Ferrate (Fe(VI)) Application for Municipal Wastewater Treatment: A Novel Process for Simultaneous Micropollutant Oxidation and Phosphate Removal

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A novel technology for enhanced municipal wasterwater treatment was assessed based on the dual functions of Fe(VI) to oxidize micropollutants and remove phosphate by formation of ferric phosphates. Second-order rate constants (k) for the reactions of selected pharmaceuticals, endocrine disruptors, and organic model compounds with Fe(VI) were in the range of 1 (trimethylamine) to 9000 M^{-1} s^{-1} (aniline) in the pH-range 7−8. The selected compounds contained electron-rich moieties (ERM) such as phenols, anilines, amines, and olefins. Oxidation experiments in wastewater spiked with micropollutants at concentrations in the low μM range at pH 7 and 8 showed that Fe(VI) doses higher than 5 mg Fe L^{-1} are capable of eliminating various ERM-containing micropollutants by more than 85%. In comparison to ozone, Fe(VI) was as effective or slightly less effective in terms of micropollutants oxidation, with Fe(VI) having the benefit of phosphate removal. To lower phosphate from 3.5 to 0.8 mg PO_4−P L^{-1} (regulatory limit for wastewater discharge in Switzerland), a Fe(VI) dose of 7.5 mg Fe L^{-1} was needed. Overall, this study demonstrates Fe(VI) as a promising tool for an enhanced wastewater treatment to remove micropollutants as well as to control phosphate in a single treatment step.

Introduction

Phosphate removal from municipal wastewater has been practiced for a long time to prevent eutrophication of the receiving waters. In Switzerland, the regulatory limit for phosphate in wastewater effluents is 0.8 mg PO_4−P L^{-1} (*1*). Addition of ferric salts and subsequent ferric-phosphate precipitation is one of the common practices in municipal wastewater treatment plants (WWTPs) to meet the phosphate standards (*2*). Recently, effluents of municipal WWTPs have also been identified as a major source of emerging micropollutants, such as hormones, pharmaceuticals, and personal care products for the aquatic environments (*3*). Strategies for the removal of these compounds from municipal wastewaters are currently discussed. Oxidation processes with ozone (O_3) in laboratory- and pilot-scale studies have been shown to be an option for the removal of micropollutants (*4, 5*).

As an alternative, ferrate (Fe(VI)) is a potential water treatment chemical due to its dual functions as an oxidant and a subsequent coagulant/precipitant as ferric hydroxide (*6, 7*). Hence, an application of Fe(VI) to wastewater could achieve both oxidative elimination of various micropollutants and removal of phosphate by a subsequent ferric-phosphate precipitation. However, up to now, Fe(VI) has neither been suggested nor investigated in detail for this novel application.

Fe(VI) has been known to react with electron-rich organic moieties (ERM), such as phenols (*8, 9*), anilines (*10*−*12*), amines (*10, 13, 14*), and olefins (*15*). Therefore, ERM-containing compounds can be potentially transformed during Fe(VI) oxidation. This has been demonstrated in a few previous kinetic studies for the Fe(VI) reaction with emerging micropollutants such as steroid estrogens (*9*), sulfonamide antimicrobials (*12*), and carbamazepine (*15*). Nevertheless, kinetic information is still limited for the reactions of Fe(VI) with various organic compounds in the pH range relevant to water treatment (pH 6−9).

The aim of this study was to assess the potential of Fe(VI) to oxidize selected micropollutants and remove phosphate during enhanced treatment of municipal wastewater in a single treatment step. Second-order rate constants (k) for the reaction of Fe(VI) with selected micropollutants and organic model compounds were determined as a function of pH. The oxidative elimination of a wide range of micropollutants was then investigated in wastewater for varying experimental conditions for pH (7 and 8) and Fe(VI) dose (0.1−15 mg Fe L^{-1}). In addition, the performance of Fe(VI) to oxidize micropollutants in a wastewater matrix was compared to O_3. Furthermore, jar tests with Fe(VI) were performed in wastewater to evaluate the oxidative elimination of selected micropollutants in combination with the subsequent removal of phosphate. Finally, Fe(VI) was compared to Fe(III) and Fe(II) with regard to the phosphate removal efficiency.

Experimental Section

Standards and Reagents. All chemicals and solvents (purity ≥95%) were purchased from various commerical suppliers. Description on preparation and quantification of oxidants (Fe(VI) and O_3), coagulants (Fe(II) and Fe(III)), stock solutions of micropollutants, and organic model compounds are provided in the Supporting Information, Text S1.

Kinetics of Fe(VI) Reactions with Micropollutants and Organic Model Compounds. All kinetic experiments were performed at room temperature (23 ± 2 °C). Second-order rate constants were mostly determined by measuring the Fe(VI) decrease in the presence of excess compound (pseudo-first-order conditions) in the pH range 5−11. For diclofenac, second-order rate constants were determined by measuring the diclofenac decrease in the presence of excess Fe(VI). For details, see the Supporting Information, Text S2.

Oxidation of Micropollutants by Fe(VI) in a Wastewater Matrix. Bench-scale experiments were performed to investigate the elimination of micropollutants spiked in a secondary effluent from a pilot WWTP in Dübendorf, Switzerland (DDWW) at various Fe(VI) doses at 23 ± 2 °C and pH 7−8. Secondary effluent was chosen to investigate the potential of Fe(VI) as a polishing step for enhanced removal of

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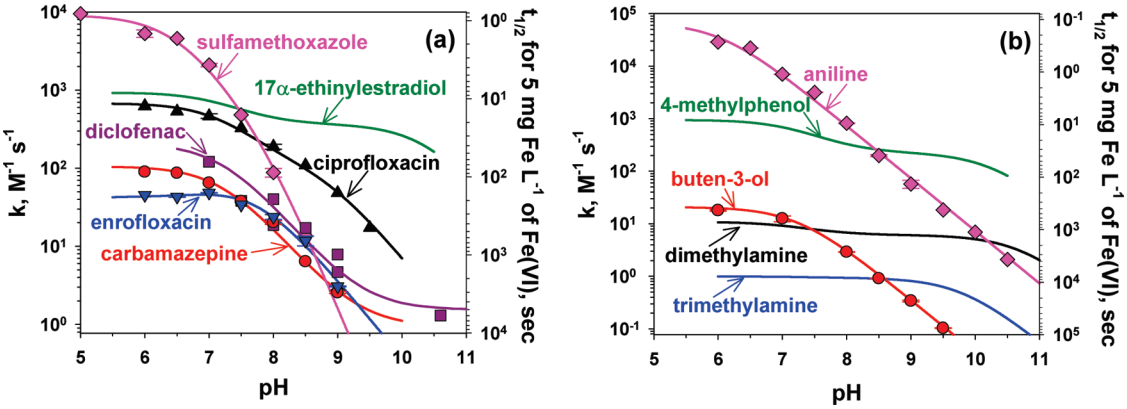


FIGURE 1. Second-order rate constants and half-lives ($t_{1/2}$) for the reactions of Fe(VI) with (a) selected micropollutants and (b) organic model compounds as a function of pH (5−11) and at $T = 23 \pm 2$ °C. The symbols represent the measured data, and the lines represent the model fits from the present study. The half-lives are calculated for a Fe(VI) concentration of 5 mg Fe L^{-1} (90 μM). Kinetic data for 17α-ethinylestradiol and 4-methylphenol are taken from ref *9* and for dimethylamine and trimethylamine from ref *13*, and only the model calculations are provided here.

micropollutants as well as phosphate. The micropollutants were selected as representative substances with different reactive moieties that belong to different usage classes and have an environmental relevance (*3*). Each micropollutant was spiked separately at concentrations of 0.2−1 μM into 20 mL of the wastewater buffered at pH 7 (10 mM carbonate buffer) or 8 (20 mM borate buffer). After Fe(VI) was completely consumed (3−5 h after Fe(VI) addition), residual micropollutant concentrations were analyzed with a HPLC/UV-fluorescence system (Supporting Information, Text S3). Fe(VI) decrease was measured spectrophotometrically as a function of the reaction time with the ABTS method (*16*). Further experimental details, the characteristics of the wastewater, and the analytical procedures are described in the Supporting Information, Text S4.

Oxidation of Micropollutants by Fe(VI) and O_3 in the Same Wastewater Matrix. DDWW was spiked with each of the selected micropollutants at pH 8 (20 mM borate buffer) and treated with a range of Fe(VI) or O_3 doses. After 3−5 h (total Fe(VI) or O_3 consumption), residual micropollutant concentrations were analyzed by a HPLC/UV-fluorescence system (Supporting Information, Text S3).

Jar Tests for Phosphate Removal. Phosphate removal experiments were carried out with a standard jar test apparatus with a reactor volume of 0.5 L. DDWW was spiked with phosphate (3.5 mg PO_4−P L^{-1}, a realistic scenario for a high phosphate concentration) and selected micropollutants at pH 7 (typical pH conditions of municipal wastewaters). Carbamazepine, diclofenac, and sulfamethoxazole were chosen based on their moderate reactivity toward Fe(VI) and relevance in municipal wastewaters. Thereafter, a range of Fe(VI) doses (1−15 mg Fe L^{-1}) were added. For comparison of the phosphate removal efficiency, Fe(II) ($FeCl_2$) and Fe(III) ($FeCl_3$) were also used. Concentrated stock solutions of Fe(II) and Fe(III) were freshly prepared and quickly applied to the wastewater (see Supporting Information, Text S1 for details). The jar test procedure for the removal of phosphate was composed of three steps: i) rapid mixing at 200 rpm for 0.5 min, ii) slow mixing at 50 rpm for 15 min, and iii) settling for >15 min. After settling, the supernatant samples were collected and filtered through 0.45 μm Nylon or RC filters (BGB Analytik AG, Switzerland) prior to analysis of the residual phosphate and micropollutant concentrations. Phosphate concentrations were analyzed according to a standard method (ascorbic acid-molybdate blue method) (*17*). All experiments were performed in triplicate.

Results and Discussion

Kinetics for the Reactions of Fe(VI) with Micropollutants and Organic Model Compounds. To assess the reactivity of Fe(VI) toward a broad range of micropollutants, second-order rate constants (k) were determined for the reaction of Fe(VI) with selected micropollutants and organic model compounds as a function of pH. The investigated micropollutants were selected based on their environmental relevance and their reactivity to other water treatment oxidants, such as O_3 (*4, 18*), due to electron-rich moieties (ERM). For example, 17α-ethinylestradiol contains a phenolic-, carbamazepine an olefine-, ciprofloxacin and enrofloxacin an amine-, and sulfamethoxazole and diclofenac an aniline-moiety.

Fe(VI) shows an appreciable reactivity with the selected micropollutants. In the pH range 7−8, the second-order rate constant k varied between 20 and 2090 M^{-1} s^{-1} (Figure 1a). In general, k for the selected micropollutants (Figure 1a) and organic model compounds (Figure 1b) increases with decreasing pH. These pH-dependent variations in k could be explained by considering species-specific reactions between Fe(VI) species ($HFeO_4^- \leftrightharpoons FeO_4^{2-} + H^+$, $pK_{HFeO4} \leftrightharpoons 7.2$) and acid−base species of an ionizable substrate ($XH = X^- + H^+$, $pK_{a,\,XH}$) (*9, 13*). The speciation of Fe(VI) as a function of pH can be found in Figure S5. According to that, eq 1 applies for the loss of Fe(VI)

$$-\frac{d[Fe(VI)_{tot}]}{dt} = k[Fe(VI)_{tot}][XH_{tot}] = k_1[HFeO_4^-][XH] + k_2[HFeO_4^-][X^-] + k_3[FeO_4^{2-}][XH] + k_4[FeO_4^{2-}][X^-] \quad (1)$$

and, therefore, k can be expressed by eq 2

$$k = k_1\alpha_1\beta_1 + k_2\alpha_1\beta_2 + k_3\alpha_2\beta_1 + k_4\alpha_2\beta_2 \quad (2)$$

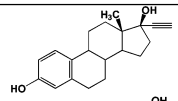
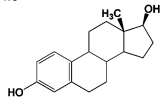
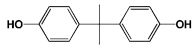
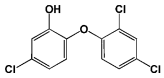
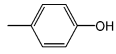
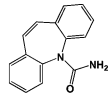
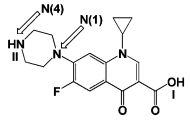
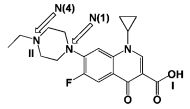
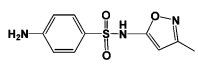
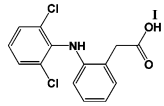
where $[Fe(VI)_{tot}] = [HFeO_4^-] + [FeO_4^{2-}]$ and $[XH_{tot}] = [XH] + [X^-]$, k_1, k_2, k_3, and k_4 represent species-specific rate constants, α_1 and α_2 represent the fraction of $HFeO_4^-$ and FeO_4^{2-}, respectively, and β_1 and β_2 represent the fraction of XH and X^-, respectively.

Similarly, for the reaction of Fe(VI) with nonionizable substrate, k can be expressed by eq 3:

$$k = k_5\alpha_1 + k_6\alpha_2 \quad (3)$$

The species-specific second-order rate constants, k_1−k_6, were calculated from least-squares nonlinear regressions of the experimental k data by using the software GraphPad Prism (www.graphpad.com). In all cases, the model could explain the experimental k well ($R^2 \geq 0.94$). For reactions of Fe(VI) with ionizable substrates, the reactions of FeO_4^{2-} ($k_3\alpha_2\beta_1$ and $k_4\alpha_2\beta_2$) did not appear to contribute significantly to the overall

TABLE 1. Second-Order Rate Constants k (M^{-1} s^{-1}) for the Reaction of Fe(VI) and O_3 with Selected Pharmaceuticals, Endocrine Disruptors, and Organic Model Compounds[s]

			Fe(VI)				O_3		
Compound	Structure	pK_a	Reacting species	k_1/k_2 (k_5/k_6) [a]	k (pH 7)	k (pH 8)	k_1/k_2 [b]	k (pH 7)	k (pH 8)
17α-ethinyl-estradiol		10.4 [c]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	9.4×10^2 / 5.4×10^5 [d]	7.3×10^2	4.5×10^2	1.8×10^5 / 3.7×10^9 [c]	1.6×10^6	1.5×10^7
17β-estradiol		10.4 [c]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	1.0×10^3 / 5.4×10^5 [d]	7.6×10^2	4.6×10^2	2.2×10^5 / 3.7×10^9 [c]	1.7×10^6	1.5×10^7
bisphenol-A		9.6 10.2 [c]	$HFeO_4^-$ + XH_2^+/ $HFeO_4^-$ + XH^-/ $HFeO_4^-$ + X^{2-}	8.2×10^2 / 8.0×10^4 / 2.6×10^5 [d]	6.4×10^2	4.1×10^2	1.7×10^4 / 1.1×10^9 / 1.1×10^9 [c]	2.7×10^6	2.6×10^7
triclosan		8.1 [e]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	– / $2.5(\pm0.2)\times10^4$ [f]	1.1×10^3	1.6×10^3	1.3×10^3 / 5.1×10^8 [e]	3.8×10^7	2.3×10^8
4-methylphenol		10.3 [g]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	9.6×10^2 / 2.4×10^5 [d]	6.9×10^2	3.3×10^2	3.0×10^4 [g]/ 2.0×10^9 [h]	1.1×10^6	1.1×10^7
carbamazepine		–	$HFeO_4^-$ + X/ FeO_4^{2-} + X	$1.1(\pm0.1)\times10^2$ / 0.9(±0.3)	67	16	3×10^5 [i]	3×10^5	3×10^5
buten-3-ol		–	$HFeO_4^-$ + X/ FeO_4^{2-} + X	19(±0.6) / 0.01(±0.003)	12	3	7.9×10^4 [j]	7.9×10^4	7.9×10^4
ciprofloxacin		6.2(I) 8.8(II)[k]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	$6.9(\pm0.4)\times10^2$/ $4.4(\pm0.3)\times10^3$ [l]	4.7×10^2	1.7×10^2	7.5×10^3 / 9.0×10^5 [k, l]	1.9×10^4	1.3×10^5
dimethylamine		10.7 [g]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	11 / 1.8×10^4 [m]	9	7	– / 1.9×10^7 [g]	3.8×10^3	3.8×10^4
enrofloxacin		6.1(I) 7.7(II)[k]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	43(±4) / $2.2(\pm0.2)\times10^2$ [l]	46	24	4.6×10^4 / 7.8×10^5 [k, l]	1.5×10^5	5.3×10^5
trimethylamine		9.8 [g]	$HFeO_4^-$ + XH/ $HFeO_4^-$ + X^-	1 / 3.5×10^2 [m]	1	1	– / 4.1×10^6 [g]	6.5×10^3	6.4×10^4
sulfamethox-azole		6.4 (±0.2), 7.8 (±0.3) [n]	– [o]	$9.2(\pm1.7)\times10^3$	1.8×10^3	77	2.5×10^6 [i]	2.5×10^6	2.5×10^6
aniline		6.0 (±0.2) [p]	– [q]	$6.8(\pm2.8)\times10^4$	6.6×10^3	7.2×10^2	1.4×10^7 [r]	1.4×10^7	1.4×10^7
diclofenac		4.2 (I) [i]	$HFeO_4^-$ + X^-/ FeO_4^{2-} + X^-	$2.1(\pm0.4)\times10^2$ / 1.5(±0.6)	1.3×10^2	32	1×10^6 [i]	1×10^6	1×10^6

[a] k_1 and k_2 represent the reaction rate constants of $HFeO_4^-$ with protonated and deprotonated species of substrates, respectively. The exceptions are as follows: bisphenol A for which the reaction rate constants of $HFeO_4^-$ with protonated, mono-, and di-deprotonated species are given; carbamazepine, buten-3-ol, and diclofenac of which the reaction rate constants with $HFeO_4^-$ (k_5) and FeO_4^{2-} (k_6) are given; k_3 and k_4 are not of importance as discussed in the text, [b] k_1 and k_2 represent the reaction rate constants of O_3 with protonated and deprotonated species of substrates, respectively. [c] From ref *20*. [d] From ref *9*. [e] From ref *21*. [f] Estimated from the competition kinetics in DDWW at pH 7 (see Figure S8). [g] From ref *22*. [h] Estimated from the Brown-Okamoto correlations in ref *21*. [i] From ref *4*. [j] From ref *23*. [k] From ref *18*. [l] k_1 for ciprofloxacin and enrofloxacin represent an 'effective' rate constant for the combination of zwitterionic and neutral species. [m] k from ref *13*. [n] pK_a values of hypothesized Fe(VI)-sulfamethoxazole intermediate. [o] The reaction of the fully protonated species of the intermediate (Fe(VI)-SMX-H_2^+) with sulfamethoxazole. [p] pK_a value of hypothesized Fe(VI)-aniline intermediate. [q] The reaction of the protonated species of the intermediate (Fe(VI)-AN-H) with aniline. [r] k from ref *24*. [s] Standard deviation (±σ) is given for the rate constants determined in this study.

kinetics and thus were neglected. Table 1 summarizes the determined species-specific rate constants.

17α-Ethinylestradiol and 4-Methylphenol. The pH-dependence of k for 17α-ethinylestradiol is well explained by considering the reactions of $HFeO_4^-$ with the protonated (k_1 = 9.4×10^2 M^{-1} s^{-1}) and the deprotonated species of 17α-ethinylestradiol (k_2 = 5.4×10^5 M^{-1} s^{-1}) at the 17α-ethinylestradiol's phenolic-moiety (pK_a = 10.4, Table 1) (*9*). The magnitude and pH-dependence of k for 17α-ethinylestradiol are consistent with those for 4-methylphenol (Figure 1).

Carbamazepine and Buten-3-ol. Both compounds are not ionizable in the tested pH range 5−11. As a consequence, k for these two compounds mainly depends on the fraction of the $HFeO_4^-$ species as a function of pH. Hence, the magnitude of k exhibits a one-log decrease for each unit increase in pH. k_5 for carbamazepine is $1.1(\pm0.1) \times 10^2$ M^{-1} s^{-1}, which is about a factor of 5 higher than that for buten-3-ol (Table 1). It is assumed that Fe(VI) only attacks at the double bond and that the presence of electron-donating benzene-groups increases the reactivity to Fe(VI). k_5 for carbamazepine from this study is comparable to the value reported recently by Hu et al. ($k_5 = 1.4 \times 10^2$ M^{-1} s^{-1}) (*15*).

Ciprofloxacin and Dimethylamine. The pH-dependence of k for ciprofloxacin is well explained by considering the reactions of $HFeO_4^-$ with the protonated ($k_1 = 6.9(\pm0.4) \times 10^2$ M^{-1} s^{-1}) and the deprotonated species of ciprofloxacin ($k_2 = 4.4(\pm0.3) \times 10^3$ M^{-1} s^{-1}) at ciprofloxacin's secondary amine moiety (N(4), $pK_{a,II} = 8.8$, Table 1). This is consistent with the case of O_3 where only the N(4) amine, not the N(1) amine nor the quinolone moiety, of the ciprofloxacin is the main site for oxidation (*18*). The pH-dependent k for ciprofloxacin is much higher than that of dimethylamine, because of the higher pK_a value of dimethylamine (10.7, Table 1).

Enrofloxacin and Trimethylamine. Similar to the case of ciprofloxacin, the pH-dependence of k for enrofloxacin is governed by deprotonation at enrofloxacin's tertiary amine moiety (N(4), $pK_{a,II} = 7.7$, Table 1) which was shown for ozone as well (*18*). k of enrofloxacin is much higher than that of trimethylamine, because of the higher pK_a value of trimethylamine (9.8, Table 1). In addition, enrofloxacin reacts with Fe(VI) at lower rates than ciprofloxacin which is consistent with the lower reactivity of tertiary amines.

Sulfamethoxazole and Aniline. These two compounds show a strong pH-dependence with k increasing more than 4 orders of magnitude with a decrease of the pH from 11 to 5. The pH- dependence of k for sulfamethoxazole and aniline could not be explained by eq 1 or eq 2. k steadily increases even at pH < 7.2 where the $HFeO_4^-$ concentration is at its maximum. Furthermore, k for sulfamethoxazole exhibits more than a one-log unit increase for each unit decrease of pH from 9 to 7. Including the reactions of H_2FeO_4 ($H_2FeO_4 \leftrightarrow HFeO_4^- + H^+$, $pK_{H2FeO4} = 3.5$ (*19*)) into the model calculations did not improve the predictions. However, this unusual pH-dependence could be explained by employing the following tentative reaction mechanism: Fe(VI) reacts with R-NH_2 by forming an intermediate complex, such as 'Fe(VI)-NH_2-R' which also has an acid−base equilibrium. For aniline, the pK_a of the corresponding intermediate was estimated to be 6.0(±0.2) (i.e., Fe(VI)-AN-H ⇔ Fe(VI)-AN^- + H^+, $pK_a = 6.0$ where AN represents the aniline side). For sulfamethoxazole, the existence of two pK_a at 6.4(±0.2) and 7.8(±0.3) was necessary to explain the observed pH-dependence of k (i.e., Fe(VI) -SMX-H_2^+ ⇔ Fe(VI)-SMX-H + H^+, $pK_{a,1} = 6.4$ and Fe(VI)-δMX^- + H^+ ⇔ Fe(VI)-SMX + H^+, $pK_{a,2} = 7.8$ where SMX represents the sulfamethoxazole side). The (de)-protonation may occur either at the Fe(VI)- or aniline-side of the intermediate. The rate determining step will be the reaction of these intermediates with an additional aniline (or sulfamethoxazole) because the reaction was found to be first-order with respect to both Fe(VI) and aniline (or sulfamethoxazole) (Figure S3). A similar reaction mechanism has been proposed in a previous study for the aniline oxidation by Fe(VI) (*10*). The nonlinear regression of the k with the above proposed model revealed that only the reaction of the protonated species of the intermediate (Fe(VI)-AN-H) with aniline ($k = 6.8(\pm2.8) \times 10^4$ M^{-1} s^{-1}, Table 1) is contributing to the pH-dependence for the reaction between Fe(VI) and aniline. Similary, for the reaction between Fe(VI) and sulfamethoxazole, the reaction of the fully protonated species of the intermediate (Fe(VI)-SMX-H_2^+) with sulfamethoxazole ($k = 9.2(\pm1.7) \times 10^3$ M^{-1} s^{-1}, Table 1) is controlling the pH-dependence. Further details of the reaction scheme for aniline and sulfamethoxazole are described in the Supporting Information, Text S5.

The k for aniline and sulfamethoxazole has been reported in previous studies (*10*−*12*). The k values for aniline and sulfamethoxazole determined in the present study are comparable to those of Huang et al. 2001 (*11*) and Sharma et al. 2006 (*12*), respectively, but different within a factor of 5 from those of Hornstein 1999 (*10*). In addition, the intepretation of the pH- dependence of k in the studies of Huang et al. (*11*) and Sharma et al. (*12*) is different from that of the present study. A comparison of the k for aniline and sulfamethoxazole with literature data is provided in the Supporting Information, Text S6.

Diclofenac. The pH-dependence of k for diclofenac in the pH-range 7−11 is well explained by considering the reactions of diclofenac with $HFeO_4^-$ ($k_5 = 2.1(\pm0.4) \times 10^2$ M^{-1} s^{-1}) and FeO_4^{2-} ($k_6 = 1.5(\pm0.6)$ M^{-1} s^{-1}). It is assumed that the protonation on diclofenac's carboxylic acid moiety ($pK_a = 4.0$, Table 1) does not have any influence on the kinetics within the tested pH range.

Oxidation of Individually Spiked Micropollutants by Fe(VI) in a Wastewater Matrix. The significant reactivity of Fe(VI) toward the ERMs shown in the previous section indicates that many micropollutants containing these ERMs can be considerably eliminated during oxidation by Fe(VI). To confirm this, experiments for the elimination of selected micropollutants were performed in real wastewaters.

Figure 2 shows the oxidative elimination of individually spiked ERM-containing micropollutants in a wastewater (DDWW) at a concentration of 0.2−1.0 μM (0.05−0.32 mg L^{-1}) and at pH 7 for Fe(VI) doses ranging from 0.25 to 5.0 mg Fe L^{-1}. For the micropollutants containing a phenolic-moiety, such as 17α-ethinylestradiol, 17β-estradiol, bisphenol A, and triclosan, a Fe(VI) dose of 2 mg Fe L^{-1} achieved an elimination of >95%. The rate constant k for the reaction of triclosan with Fe(VI) at pH 7 could be estimated from the elimination of triclosan relative to the other phenolic micropollutants in DDWW. Figure S8 shows a competition kinetic plot for triclosan versus 17α-ethinylestradiol, 17β-estradiol, and bisphenol A, respectively. A second-order rate constant of $1.1(\pm0.1) \times 10^3$ M^{-1} s^{-1} was obtained for triclosan at pH 7. Based on this rate constant, the second-order rate constant (k_2) between $HFeO_4^-$ and deprotonated triclosan species was estimated to be $2.5(\pm0.2) \times 10^4$ M^{-1} s^{-1}. Even though k_2 for triclosan is >10-fold lower than the corresponding rate constants for the other phenolic micropollutants, the reactivity of triclosan at pH 7 or 8 is higher due to a lower pK_a value of triclosan ($pK_a = 8.1$, Table 1).

An electrophilic attack on phenolic moieties is expected for both Fe(VI) and O_3. Therefore, a correlation between the corresponding Fe(VI) and O_3 rate constants can be developed. Figure S9 shows a good linear correlation between log(k_{HFeO4-}) and log(k_{O3}) for selected phenolic compounds. k_{HFeO4-} and k_{O3} represent the second-order rate constant of $HFeO_4^-$ and O_3, respectively, with deprotonated phenolic compounds. The obtained correlation was $\log(k_{HFeO4-}) = 1.91 \cdot (\pm0.19) \log(k_{O3}) - 12.50$ (±1.74), $R^2 = 0.94$, $n = 8$. For a given phenolic compound, the rate constant for O_3 is about 4−5 orders of magnitude higher than for $HFeO_4^-$.

For the other micropollutants such as sulfamethoxazole, diclofenac, enrofloxacin, ciprofloxacin, and carbamazepine, a Fe(VI) dose of 5 mg Fe L^{-1} was necessary to obtain an elimination of >85%. The compounds with an amine or olefine moiety have a lower reactivity with Fe(VI) (Table 1) and were therefore eliminated less efficiently than the phenolic compounds.

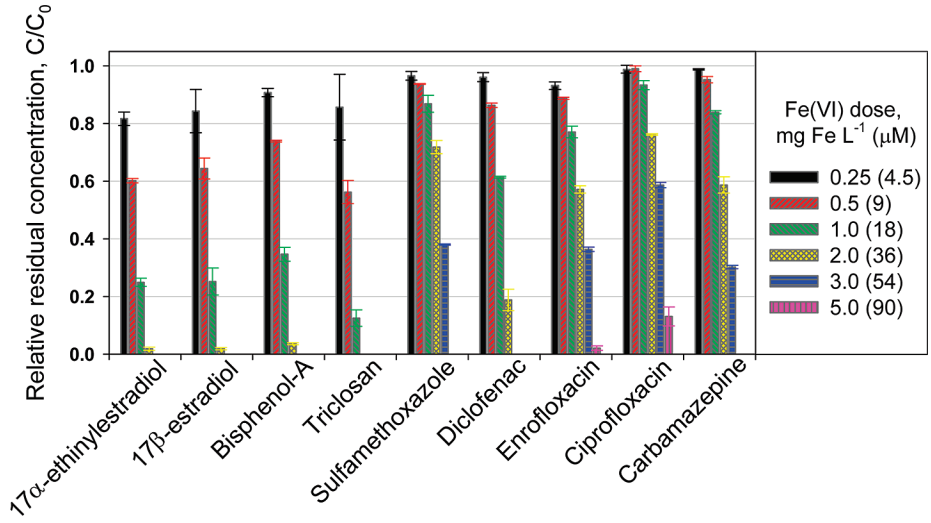


FIGURE 2. Relative residual concentration of selected micropollutants during treatment of a wastewater (DDWW) as a function of the Fe(VI) dose (0.25−5.0 mg Fe L^{-1}) after complete Fe(VI) consumption (3−5 h). Experimental conditions: [micropollutants]$_0$ = 0.2−1 μM (0.05−0.32 mg L^{-1}), [phosphate]$_0$ = 3.5 mg PO_4−P L^{-1}, [DOC] = 5.1 mg C L^{-1}, pH = 7 (10 mM bicarbonate buffer), and T = 23 ± 2 °C. For the four phenolic micropollutants, Fe(VI) doses were applied up to 2.0 mg Fe L^{-1}. If no bar is shown, the residual concentration was below 4% of the initial concentration.

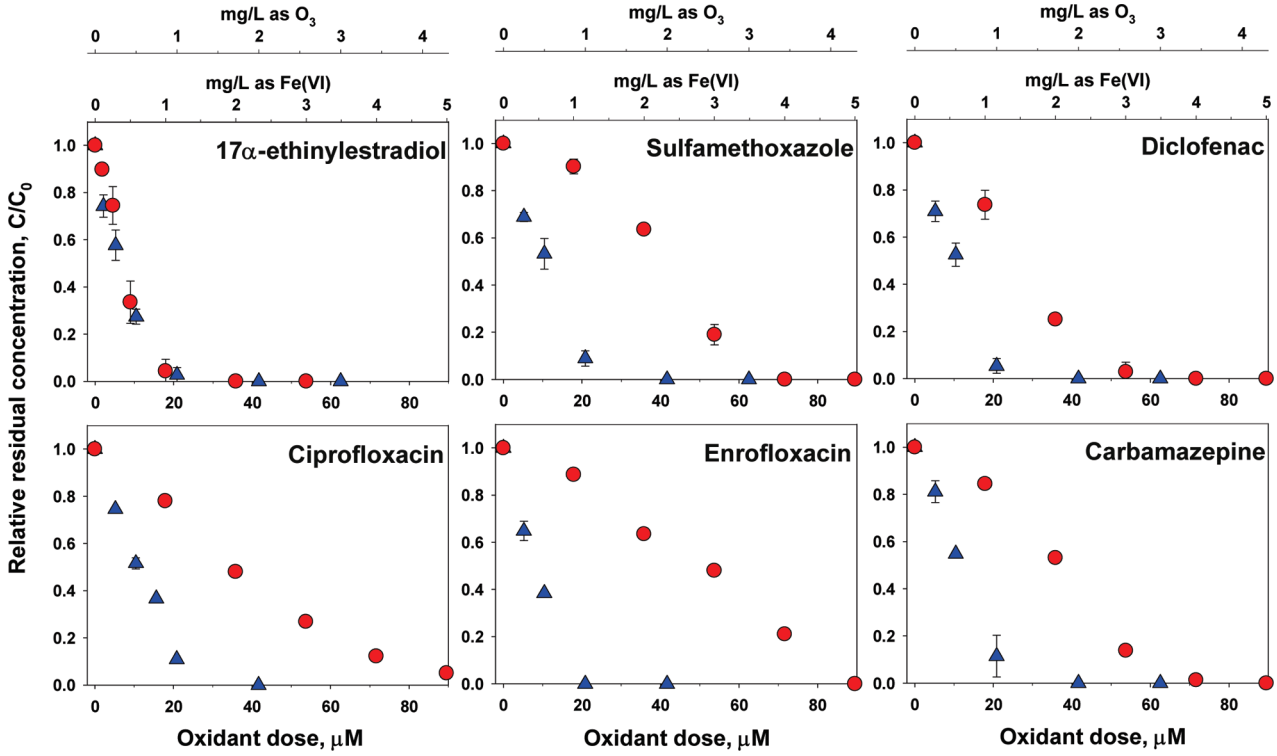


FIGURE 3. Comparison of the relative residual concentration after oxidation of selected micropollutants by Fe(VI) (red circles) and O_3 (blue triangles) as a function of the oxidant dose in a wastewater (DDWW). Experimental conditions: [micropollutants]$_0$ = 0.2−1 μM (0.05−0.32 mg L^{-1}), [DOC] = 5.0 mg C L^{-1}, pH = 8 (20 mM borate buffer), T = 23 ± 2 °C.

Compounds without the ERMs were also treated by Fe(VI) in the same wastewater. Figure S10 shows that bezafibrate, iopromide, and ibuprofen were eliminated by less than 40% even at a Fe(VI) dose of 15 mg Fe L^{-1}. Therefore, significant eliminations are not expected for other micropollutants without the ERMs.

The oxidative elimination of a micropollutant (M) by Fe(VI) can be predicted by using the determined second-order rate constants ($k_{Fe(VI)}$, Table 1) according to eq 4

$$\frac{[M]_\tau}{[M]_0} = \exp\left[-k_{Fe(VI)} \int_0^\tau [Fe(VI)]dt\right] \quad (4)$$

where $\int_0^\tau$[Fe(VI)]dt represents the Fe(VI) exposure (Fe(VI) concentration integrated over time). Equation 4 is derived from the second-order reaction kinetics for the reaction between M and Fe(VI) under the condition of [M] ≪ [Fe(VI)].

Figure S11 shows the time-dependent Fe(VI) concentrations in DDWW at pH 7 for various Fe(VI) doses. Most of the Fe(VI) added to the wastewater was consumed within 30 min. In general, the Fe(VI) decrease is caused by its reaction with the ERMs in the dissolved organic matter and by the Fe(VI) self-decay (*9*, *19*). Hence, as an example, when a Fe(VI) dose of 2.5 mg Fe L^{-1} was applied to the wastewater, a Fe(VI) exposure of 7.7 mg Fe L^{-1} min (= 8.3 mM s) was obtained

(Figure S11). Based on the Fe(VI) exposures in Figure S11, the measured and predicted relative residual concentrations of selected micropollutants are compared in Figure S12 during treatment of DDWW with Fe(VI) at pH 7. For 17α-ethinylestradiol, carbamazepine, and enrofloxacin, the eliminations were reasonably well predicted. However, the predictions overestimated the eliminations of ciprofloxacin and sulfamethoxazole and underestimated the elimination of diclofenac (Figure S12).

The oxidative elimination experiments of selected compounds by Fe(VI) were also performed at pH 8 in DDWW to investigate the effect of pH. Figure 3 shows that similar degrees of elimination were observed for the selected micropollutants at pH 8 compared to the data at pH 7 presented in Figure 2. 17α-Ethinylestradiol as a phenolic micropollutant was oxidized by >95% at a Fe(VI) dose of 1 mg Fe L^{-1}. The other investigated micropollutants, such as sulfamethoxazole, diclofenac, ciprofloxacin, enrofloxacin, and carbamazepine, were eliminated by >95% at a Fe(VI) dose of 5 mg Fe L^{-1}. The similar degrees of the elimination at pH 7 and 8 (Figure 2 vs Figure 3), even though the apparent k for the selected micropollutants is higher at pH 7 than pH 8 (Table 1), can be understood by considering the longer lifetime of Fe(VI) and hence the higher Fe(VI) exposure at pH 8 (Figure S13) compared to pH 7 (Figure S11). For example, when a Fe(VI) dose of 5 mg Fe L^{-1} was applied, a Fe(VI) exposure of 58 mg Fe L^{-1} min was obtained at pH 8 (Figure S13), whereas at pH 7 it was only 20 mg Fe L^{-1} min (Figure S11). Based on the Fe(VI) exposures derived from Figure S13, a comparison of the predicted relative residual concentration of selected micropollutants at pH 8 in DDWW with the measured data is shown in Figure 4. Comparable to pH 7 (Figure S12), 17α-ethinylestradiol and enrofloxacin eliminations were well predicted, while ciprofloxacin elimination was again overestimated (Figure 4). Carbamazepine and diclofenac eliminations were well predicted at a Fe(VI) dose of 1 mg Fe L^{-1}, however, increasingly underestimated by increasing the Fe(VI) doses to 3 and 4 mg Fe L^{-1}. Sulfamethoxazole elimination was well predicted at Fe(VI) doses of 1 and 3 mg Fe L^{-1}, however, underestimated at a Fe(VI) dose of 4 mg Fe L^{-1} (Figure 4).

There are several possible reasons for the discrepany between the measured and predicted eliminations. One of the possibilities is the difference of k which is measured by Fe(VI) decrease and micropollutant decrease. The method monitoring the Fe(VI) decrease (which is mainly employed in the current study) can yield a k which differs from that obtained by the method monitoring the micropollutant decrease, by the stoichiometric factor η, which defines the number of Fe(VI) molecules consumed per molecule of target micropollutant under the experimental conditions. Deviations from $\eta = 1$ can be caused by fast side reactions of Fe(VI) with products of the primary (or secondary) reactions. Little is known about the η values of Fe(VI) reactions with organic compounds. Only Sharma et al. 2006 (*12*) reported a η value of ~4 for the Fe(VI) reaction with sulfamethoxazole. If we assume that the η values for Fe(VI) reactions range from 1 to 4 (based on the case of sulfamethoxazole), k which is measured by monitoring the Fe(VI) decrease can overestimate the transformation of a micropollutant by up to a factor of 4. The difference in the k from the two kinetic methods can partially explain the observed lower than predicted elimination of sulfamethoxazole and ciprofloxacin at pH 7 (Figure S12) and ciprofloxacin at pH 8 in DDWW (Figure 4).

The other possibility is the contribution of Fe(V) or Fe(IV) species to the enhanced oxidation of the compounds. Fe(VI) has been known to react via a one- or two-electron transfer depending on its reaction counterparts, generating Fe(V) or Fe(IV) species, respectively (*8, 10, 19, 25*). Since Fe(V) is known

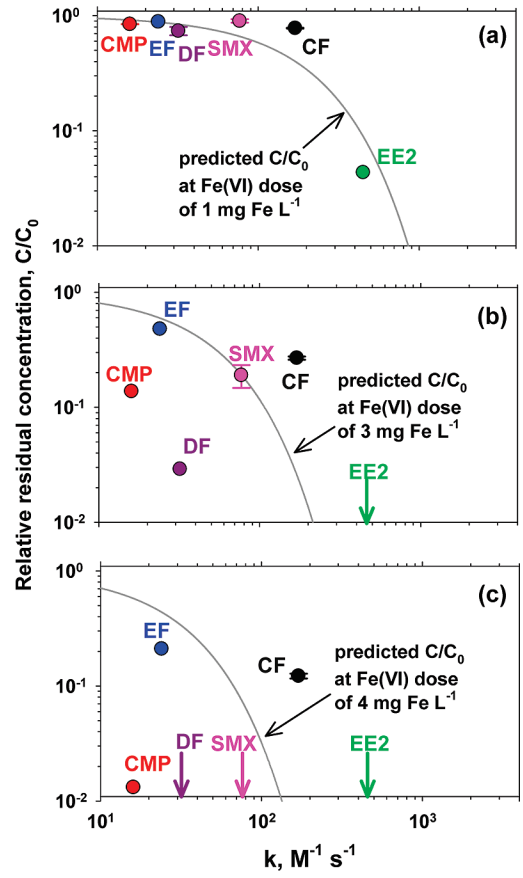


FIGURE 4. Measured and predicted relative residual concentration (C/C_0) of selected micropollutants during treatment of a wastewater (DDWW) at pH 8 with Fe(VI). Predicted relative residual concentration (lines) at Fe(VI) doses of (a) 1.0 mg Fe L^{-1}, (b) 3.0 mg Fe L^{-1}, and (c) 4.0 mg Fe L^{-1} was calculated by using eq 4 and the resulting Fe(VI) exposures of (a) 5.0 mg Fe L^{-1} min, (b) 34 mg Fe L^{-1} min, and (c) 46 mg Fe L^{-1} min (Figure S13). Abbreviations: EE2 = 17α-ethinylestradiol, EF = enrofloxacin, CF = ciprofloxacin, CMP = carbamazepine, SMX = sulfamethoxazole, DF = diclofenac. Circles represent measured relative residual concentrations at the respective Fe(VI) doses shown in Figure 3. The arrows indicate that the relative residual concentration of the respective micropollutant is below its quantification limit (4% of the initial concentration) at the corresponding Fe(VI) dose.

to be significantly more reactive than Fe(VI) (*8, 19, 25*), oxidative elimination rates of micropollutants by Fe(VI) may be enhanced when reactions are conducted in the presence of reducing substrates such as dissolved organic matter in wastewater. This might be the case for the higher elimination of diclofenac at pH 7 (Figure S12) and sulfamethoxazole, diclofenac, and carbamazepine at pH 8 in DDWW (Figure 4). The mechanisms of Fe(VI) reactions with organic compounds are currently poorly understood, and therefore a comprehensive discussion of the underlying processes is beyond the scope of this study.

Comparison between Fe(VI) and O_3. Recent studies have demonstrated that ozonation might be a powerful tool for the elimination of various micropollutants during enhanced wastewater treatment (*5, 18*). Therefore, it is of interest to compare the ability of Fe(VI) to oxidize various micropollutants in wastewater with O_3. Figure 3 shows a comparison between Fe(VI) and O_3 for the eliminations of ERM-containing micropollutants as a function of the oxidant dose in a wastewater (DDWW) at pH 8. For 17α-ethinylestradiol, Fe(VI) and O_3 showed almost the same elimination efficiency. An oxidant dose of 20 μM (~1 mg L^{-1} for Fe(VI) and O_3) achieved

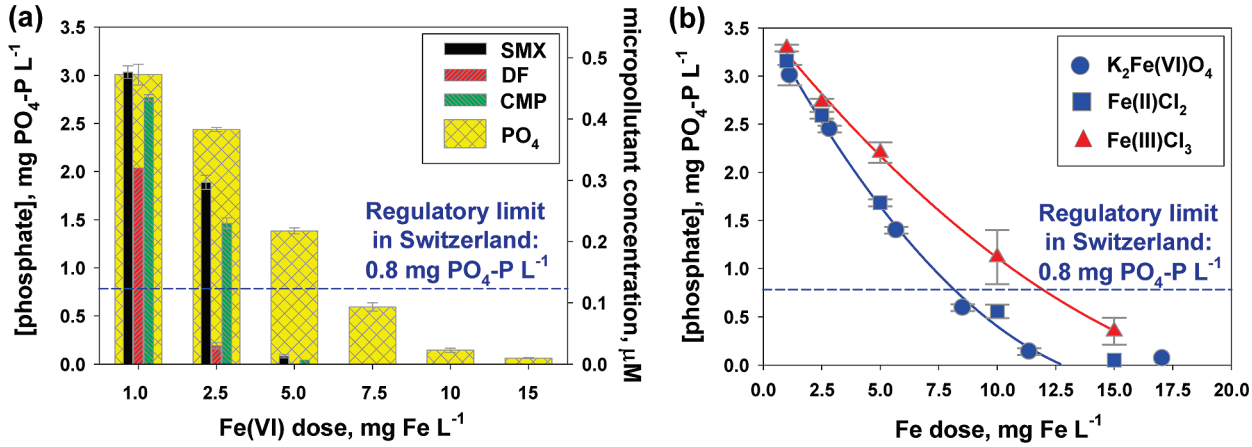


FIGURE 5. (a) Oxidative elimination of selected micropollutants and subsequent removal of phosphate during treatment of a wastewater (DDWW) as a function of the Fe(VI) dose (1.0−15 mg Fe L^{-1}) and (b) comparison of phosphate removal efficiency for various forms of iron. A standard jar test protocol was applied for ferric-phosphate precipitation (see the Materials and Methods section for details). Experimental conditions: $[micropollutants]_0$ = 0.5−1 μM, $[phosphate]_0$ = 3.5 mg PO_4−P L^{-1}, [DOC] = 5.1 mg C L^{-1}, pH = 7 (10 mM bicarbonate buffer), and T = 23 ± 2 °C. The blue dashed lines represent the regulatory limit for phosphate (0.8 mg PO_4−P L^{-1}) in effluents of wastewater treatment plants in Switzerland (*1*). Abbreviations: SMX = sulfamethoxazole, DF = diclofenac, and CMP = carbamazepine.

a >95% elimination of 17α-ethinylestradiol. For the other micropollutants, O_3 was more efficient than Fe(VI) within a factor of 3 in terms of oxidant dose required to achieve >95% elimination. The k values for Fe(VI) reactions with the investigated micropollutants in Figure 3 are several orders of magnitude lower than those for O_3 (Table 1). Nevertheless, the observed comparable elimination efficiency of Fe(VI) relative to O_3 can be understood because of the much higher stability of Fe(VI) in a wastewater matrix. As an example, Figure S14 shows the decrease of Fe(VI) and O_3 in a secondary effluent from a WWTP in Regensdorf, Switzerland at pH 8 for an oxidant dose of 40−45 μM. Fe(VI) was consumed within >30 min, whereas O_3 was completely consumed in less than 5 min.

Phosphate Removal from a Wastewater Matrix. Figure 5a demonstrates the ability of Fe(VI) to eliminate micropollutants and subsequently remove phosphate during treatment of DDWW. A Fe(VI) dose of 7.5 mg Fe L^{-1} lowered the phosphate concentration from initially 3.5 to below 0.8 mg PO_4−P L^{-1} (~80% removal), the regulatory limit for wastewater discharge in Switzerland. Selected micropollutants, sulfamethoxazole, diclofenac, and carbamazepine were eliminated >97% at a Fe(VI) dose of 5 mg Fe L^{-1}. It can be predicted that at Fe(VI) doses at which >80% removal of phosphate is achieved (≥8 mg Fe L^{-1}), many ERM-containing micropollutants can be significantly eliminated. Figure 5b compares the phosphate removal efficiency during treatment of DDWW with different forms of iron (Fe(VI), Fe(II), and Fe(III)). Fe(VI) shows a similar efficiency as Fe(II) and a slightly better efficiency than Fe(III) (within a factor of 1.5). This can be understood by considering a relative homogeneous formation of Fe(III) by Fe(VI) and Fe(II) leading to higher specific surface areas compared to Fe(III) where larger aggregates are formed (*2*).

Implications for Enhanced Wastewater Treatment. This study has demonstrated that Fe(VI) is a powerful tool to eliminate various micropollutants containing electron-rich moieties as well as to remove phosphate during enhanced treatment of secondary wastewater effluents. Fe(VI) doses required to achieve significant eliminations of micropollutants in the tested wastewater (e.g., > 5 mg Fe L^{-1} per 5 mg C L^{-1} of DOC) were lower than those for a significant phosphate removal (≥8 mg Fe L^{-1} for 3.5 to 0.8 mg PO_4−P L^{-1}, the regulatory limit for wastewater discharge in Switzerland). Therefore, a combined use of Fe(VI) and Fe(III) as an additional coagulant could be a practical method, since Fe(VI) is significantly more expensive than Fe(III). This study mainly focused on the application of Fe(VI) to secondary effluents to eliminate micropollutants and lower the phosphate level in the final effluent significantly (e.g., < 0.8 mg PO_4−P L^{-1}). The application of Fe(VI) can also be considered during primary or secondary treatment of wastewater. In this case, a higher consumption of Fe(VI) by higher concentrations of suspended (e.g. sludge) or dissolved organic matter is expected, which decreases the oxidation efficiency for micropollutants. Finally, for the wastewater treatment plants already practicing a chemical phosphorus removal, it can be straightforward to switch to a Fe(VI) treatment because the existing facilities for pumping and mixing can be used. However, technologies for on-site production of aqueous Fe(VI) and its rapid application are required because of the unstable nature of Fe(VI) in contact with water. Furthermore, additional research is needed to assess the feasibility of the Fe(VI) treatment process in pilot- or full-scale wastewater treatment plants.

Acknowledgments

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Supporting Information Available

Information addressing materials, experimental procedures, and additional data (Texts S1−S9 and Figures S1−S14). This material is available free of charge via the Internet at http://pubs.acs.org.

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