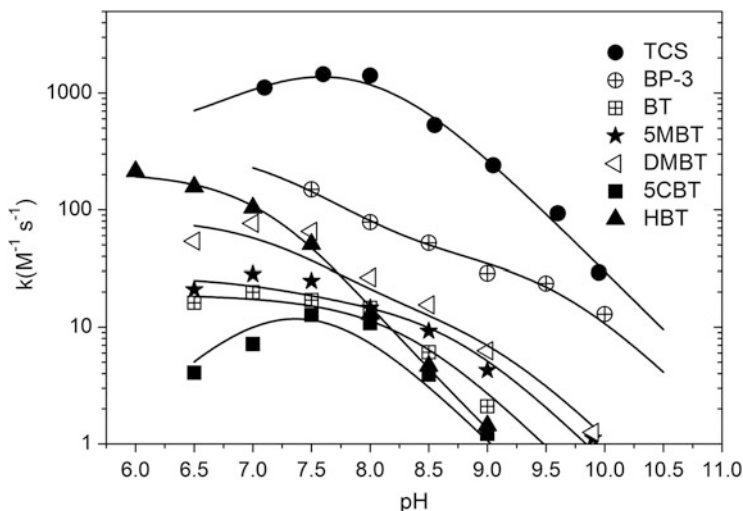


Fig. 3 Apparent second-order rate constants and associated model simulation for the reactions of PCPs with Fe(VI) as a function of pH (6.0–10.0) at the room temperature ($24 \pm 1^\circ\text{C}$)

Fe(VI) and PCPs; i and j represent each of the three Fe(VI) species and PCP species, respectively; and k_{ij} represents the species-specific second-order rate constant for the reaction between the Fe(VI) species i with the PCP species j . Consequently, the k_{ij} is calculated from least-squares nonlinear regressions of the experimental k_{app} data by using SigmaPlot 10.0 (Systat Software Inc.). Table 2 summarizes the determined k_{12} , k_{21} , and k_{22} values for each PCPs. The k_{22} was magnitude higher than k_{21} because the deprotonated species are better electron donors. Thus, the reaction between HFeO_4^- and the dissociated PCPs controls the overall reaction of Fe(VI) with PCPs. Besides, the k_{12} is 10^4 times higher than k_{22} for HBT, which indicates H_2FeO_4 has a higher reactivity than HFeO_4^- . However, reactions of the deprotonated Fe(VI) species (FeO_4^{2-}) with PCP species have a low contribution to the overall reactivity. Moreover, density functional theory (DFT) calculations have shown that the protonated species of Fe(VI) has a larger spin density on the oxo ligands than the deprotonated species of Fe(VI), which increases the oxidation ability of protonated Fe(VI) [32]. Above results demonstrate that the order of oxidizing power of Fe(VI) species for PCPs in aqueous solution is following $\text{H}_2\text{FeO}_4 > \text{HFeO}_4^- > \text{FeO}_4^{2-}$.

3.3 Linear Free-Energy Relationships

Linear free-energy relationships have been widely used in oxidation/disinfection reaction for the understanding of the reaction mechanisms and prediction of reaction rates [12, 22, 23, 25, 33, 34]. The Hammett-type correlations between

Table 2 Species-specific second-order rate constants for the reactions of Fe(VI) with selected PCPs

Chemical name	pK_a	$H_2FeO_4 + X^-$ (k_{12} , $M^{-1} s^{-1}$)	$HFeO_4^- + XH$ (k_{21} , $M^{-1} s^{-1}$)	$HFeO_4^- + X^-$ (k_{22} , $M^{-1} s^{-1}$)	k_{app} at pH 7.0 ($M^{-1} s^{-1}$)	$t_{1/2}$ (s) ^a
Triclosan (TCS)	8.1		$4.1 (\pm 3.5) \times 10^2$	$1.8 (\pm 0.1) \times 10^4$	1,111	12
Benzophenone-3 (BP-3)	9.57		$3.4 (\pm 0.5) \times 10^2$	$8.5 (\pm 0.7) \times 10^3$	228	60
1H-benzotriazole (BT)	8.37		$1.9 (\pm 0.4) \times 10^1$	$1.9 (\pm 0.2) \times 10^2$	20	690
5-Methyl-1H-benzotriazole (5MBT)	8.5		$2.7 (\pm 0.5) \times 10^1$	$4.3 (\pm 0.5) \times 10^2$	28	486
5,6-Dimethyl-1H-benzotriazole (DMBT)	8.98		$8.5 (\pm 1.7) \times 10^1$	$7.3 (\pm 1.4) \times 10^2$	77	180
5-Chloro-1H-benzotriazole (5CBT)	7.5		$2.0 (\pm 0.2) \times 10^0$	$6.6 (\pm 0.6) \times 10^1$	7	1917
1-Hydroxybenzotriazole (HBT)	7.39	$1.6 (\pm 0.1) \times 10^6$		$7.7 (\pm 0.6) \times 10^1$	104	132

^aEstimated by assuming pseudo-first-order conditions with a Fe(VI) excess ($[Fe(VI)] = 10 \text{ mg L}^{-1}$, pH 7.0)

the k_{ij} of the above PCP reaction with Fe(VI) and free-energy descriptors (σ_p^+ or σ_p) have been successfully established according to the relationship $\log(k_{ij}) = y_0 + \rho\sigma$ as shown in Eqs. (12)–(15) [30]. A negative Hammett slope (ρ) illustrated the electrophilic oxidation mechanism for Fe(VI) reaction with PCPs. The Hammett-type relationships of substituted phenols for TCS (Eqs. (12) and (13)) verify the dependence of TCS and Fe(VI) reaction kinetics on phenol substituent effects, illustrating the Fe(VI) reacts initially with TCS by electrophilic attack at the latter's phenol moiety. Similarly, 1,2,3-triazole moiety of BT can be initially electrophilic attacked by Fe(VI) (Eqs. (14) and (15)), but the initial attack site of HBT may be at the N–OH bond by Fe(VI).

Substituted phenols for TCS:

$$\log(k_{21}) = 2.30(\pm 0.08) - 2.20(\pm 0.26)\sigma_p^+ \quad R^2 = 0.91, n = 8, \quad (12)$$

$$\log(k_{22}) = 4.42(\pm 0.04) - 3.13(\pm 0.13)\sigma_p^+ \quad R^2 = 0.99, n = 8. \quad (13)$$

BTs:

$$\log(k_{21}) = 1.00(\pm 0.08) - 2.86(\pm 0.38)\sigma_p \quad R^2 = 0.95, n = 4, \quad (14)$$

$$\log(k_{22}) = 2.27(\pm 0.02) - 1.94(\pm 0.10)\sigma_p \quad R^2 = 0.99, n = 4. \quad (15)$$

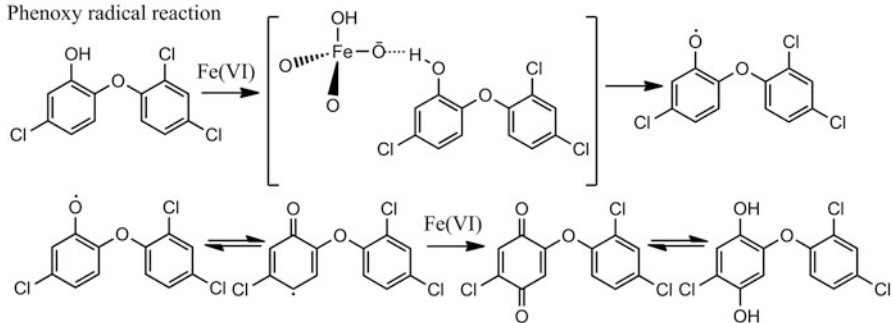
3.4 Products Identification

During Fe(VI) oxidation treatment, numerous transformation products may be formed and persist even after the parent compound has been fully removed [35–39]. Thus, the oxidation products of some PCPs (i.e., TCS, BP-3, and BTs) reaction with Fe(VI) were tentatively identified by gas chromatography–mass spectrometry (GC–MS) and rapid resolution liquid chromatography–tandem mass spectrometry (RRLC–MS/MS) techniques [29–31]. For the reaction between Fe(VI) and TCS, four products of chlorophenol, 2-chlorobenzoquinone, 2,4-dichlorophenol, and 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol were identified in the reaction solution by GC–MS and RRLC–MS/MS. In addition, the dimerization of some TCS degradation products, such as 5-chloro-3-(chlorohydroquinone)phenol, 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol, and 3-chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy)phenol, was also identified by RRLC–MS/MS. But, only two reaction products of 4-methoxybenzophenone and 4-methoxybenzoyl cation were found during Fe(VI) degradation of BP-3. However, no obvious transformation products were found in the Fe(VI) reaction with BTs.

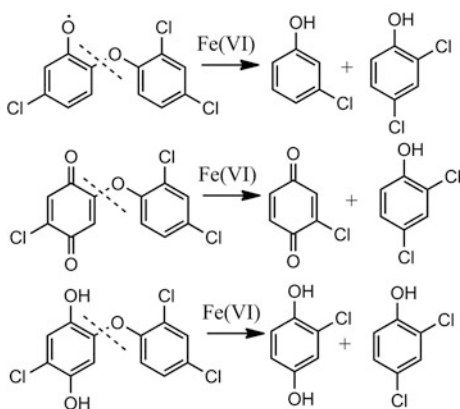
According to the kinetic information, products identification, and the mechanism of Fe(VI) reaction with phenols [36, 40, 41], a plausible reaction scheme for Fe(VI) oxidation of phenolic PCPs (TCS and BP-3) is proposed in Fig. 4. Initially, the reaction mixture of Fe(VI) with phenol moiety of TCS and BP-3 may proceed through an associative type of mechanism and involve hydrogen bond formation in the activated complex accompanied by intermolecular electron transfer. Consequently,

Triclosan (TCS):

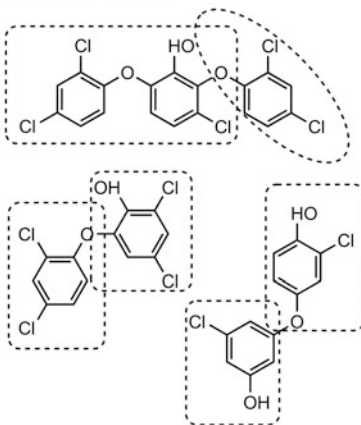
Phenoxy radical reaction



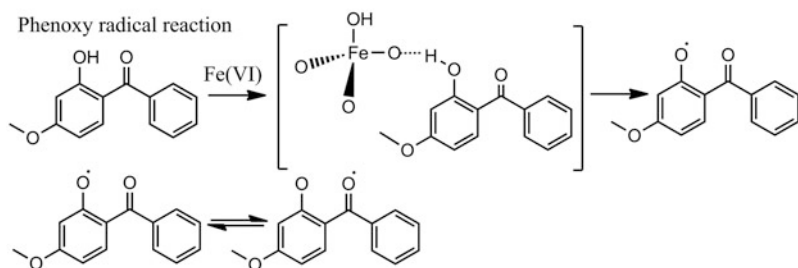
Degradation reaction



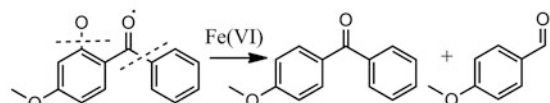
Coupling reaction

**Benzophenone-3 (BP-3):**

Phenoxy radical reaction



Degradation reaction

**Fig. 4** Proposed reaction schemes for oxidation of TCS and BP-3 by Fe(VI)

Fe(VI) oxidizes the phenol moiety by one electron transfer generating corresponding phenoxyl radical and Fe(V) as the first step. For TCS, the phenoxyl radical transferred to the para-position of TCS molecule and reacts with ferrates (Fe(VI) and Fe(V)) generating 2-chloro-5-(2,4-dichlorodichlorophenoxy)-[1,4] benzoquinone through two-electron oxidation. It can be converted into 2-chloro-5-(2,4-dichlorophenoxy) benzene-1,4-diol. Fe(VI) then goes on to break C–O bond leading to the formation of chlorophenol, 2,4-dichlorophenol, chlorocatechol, and 2-chlorobenzoquinone. Coupling reaction may also occur during Fe(VI) oxidation of TCS. This is especially likely given the large excess of phenol in the reaction mixture. Phenoxyl radical of 2,4-dichlorophenol reacted with another triclosan and 2,4-dichlorophenol forming products 3-chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy) and 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol. Phenoxyl radical of 2-chlorocatechol and m-chlorophenol produced 5-chloro-3-(chlorohydroquinone)phenol. For BP-3, the activated electron in phenoxyl radical could be transferred to the oxygen atom of phenyl methanone moiety. Ferrates (Fe(VI) or Fe(V)) then break C–O bond of phenol or eliminate benzene of BP-3 leading to the formation of 4-methoxybenzophenone and 4-methoxybenzoyl cation. But, coupling reaction of BP-3 products has not been found in the reaction solutions. Overall, transformation products could undergo further oxidation reactions with Fe(VI), yielding low molecular weight organic products.

3.5 Toxicity Evaluation

The Fe(VI) oxidation process will undoubtedly render the transformation products a different biological binding property [35, 37, 42]. For example, the antibacterial activity of the TCS molecule is derived primarily from its phenol ring, via van der Waals and hydrogen-bonding interactions with the bacterial enoyl–acyl carrier protein reductase enzyme [43]. Thus, oxidation of the TCS molecule by Fe(VI) leads to the breakage of C–O bond or phenol ring changing, which is considered to reduce or eliminate its toxicity. Using algae growth inhibition tests of TCS and its products to *Pseudokirchneriella subcapitata*, Yang et al. [29] demonstrated that the dose–response relationships of the Fe(VI) treated TCS samples and TCS standards are almost the same, indicating that the generated oxidation products of TCS did not exhibit any appreciable degree of inhibitory effect, only relative to TCS itself. Moreover, the Fe(VI) dosage used in this study did not appear to inhibit green algae growth, which reconfirms previous assumption that Fe(VI) can be an “environmentally friendly” oxidant for water treatment applications.

Similarly, the UV filter of BP-3 is an important representative hydroxylated benzophenone derivative which has potential endocrine-disrupting effects such as estrogenic and antiandrogenic activities [44–46]. However, the oxidation product of 4-methoxybenzophenone has been manifested to possess no estrogenic activity [47]. Thus, Fe(VI) oxidation treatment not only removes hydroxylated benzophenone derivatives in water but also produces by-products that are expected to have less endocrine-disrupting effects.

4 Removal of Personal Care Products During Water Treatment with Ferrate(VI)

4.1 Influence of Coexisting Constituents on PCP Removal

PCPs containing the electron-rich organic moieties mentioned above can be potentially removed during water treatment by Fe(VI) oxidation. Moreover, the coexisting constituents present in source water are also responsible for a rapid Fe(VI) consumption, which determine its ability to remove PCPs. The influence of coexisting constituents such as dissolved organic matter (humic acid (HA)), inorganic ions (Br^- , NH_4^+ , and NO_3^-), metal cations (Cu^{2+} , Mn^{2+} , Fe^{3+} , and Fe^{2+}), or ionic strength (NaCl) on PCP removal during Fe(VI) treatment is discussed in the following with BP-3 as an example [31].

4.1.1 Dissolved Organic Matter

Humic substances are the principal component of dissolved organic matter in aquatic systems. HA can decrease the removal efficiency of BP-3 during Fe(VI) treatment [31]. When the spiked concentration of HA reached 15 mg L^{-1} , the removal efficiency of BP-3 reduced from 60% to 31% and 17% at pH 7.0 and 8.0, respectively. The significant consumption of Fe(VI) and the competition reaction with BP-3 by HA may be responsible for remarkably decreased removal efficiency. Besides, Lee and von Gunten [48] suggested that the competition can disappear rapidly after the electron-rich organic moieties present in effluent organic matter are consumed during Fe(VI) treatment.

4.1.2 Inorganic Ions

Selected Br^- , NH_4^+ , and NO_3^- are important inorganic species in aquatic systems. The effect of Br^- on the Fe(VI) removal of BP-3 is related to the pH of the reaction solution [31]. When the reaction solution was at pH 7.0, Br^- significantly enhanced the removal efficiency of BP-3, from 58% to 84% at $100 \mu\text{M}$ of Br^- , but it showed no effect at pH 8.0. Besides, BP-3 removal is not affected by the presence of NH_4^+ and NO_3^- . This may be due to the low reactivity of Fe(VI) with NH_4^+ and NO_3^- [48, 49].

4.1.3 Metal Cations

The removal efficiency of BP-3 is slightly enhanced by the presence of Cu^{2+} [31]. At the Cu^{2+} concentration of $20 \mu\text{M}$, the removal efficiency of BP-3 was increased from 60% to 83% and 79% at pH 7.0 and pH 8.0, respectively. However,

Mn^{2+} significantly decreases the removal efficiency of BP-3. This may be due to the reducing state of the manganese ion under the alkaline condition [50], which may accelerate the decomposition of Fe(VI). Besides, Fe^{3+} and Fe^{2+} have little effects on BP-3 removal.

4.1.4 Ionic Strength

NaCl is ordinarily used to adjust the ionic strength of aqueous solutions. NaCl only have a small effect on the removal efficiency of BP-3 during Fe(VI) treatment [31]. Even when the concentration of NaCl increased to 35 g L^{-1} , the removal efficiency of BP-3 decreased from 60% to 33% and 43% at pH 7.0 and 8.0, respectively. An explanation may be that the pH values of the reaction solution were decreased with the increasing NaCl which consumed more amount of Fe(VI), resulting in the decreased removal of BP-3.

The removal of BP-3 spiked in the natural water (groundwater, river water, and wastewater) during Fe(VI) treatment was also conducted in Fe(VI) excess to confirm the effects of coexisting constituents as shown in Fig. 5 [31]. With the increasing reaction times, the residual concentrations of BP-3 gradually decreased in all the natural water samples. Before complete removal of BP-3, the residual concentrations follow the decreasing order of wastewater > groundwater-1 > river water > groundwater-2, which is in accordance with the trends of dissolved organic

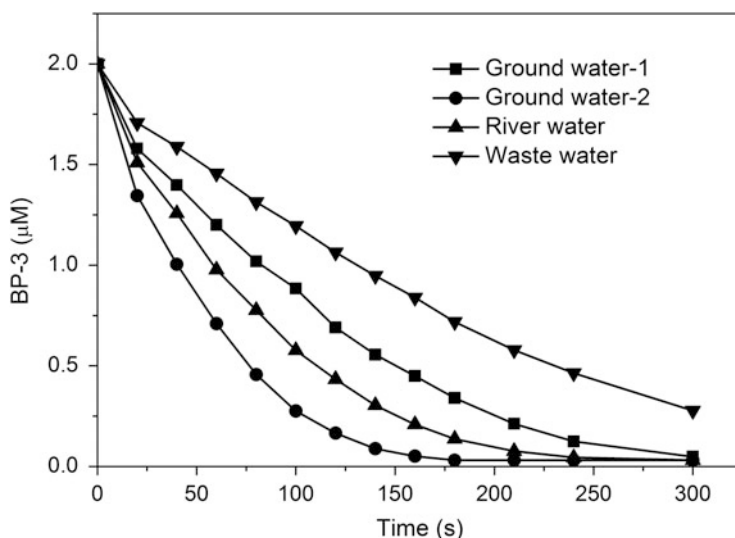


Fig. 5 Oxidation removal of BP-3 by Fe(VI) during the treatment of groundwater, river water, and wastewater. Experimental conditions: $[BP-3]_0 = 2\ \mu\text{M}$, $[Fe(VI)]_0 = 100\ \mu\text{M}$, pH 8.0 (20 mM borate buffer), $T = 24 \pm 1^\circ\text{C}$

carbon (DOC) values: 2.51 mg L^{-1} (wastewater) $> 0.78 \text{ mg L}^{-1}$ (river water) $> 0.24 \text{ mg L}^{-1}$ (ground water). The residual concentrations of BP-3 in groundwater-1 are higher than in river water; this is because groundwater-1 has higher conductivity of $183.8 \text{ }\mu\text{S/cm}$ than that of river water ($49.4 \text{ }\mu\text{S/cm}$). So, the differences of water quality parameters caused mainly by the presence of coexisting constituents can significantly influence the removal efficiencies of BP-3 during Fe(VI) treatment. However, BP-3 can achieve complete removal in all natural water samples after 300 s (Fig. 5), indicating complete removal of BP-3 can be achieved by dosing more Fe(VI) in order to reduce the effects of coexisting constituents present in natural waters.

4.2 *In Situ Production of Fe(VI) Solution for PCP Removal*

The exploration of the use of Fe(VI) for removal of typical PCPs spiked in a natural water matrix has been well addressed in the laboratory studies. However, challenges still exist for the implementation of Fe(VI) oxidation treatment in a pilot or full-scale application for PCP removal during water treatment due to the instability of a Fe(VI) solution or high production cost of solid Fe(VI) products. Up to now, one promising approach is the in situ production of Fe(VI) in solution and its direct use in water treatment.

The Ferrator[®], invented by Ferrate Treatment Technologies, LLC (FTT, Orlando, Florida), is a commercial reactor to synthesize liquid Fe(VI) in situ in bulk quantities for broad industrial use [51]. The Fe(VI) solution is synthesized based on wet oxidation method from commodity feedstocks such as alkali hydroxide, hypochlorite, and ferric chloride. Ferrator[®] reduces the production steps from 23 to 5 by eliminating the storage, handling, and transportation overheads required for a prepackaged product. Thus, the costs of production can be cut by 85% than traditional Fe(VI) deployment. But the disadvantage of this strategy is that addition of a sufficient amount of Fe(VI) solution leads to strong alkalization of the treated water to a pH of about 12; it has to utilize the ferric chloride, sulfuric acid, or CO₂ for adjusting the pH of treated water in actual applications.

Electrochemical Fe(VI) synthesis may be the most promising and economically competitive process on an industrial scale for the purpose of water treatment. Licht and Yu [24] proposed a schematic of online electrochemical Fe(VI) water purification system. Fe(VI) solution can be electrochemically prepared with a coiled iron wire anode immersed in 40 mL of 10 M NaOH at a constant oxidative current applied by Pine AFRDE5 bipotentiostat. The generated Fe(VI) was separated from the cathode by a Nafion 350 alkali-resistant, anion-impermeable membrane and then dosed into a continuous flow of effluent. This process also causes the strong alkalization of the treated water, but recent studies of pilot and full-scale trials demonstrated that with the use of highly concentrated NaOH, high current density, and anodic surface cleaning procedures, the yield efficiency of the in situ-generated Fe(VI) was up to 70%, and the concentration of the resulting Fe(VI) solution was as

high as 9 g L^{-1} [52–54]. Thus, very low volume dose of Fe(VI) solution is required for water treatment and the final pH value of treated water can be controlled below 9.

In summary, several attempts have been made to commercialize in situ Fe(VI) synthesis, but in situ production of Fe(VI) solution for removal of PCPs during water treatment needs to be further validated.

Conclusions

Fe(VI) has been demonstrated to have remarkable performance in the oxidative removal of PCPs in water. By Fe(VI) treatment, phenolic PCPs are more easily oxidized than those nitrogen-containing PCPs. The reactions between Fe(VI) and the above PCPs follow second-order reaction kinetics, with the determined k_{app} values ranging from $7 \text{ M}^{-1} \text{ s}^{-1}$ (5CBT) to $1,111 \text{ M}^{-1} \text{ s}^{-1}$ (TCS) at pH 7.0. The reactivity of Fe(VI) species with PCPs is following the decreasing order of $\text{H}_2\text{FeO}_4 > \text{HFeO}_4^- > \text{FeO}_4^{2-}$. Hammett-type relationships illustrate the electrophilic oxidation mechanism of the above reactions. Fe(VI) can transform the phenolic PCP molecules through phenoxy radical reaction, degradation, and coupling reaction. More importantly, the oxidation of each phenolic PCPs by Fe(VI) leads to the loss of its corresponding toxicity. However, the coexisting constituents present in source water could have significant effects on PCP removal during Fe(VI) oxidation treatment. In situ production of Fe(VI) solution appears to be a promising technology for removal of PCPs during pilot and full-scale water treatment. The potential future research directions are proposed as follows:

1. The removal of other categories of PCPs through Fe(VI) oxidation treatment should be carried out in batch experiments, since the numerous PCPs ubiquitous in aquatic environment have different reaction mechanisms with Fe(VI).
2. The information on radical formation and valence of iron intermediates should be studied by the application of electron paramagnetic resonance spectroscopy and Mössbauer spectroscopic techniques, to advance our understanding of the oxidative chemistry of Fe(VI) with PCPs.
3. The potential transformation products of PCP reaction with Fe(VI) should be identified by GC–MS and LC–MS/MS techniques, and the toxicity of transformation products should be evaluated by using various bioassays.
4. The in situ production of Fe(VI) solution for PCP removal should be conducted in pilot and full-scale trials to validate the treatment performance obtained in the laboratory studies and evaluate economic suitability of using Fe(VI) oxidation treatment.

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