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Enhanced Degradation of Micropollutants in a Peracetic Acid−Fe(III) System with Picolinic Acid

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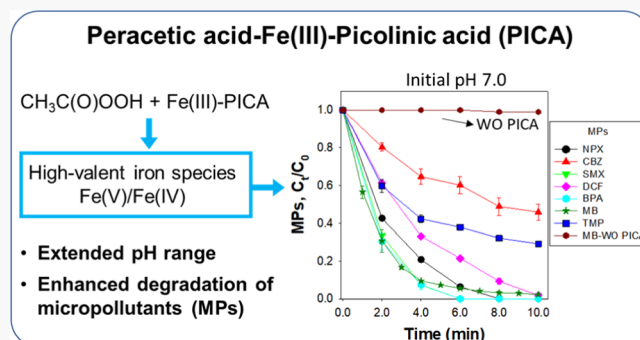
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ABSTRACT: Activation of peracetic acid (PAA) with iron species is an emerging advanced oxidation process (AOP). This study investigates the use of the chelating agent picolinic acid (PICA) to extend the pH range and enhance the performance of the PAA−Fe(III) AOP. Compared to the PAA−Fe(III) system, the PAA−Fe(III)−PICA system degrades various micropollutants (MPs: methylene blue, naproxen, sulfamethoxazole, carbamazepine, trimethoprim, diclofenac, and bisphenol-A) much more rapidly at higher pH, achieving almost complete removal of parent compounds within 10 min. PAA significantly outperforms the coexistent H_2O_2 and is the key oxidant for rapid compound degradation. Other chelating agents, EDTA, NTA, citric acid, proline, and nicotinic acid, could not enhance MP degradation in the PAA−Fe(III) system, while 2,6-pyridinedicarboxylic acid with a structure similar to PICA moderately enhanced MP degradation. Experiments with scavengers (*tert*-butyl alcohol and methyl phenyl sulfoxide) and a probe compound (benzoic acid) confirmed that high-valent iron species [Fe(IV) and/or Fe(V)], rather than radicals, are the major reactive species contributing to MP degradation. The oxidation products of methylene blue, naproxen, and sulfamethoxazole by PAA−Fe(III)−PICA were characterized and supported the proposed mechanism. This work demonstrates that PICA is an effective complexing ligand to assist the Fenton reaction of PAA by extending the applicable pH range and accelerating the catalytic ability of Fe(III).

KEYWORDS: peracetic acid, picolinic acid, Fenton-like reaction, high-valent iron species, Fe(V)/Fe(IV)

Peracetic acid-Fe(III)-Picolinic acid (PICA)

$CH_3C(O)OOH$ + Fe(III)-PICA

High-valent iron species Fe(V)/Fe(IV)

- Extended pH range
- Enhanced degradation of micropollutants (MPs)

INTRODUCTION

Peracetic acid [PAA, $CH_3C(O)OOH$] is a widely used oxidant/disinfectant in various industries, including medicine, food processing, textile, and pulp and paper industries.[1−4] PAA is also used in municipal wastewater treatment[5−7] owing to its disinfection effectiveness and little formation of toxic by-products compared to the conventional chlorine oxidants.[8,9] PAA has been applied in full-scale wastewater treatment plants (WWTPs) in the United States, Canada, and parts of Europe.[10−12] The global PAA market was worth $650 million in 2017 and is projected to grow to $1.3 billion by 2026, including a steady annual 8% increase in wastewater treatment usage.[13] More recently, PAA has been studied for the degradation of harmful micropollutants (MPs) in waste-water.[14−25] PAA itself is a highly selective oxidant toward chemical species with the reported rate constants ranging from 3.2×10^{-6} to $>1.0 \times 10^5$ $M^{-1}s^{-1}$.[26] However, PAA can be activated by energy or catalysts to generate highly reactive species which are capable of efficiently degrading a wide range of MPs. Previous studies have proposed the formation of radicals, including $^\bullet OH$, $CH_3C(O)O^\bullet$, and $CH_3C(O)OO^\bullet$, and high-valent metal species in the activated PAA systems.[21,22,27,28]

Previous research has employed a variety of metals, such as Fe(II/III/VI), Co(II/III), Mn(II/III/IV), Ru(III), and V(IV/V), to activate PAA.[16,20−22,29−31] Among them, Fe is environmentally abundant and benign. The Fenton reaction was first discovered by Fenton,[32] and it has been applied for pollution remediation since the late 1960s.[33] Fenton-related reactions with various oxidants (e.g., H_2O_2, persulfate, and PAA) have been extensively studied, and the formation of radicals (e.g., $^\bullet OH$, $HO_2^\bullet$, $SO_4^{\bullet-}$, and $CH_3C(O)O^\bullet$) have been well documented. Moreover, the generation of ferryl ($Fe^{IV}=O$) species especially under high pH conditions has been proposed based on the detection of nonhydroxylated degradation products and the minimal impact of radical scavengers.[34,35] In the Fe(III)−H_2O_2 system, it has been postulated that the generation of $Fe^{IV}=O$ species is derived by the homolytic O−O bond cleavage in the Fe^{III}−OOH

complex.[36] The formation of Fe(IV) is advantageous because Fe(IV) is less susceptible to scavengers compared to radicals such as $^{\bullet}OH$ and thus can have a longer lifetime in waters containing a variety of constituents to oxidize contaminants.[37]

However, the Fenton reactions have several limitations, one of which is that the solution pH should be maintained below 3.0 to avoid the formation of insoluble, much less reactive Fe(III) oxides. The acidification of water requires additional treatment processes to neutralize it before discharge, and it may cause other problems such as increased solution salinity, sludge formation, and release of harmful gases of sulfide or cyanide.[34,38] Chelating agents (CAs) can be used to render Fe ions soluble at neutral to alkaline pH by forming complexes. Efficient CAs should have at least two functional groups, such as NH_2 and $COOH$, which can donate a pair of electrons to the Fe cation. A variety of CAs, such as ethylenediaminetetraacetic acid (EDTA),[39−41] ethylenediamine-*N,N′*-disuccinic acid (EDDS),[41,42] and protocatechuic acid,[43] have been studied for Fenton-related oxidation. CAs can alter the Fe(III)/Fe(II) reduction potential via the preferential stabilization of one oxidation state over the other due to ligand-field effects,[44,45] which can affect the reactivity of the Fe(III) species with oxidants.[46] CAs may also compete with MPs for the reactive species.[44,47]

Many different types of pyridine derivatives have been applied as CAs in the fields of pharmaceuticals, medicine, and cosmetics; thus, they are frequently detected in wastewaters.[48,49] Picolinic acid (2-pyridinecarboxylic acid; PICA), one of the pyridine derivatives, is an intermediate metabolite of tryptophan. PICA has been well studied as a bidentate ligand to form complexes with divalent and trivalent metal ions, such as Cr, Zn, Mn, Cu, Mo, and Fe.[50] PICA includes the nitrogen atom in the pyridine ring and the oxygen atom in the carboxyl group, which can participate in the chelation of metal ions. Yang et al.[51] recently reported that PICA can assist in the reaction of Fe(III) with H_2O_2 to degrade atrazine, sulfamethazine, and substituted phenols at pH 5.5. They suggested that the $^{\bullet}OH$ radical and intermediate PICA−Fe(III)−OOH complex serve as the reactive species to degrade MPs in the H_2O_2−Fe(III)−PICA system. Their study motivated us to consider PICA among candidate CAs to enhance the PAA Fenton system, which has not been investigated previously.

This study was motivated to investigate whether CAs can facilitate the PAA−Fe(III) system for the degradation of MPs in water, especially under higher pH conditions. A variety of CAs [PICA, nicotinic acid (NA), 2,6-pyridinedicarboxylic acid (2,6-DCA), proline (PL), EDTA, and citric acid (CIA)] were investigated for the oxidation of a model compound (methylene blue, MB) in the PAA−Fe(III) system. As will be shown later, PICA exhibited the best effectiveness. Additional study objectives included (i) investigating the degradation of MB and representative MPs [naproxen (NPX) and sulfamethoxazole (SMX)] by the PAA−Fe(III)−PICA system in depth under various reaction conditions (i.e., solution pHs, molar ratios of Fe(III) to PAA, and buffers), (ii) identifying the major reactive species and reaction mechanism in the PAA−Fe(III)−PICA system by using scavengers and probe compounds, as well as determining oxidation products (OPs), and (iii) demonstrating the application of the PAA−Fe(III)−PICA oxidation process for the abatement of other MPs of different properties [carbamazepine (CBZ), trimethoprim (TMP), diclofenac

(DCF), and bisphenol-A (BPA)] in water and wastewater at higher pH.

EXPERIMENTAL SECTION

Chemicals. Sources of chemicals and reagents used in this study are provided in the Supporting Information Text S1.

Experimental Procedures. The Fe(III)−PICA solutions with different molar ratios ([Fe(III)]/[PICA] = 1.0:0.5−1.0:4.0) were prepared by adding 10.0 mM ferric sulfate into the PICA solution at the desired concentrations. The Fe(III)−PICA solutions were thoroughly mixed for 60 min.

The oxidation of MPs by the PAA−Fe(III)−PICA system was conducted in a 50 mL amber borosilicate reactor with magnetic stirring ([PAA]$_0$ = 100.0−500.0 μM, [Fe(III)]$_0$ = 50.0−400.0 μM, [PICA]$_0$ = 25.0−1000.0 μM, [MP]$_0$ = 15.0 μM). The reaction solution containing the MPs and oxidant (PAA or H_2O_2) was first prepared in the glass reactor, and the initial pH was adjusted by adding a few microliters of NaOH (1.0 M) and/or H_2SO_4 (1.0 M) into the solution. The degradation of MPs by PAA alone or H_2O_2 alone was confirmed to be negligible. Soon, the reaction was initiated by adding a desired amount of the Fe(III)−PICA solution, and sample aliquots were taken periodically up to 10 min. The MB concentration was immediately measured spectrophotometrically at 665 nm (Beckman DU 520 UV−visible spectrophotometer, Beckman Coulter, Inc., Fullerton, CA, USA). For other MPs, sample aliquots were added into vials containing excess $Na_2S_2O_3$ ([$Na_2S_2O_3$]/[PAA]$_0$ > 10.0) to quench the oxidant and stored at 5 °C prior to analysis. The solution pH was checked again after the reaction (10 min), and pH decrease was approximately 0.0−2.3 pH units for the initial pH 3.0−7.0, respectively.

The same reaction procedures were repeated for evaluating the influence of $^{\bullet}OH$ or high-valent iron species [Fe(V)/Fe(IV)] with scavengers [50.0 mM *tert*-butyl alcohol (TBA) or 5.0 mM methyl phenyl sulfoxide (PMSO)], which were added into the reaction solution before adding the Fe(III)−PICA solution. The oxidation of PMSO to PMSO$_2$ (methyl phenyl sulfone) was monitored. Benzoic acid (BA) was selected as a probe compound due to its inertness to Fe(V)/Fe(IV)[52] and investigated for degradation in the PAA−Fe(III)−PICA system. Different CAs (EDTA, CIA, NA, 2,6-DCA, and PL) and BA were also tested for their effects on degrading MB in the PAA−Fe(III) system and compared with PICA. Control experiments without Fe(III) and/or CAs were conducted to assess the degradation of MPs by PAA alone and PAA−Fe(III). Additionally, the degradation of three MPs (SMX, TMP, and BPA) was evaluated in the real wastewater sample (i.e., tertiary effluent from a municipal WWTP). The chemical properties of the MPs and probe compounds used in this study are provided in Supporting Information Table S1. All experiments were conducted in duplicate or more.

Analytical Methods. The PAA concentration was measured by the DPD method.[15,53] The cumulative Fe(II) concentrations were determined by the ferrozine method.[51,54] The concentrations of MPs were analyzed by high-performance liquid chromatography (HPLC) with UV detection. The reaction products were analyzed by HPLC coupled with time-of-flight high-resolution mass spectrometry (LC-HRMS) (Agilent Technologies, USA). The detailed methods are provided in Supporting Information Text S2.
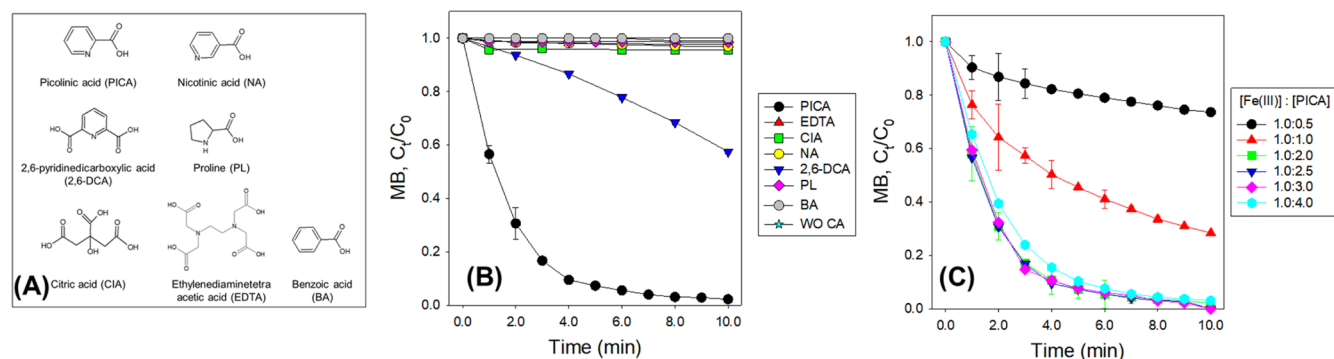
Figure 1. (A) Structures of CAs used in this study. (B) Effect of different CAs on MB degradation by PAA−Fe(III). (C) Effect of the molar ratios of Fe(III) to PICA on the degradation of MB by the PAA−Fe(III)−PICA oxidation process (experimental conditions: $[MB]_0 = 15.0\ \mu M$, $[PAA]_0 = 500.0\ \mu M$, $[Fe(III)]_0 = 50.0\ \mu M$, $[CA]_0 = 125.0\ \mu M$ for (A) and (B), $[PICA]_0 = 25.0-200.0\ \mu M$ for (C), initial pH = 5.04 ± 0.05, $T = 22 \pm 1$ °C).
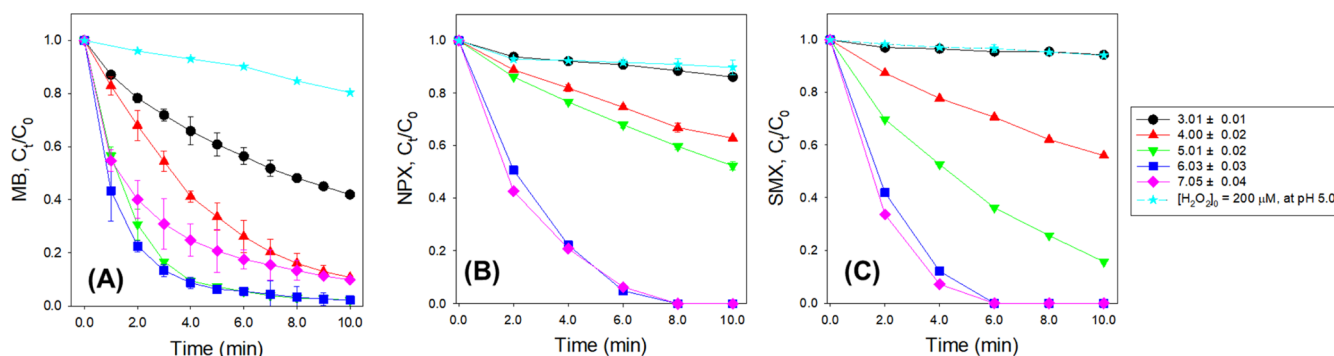

Figure 2. Effects of the initial pH on the degradation of MPs [MB (A), NPX (B), and SMX (C)] by PAA−Fe(III)−PICA (experimental conditions: $[MP]_0 = 15.0\ \mu M$, $[PAA]_0 = 500.0\ \mu M$, $[Fe(III)]_0 = 50.0\ \mu M$, $[PICA]_0 = 125.0\ \mu M$, $T = 22 \pm 1$ °C).

■ RESULTS AND DISCUSSION

PAA−Fe(III) System with Various CAs. The effects of six CAs (PICA, NA, 2,6-DCA, PL, EDTA, and CIA, Figure 1A), as well as BA, on the degradation of MB by the PAA−Fe(III) system were investigated (Figure 1B), where the [Fe(III)]/[CA] molar ratio was 1:2.5 (conditions: $[MB]_0 = 15.0\ \mu M$, $[PAA]_0 = 500.0\ \mu M$, $[Fe(III)]_0 = 50.0\ \mu M$, $[CA]_0 = 125\ \mu M$, pH = 5.0). Note that the PAA−Fe(III) system without the CA led to a minimal removal of MB. The initial first-order rate constant ($k_{initial}$ in min^{-1}) was obtained from the slope of $\ln C_t/C_o$ versus time during the initial stage of the reaction where the reaction kinetics could be approximated by pseudo-first-order kinetics (Supporting Information Table S3). The degradation % of MB ($[MB]_{removal,\%}$) was also calculated for 10 min of reaction time.

Based on $k_{initial}$ and $[MB]_{removal,\%}$, PICA was the most efficient CA to enhance MB degradation by the PAA−Fe(III) system. PICA has one N atom in the pyridine ring and a carboxyl substituent at position 2, where N and O donors can bind with the Fe(III) ion to form a stable five-membered chelate ring.[55,56] The N atom in the pyridine ring has σ-donor (and weak π-acceptor) properties, which enhances the nucleophilicity of the metal center and increases the catalytic activity of the metal complex.[56] Compared to PICA, NA, also containing the pyridine ring but with the carboxyl substituent at position 3, showed limited chelating efficiency due to the fact that N and O atoms are too far apart to chelate the iron atom. Thus, NA complexation with Fe(III) is likely similar to that of carboxylates, such as BA. The binding of Fe(III) with

NA or BA showed little effect to improve the catalytic activity of Fe(III). 2,6-DCA showed lower promoting effect than PICA but greater than the other ligands. 2,6-DCA contains the pyridine ring and two carboxyl substituents at positions 2 and 6. It is likely that the electron-withdrawing effect of the additional carboxyl group at position 6 decreases the electron density of the ring. PL has the N atom in the pyrrolidine ring with the carboxyl substituent at position 2, and thus, it can possibly form a five-membered chelate ring with the iron atom, and the stability constants of PL for metal complexation have been reported to be similar to those of PICA.[57] Nonetheless, the impact of PL on promoting MB degradation by the PAA−Fe(III) system was negligible compared to PICA. EDTA is one of the aminopolycarboxylic acids and contains two N and four O donors for coordinating with metal ions. Several studies have reported that EDTA can form the Fe(III)−EDTA complex with a high stability constant (log K = 25.1).[58] However, EDTA did not enhance MB degradation by the PAA−Fe(III) system. CIA including three carboxyl groups and one hydroxyl group also showed limited impact on the PAA−Fe(III) oxidation system.

Degradation of MB, NPX, and SMX by the PAA−Fe(III)−PICA System. Among the CAs, PICA was the most efficient to promote the PAA−Fe(III) oxidation system and thus was further investigated. Note that the doses of PAA (100.0−500.0 μM) are comparable to PAA dosages used in wastewater disinfection processes.[59]

Effect of the Fe(III)-to-PICA Molar Ratio. The effect of the molar ratios of Fe(III) to PICA on MB degradation in the PAA−Fe(III)−PICA system was investigated (Figure 1C and
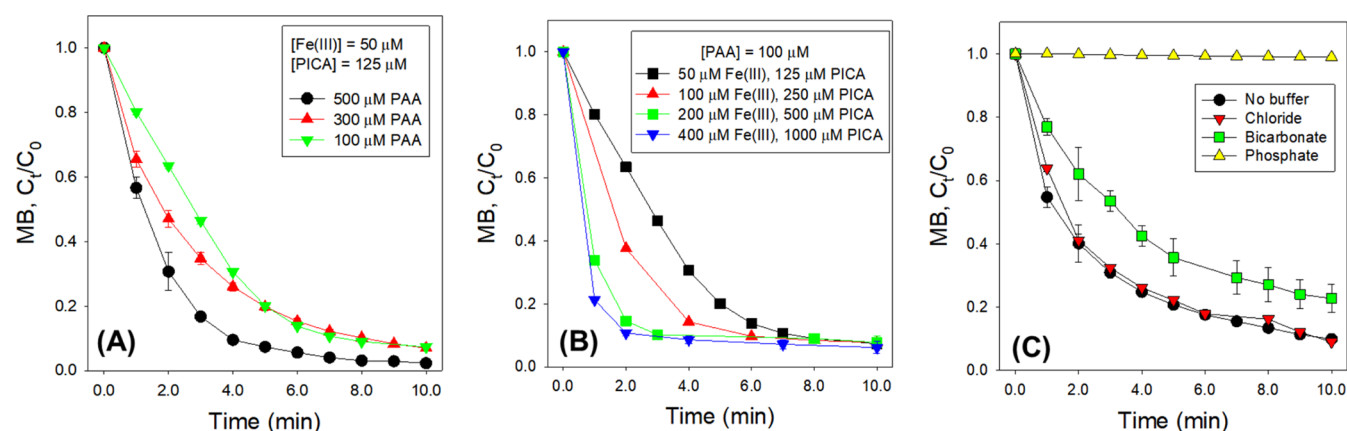
Figure 3. Effects of the molar ratio of Fe(III) to PAA (A,B) and buffers (C) on the degradation of MB by the PAA−Fe(III)−PICA oxidation process (experimental conditions: $[MB]_0 = 15.0$ μM, $[PAA]_0 = 100-500.0$ μM, $[Fe(III)]_0 = 50.0-400.0$ μM $[PICA]_0 = 125.0-1000.0$ μM, initial pH = 5.04 ± 0.05 for (A,B), $[MB]_0 = 15.0$ μM, $[PAA]_0 = 500.0$ μM, $[Fe(III)]_0 = 50.0$ μM, $[PICA]_0 = 125.0$ μM, initial pH = 7.04 ± 0.03, [buffer] = 10 mM for (C), $T = 22 \pm 1$ °C).

Supporting Information Table S4, conditions: $[MB]_0 = 15.0$ μM, $[PAA]_0 = 500.0$ μM, $[Fe(III)]_0 = 50.0$ μM, $[PICA]_0 = 25.0-200.0$ μM, initial pH = 5.0). The increase of the $[Fe(III)]/[PICA]$ ratio from 1.0:0.5 to 1.0:2.0 led to the increase in both $k_{initial}$ and $[MB]_{removal,\%}$ [$k_{initial}$ from $(5.01 \pm 0.46) \times 10^{-2}$ to $(5.48 \pm 0.01) \times 10^{-1}$ min^{-1} and $[MB]_{removal,\%}$ from 26 to 98%]. The $[Fe(III)]/[PICA]$ ratios from 1.0:2.0 to 1.0:3.0 showed similar $k_{initial}$ values and $[MB]_{removal,\%}$ [$(k_{initial} = (5.48 \pm 0.01) \times 10^{-1}-(5.60 \pm 0.01) \times 10^{-1}$ min^{-1} and $[MB]_{removal,\%} = 98-100\%$)]. However, the increase of the $[Fe(III)]/[PICA]$ molar ratio up to 1:4 led to a slight decrease in the $k_{initial}$ value [$k_{initial} =$ from $(5.51 \pm 0.02) \times 10^{-1}$ to $(4.62 \pm 0.00) \times 10^{-1}$ min^{-1}]. This result indicates that the optimum stoichiometry of the Fe(III)−PICA complex is in the range of 1.0:2.0−1.0:3.0, and PICA can scavenge reactive species when it is in excess. Indeed, the formation of the 1:2 and 1:3 complexes of Fe(III) and PICA [i.e., Fe(PICA)$_2$, Fe(PICA)$_3$, Fe(PICA)$_2$OH, and Fe$_2$(PICA)$_4$(OH)$_2$] was reported.[60,61] Yang et al.[51] also reported similar results showing the highest degradation rate of atrazine at a $[Fe(III)]/[PICA]$ ratio of 1.0:2.5 by the H$_2$O$_2$−Fe(III)-PICA system (conditions: $[atrazine]_0 = 5.0$ μM, $[H_2O_2]_0 = 4000.0$ μM, $[Fe(III)]_0 = 35.0$ μM, $[PICA]_0 = 35.0-350.0$ μM, pH = 5.5).

Effect of the Initial pH. The degradation of three MPs (MB, NPX, and SMX) by the PAA−Fe(III)−PICA system was investigated in the pH range of 3.0−7.0 (Figure 2, conditions: $[MP]_0 = 15.0$ μM, $[PAA]_0 = 500.0$ μM, $[Fe(III)]_0 = 50.0$ μM, $[PICA]_0 = 125.0$ μM). The PAA−Fe(III) system without PICA led to little degradation of these MPs at pH 5.0 (<3%, data not shown), which is likely due to the formation of insoluble Fe(III) oxides. In contrast, the addition of PICA significantly enhanced the degradation of MB, NPX, and SMX, confirming again that PICA is a good CA for promoting the catalytic ability of Fe(III) for PAA. The $k_{initial}$ values of MP degradation by PAA−Fe(III)−PICA were $(1.05 \pm 0.03) \times 10^{-1}-(6.06 \pm 0.03) \times 10^{-1}$ min^{-1}, $(1.84 \pm 0.24) \times 10^{-2}-(4.55 \pm 0.37) \times 10^{-1}$ min^{-1}, and $(8.50 \pm 1.04) \times 10^{-3}-(6.35 \pm 0.32) \times 10^{-1}$ min^{-1} for MB, NPX and SMX, respectively (Supporting Information Table S5). The $k_{initial}$ values were in the order pH 5.0−6.0 > pH 7.0 > pH 4.0 > pH 3.0 for MB and pH 6.0−7.0 > pH 5.0 > pH 4.0 > pH 3.0 for NPX and SMX, and complete degradation was observed in 10 min at pH 5.0−6.0 for MB and pH 6.0−7.0 for NPX and SMX.

The initial pH can alter the speciation of both PICA and MPs. The deprotonated species fraction of NPX (pK_a = 4.1) and SMX (pK_2 = 5.7) increased ($f_{NPX^-} = 0.07-1.00$, and $f_{SMX^-} = 0.00-0.95$) from pH 3.0 to 7.0, but MB (pK_a < 1.0) speciation was hardly changed ($f_{MB^-} = 1.00$). Deprotonated MPs are more susceptible to oxidation by reactive species; thus, NPX and SMX were less degraded at acidic pH, compared to higher pHs. Meanwhile, the ligand can be a poorer σ-donor when it is protonated;[62] thus, PICA should have less ability to form the complex with Fe(III) at acidic pH. Note that the reported pK_a value of PICA is 5.3 for pyridinium N,[51] and Fe(III)−PICA could have a lower pK_a when PICA is bound to Fe(III). These can explain the less degradation of MB, NPX, and SMX at acidic pH, compared to higher pHs. Meanwhile, PAA speciation is minimally changed in the pH range of 3.0−7.0 (neutral species fraction of PAA = 1.00−0.94) and should have limited impact.

Fe(III) can be subjected to the hydrolytic precipitation at high pH, which can cause target the MPs to adsorb and have effects on Fe(III) complexation with PICA. Note that the adsorption of MB to the Fe(III) precipitates was not significant, and preequilibration of Fe(III)−PICA−MB prior to adding PAA only slightly retarded the initial MB degradation and had a negligible effect on the overall MB degradation (Supporting Information Figure S1).

Effect of Coexistent H$_2$O$_2$. The PAA solution contained about 32% PAA and 5% H$_2$O$_2$ (w/w); thus, 185.0 μM H$_2$O$_2$ was present in a 500.0 μM PAA solution. It is important to note that the degradation of MB, NPX, and SMX by H$_2$O$_2$−Fe(III)−PICA was much slower than that by PAA−Fe(III)−PICA (Figure 2, conditions: $[MP]_0 = 15.0$ μM, $[H_2O_2]_0 = 200.0$ μM, $[Fe(III)]_0 = 50.0$ μM, $[PICA]_0 = 125.0$ μM, initial pH = 5.0). This result indicates that H$_2$O$_2$ present in the PAA solution played a minimal role in degrading MPs in the PAA−Fe(III)−PICA system.

Effects of PAA and Fe(III) Dosages. MB was selected to study the effect of the molar ratio of $[Fe(III)]/[PAA]$ on compound degradation by the PAA−Fe(III)−PICA system. Note that MB was almost completely degraded within 10 min with $[PAA]_0 = 100.0-500.0$ μM and $[Fe(III)]_0 = 50.0-400.0$ μM (Figure 3A,B). The effect of PAA dosages (100.0/300.0/500.0 μM) was investigated at initial pH 5.0 while maintaining $[Fe(III)]_0$ at 50.0 μM and $[PICA]_0$ at 125.0 μM (Figure 3A).
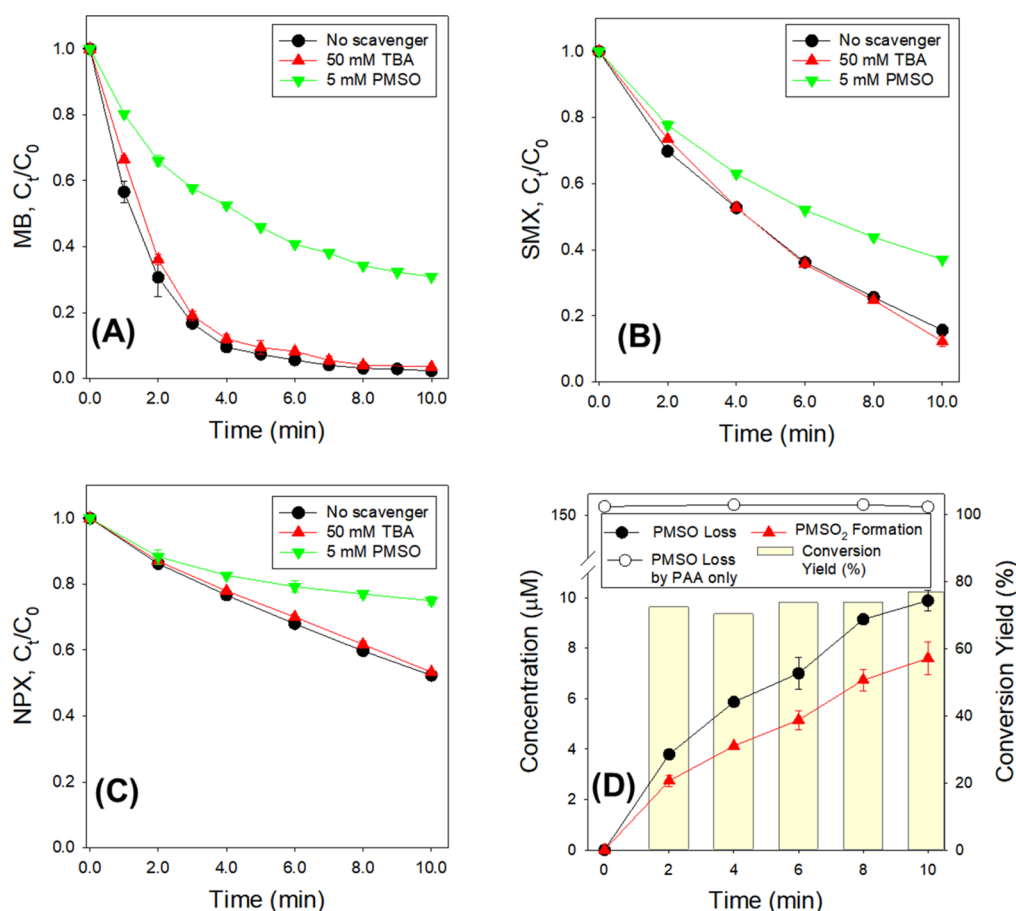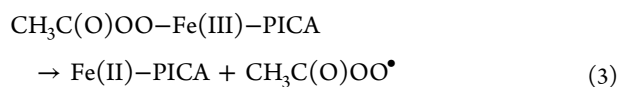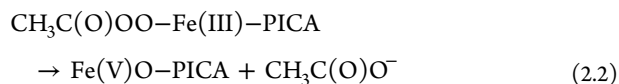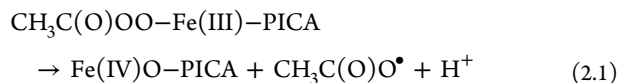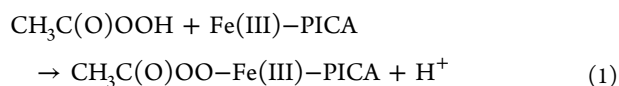
Figure 4. Degradation of MPs [MB (A), NPX (B), and SMX (C)] by PAA−Fe(III)−PICA in the presence and absence of scavengers. (D) PMSO loss ($[PMSO]_0-[PMSO]_t$) and $PMSO_2$ formation ($[PMSO_2]_t$) by the PAA−Fe(III)−PICA oxidation process. Empty dots show the change in the PMSO concentration ($[PMSO]_t$) by PAA alone, and vertical bars indicate the conversion yield (%, $\Delta[PMSO_2]/\Delta[PMSO]$) (experimental conditions for (A−C): $[MP]_0 = 15.0\ \mu M$, $[PAA]_0 = 500.0\ \mu M$, $[Fe(III)]_0 = 50.0\ \mu M$, $[PICA]_0 = 125.0\ \mu M$, $[TBA]_0 = 0$ or 50.0 mM, $[PMSO]_0 = 0$ or 5.0 mM, initial pH $= 5.02 \pm 0.04$. (D): $[PMSO]_0 = 150\ \mu M$, $[PAA]_0 = 200.0\ \mu M$, $[Fe(III)]_0 = 100.0\ \mu M$, $[PICA]_0 = 100.0\ \mu M$, initial pH $= 5.02 \pm 0.01$. $T = 22 \pm 1\ °C$).

The $k_{initial}$ value increased from $(2.72 \pm 0.14) \times 10^{-1}$ to $(5.60 \pm 0.01) \times 10^{-1}$ min^{-1} when the PAA concentration was increased from 100.0 to 500.0 μM (Supporting Information Table S3). The effect of Fe(III) dosages (50.0/100.0/200.0/400.0 μM) was investigated at the initial pH 5.0 while fixing $[PAA]_0$ at 100.0 μM (Figure 3B). The $k_{initial}$ value increased from $(2.72 \pm 0.14) \times 10^{-1}$ to $(1.20 \pm 0.12) \times 10^{0}$ min^{-1} when the Fe(III) concentration was increased from 50.0 to 400.0 μM (Supporting Information Table S3). However, the $k_{initial}$ value was not linearly related to the increase of the Fe(III) concentration, suggesting that MB degradation was inhibited at a high concentration of Fe(III), possibly due to the scavenging of the reactive species by excess Fe(III).

Effects of Water Matrix Constituents. The effects of chloride (Cl^-), bicarbonate (HCO_3^-), and phosphate ($H_2PO_4^-/HPO_4^{2-}$) (10 mM) on MB degradation by PAA−Fe(III)−PICA were investigated at the initial pH 7.0 (Figure 3C). Note that the initial pH was set after adding anions. Control experiments confirmed that MB was not degraded by PAA−Cl^-, PAA−HCO_3^-, PAA−$H_2PO_4^-/HPO_4^{2-}$, Fe(III)−PICA−Cl^-, Fe(III)−PICA−HCO_3^-, and Fe(III)−PICA−$H_2PO_4^-/HPO_4^{2-}$ (data not shown). For the PAA−Fe(III)−PICA system, the presence of Cl^- had little impact on MB degradation, which agrees well with the minimal influence of Cl^- on the PAA−Co(II) and PAA−Ru(III) reaction

systems.[20,22,25] HCO_3^- moderately retarded MB degradation [$k_{initial}$ decreasing from $(5.60 \pm 0.01) \times 10^{-1}$ to $(2.12 \pm 0.05) \times 10^{-1}$ min^{-1}] and reduced the overall abatement from 90 to 77%. Compared to Cl^- and HCO_3^-, $H_2PO_4^-/HPO_4^{2-}$ completely inhibited MB degradation by PAA−Fe(III)−PICA. Previous research showed that HCO_3^-, $H_2PO_4^-/HPO_4^{2-}$ significantly inhibited compound degradation by PAA−Co(II) but minimally influenced the PAA−Ru(III) and UV−PAA systems.[18,20,22] The impacts of buffers on compound degradation by PAA−Fe(III)−PICA are likely due to their competition with PICA and characteristics in complexing Fe(III); thus, the concentration of free ferric ions is diminished. Note that the stability constant (log $K_{Fe(III)-L}$) of Fe(III)−$PICA^-$ is 6.02[61] versus 0.61 for Fe(III)−Cl^-,[63] 7.7 for Fe(III)−CO_3^{2-},[64] $\sim$3.5 for Fe(III)−$H_2PO_4^-$,[65] and 10.6 for Fe(III)−HPO_4^{2-}.[66] HCO_3^- and $H_2PO_4^-/HPO_4^{2-}$ are expected to have significant competition effect at the employed buffer concentration (10.0 mM).
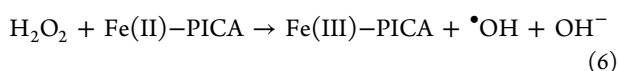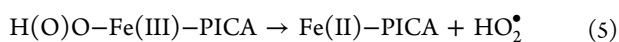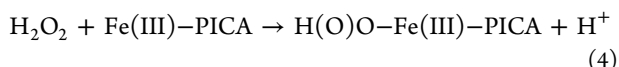
Reactive Species in the PAA−Fe(III)−PICA System. In the reactions of PAA with Fe(III)−PICA, it is likely that the initial complex of $CH_3C(O)OO$−Fe(III)−PICA is formed (eq 1), which could further decompose to form Fe(IV), Fe(V), and/or radicals $CH_3C(O)O^\bullet/CH_3C(O)OO^\bullet$ (eqs 2−3)

$$CH_3C(O)OOH + Fe(III)-PICA$$
$$\rightarrow CH_3C(O)OO-Fe(III)-PICA + H^+ \tag{1}$$

$$CH_3C(O)OO-Fe(III)-PICA$$
$$\rightarrow Fe(IV)O-PICA + CH_3C(O)O^\bullet + H^+ \tag{2.1}$$

$$CH_3C(O)OO-Fe(III)-PICA$$
$$\rightarrow Fe(V)O-PICA + CH_3C(O)O^- \tag{2.2}$$

$$CH_3C(O)OO-Fe(III)-PICA$$
$$\rightarrow Fe(II)-PICA + CH_3C(O)OO^\bullet \tag{3}$$

First, the contribution of high-valent iron species [Fe(IV) and Fe(V)] to target MPs' degradation by PAA−Fe(III)−PICA was evaluated by adding PMSO (conditions: $[MPs]_0 = 15.0 \ \mu M$, $[PAA]_0 = 500.0 \ \mu M$, $[Fe(III)]_0 = 50.0 \ \mu M$, $[PICA]_0 = 125.0 \ \mu M$, $[PMSO]_0 = 5.0$ mM, initial pH = 5.0, Figure 4A−C). The addition of PMSO inhibited the degradation of MPs by 25.4−47.5%. Moreover, PMSO was degraded over time with a high conversion yield (76.8%) to $PMSO_2$ (Figure 4D). It is known that high-valent iron species [Fe(IV) and Fe(V)] can oxidize PMSO to $PMSO_2$ via the oxygen atom transfer reaction ($k_{app,Fe(IV)/PMSO} = 2.58 \times 10^3 \ M^{-1}s^{-1}$),[67] which is different from the reaction of radicals with PMSO via one-electron transfer to generate hydroxylated PMSO and/or biphenyl compounds.[35] Thus, the PMSO study strongly suggests that Fe(IV)/Fe(V) are the major reactive species, rather than radicals.
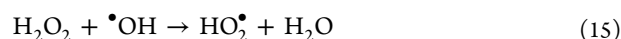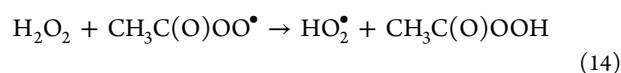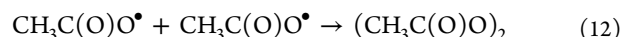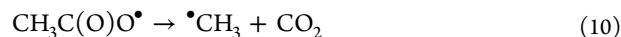
Among the radicals, the contribution of $CH_3C(O)O^\bullet$ is likely limited because $CH_3C(O)O^\bullet$ when formed can rapidly self-decay to $^\bullet CH_3$ and CO_2 ($k = (1-2.3) \times 10^5 \ s^{-1}$),[27,68] leading to a very low concentration of this radical. We used benzoic acid (BA) as a probe compound to evaluate the contribution of $CH_3C(O)OO^\bullet$ in the PAA−Fe(III)−PICA system because high-valent iron species have limited reactivity toward BA ($k_{app,Fe(IV)/BA} = 80.0 \ M^{-1}s^{-1}$).[52] Experiments found that BA was not degraded by PAA−Fe(III)−PICA (conditions: $[BA]_0 = 15.0 \ \mu M$, $[PAA]_0 = 200.0 \ \mu M$, $[Fe(III)]_0 = 50.0 \ \mu M$, $[PICA]_0 = 125.0 \ \mu M$, initial pH = 5.0, Supporting Information Figure S2A). On the other hand, BA was efficiently degraded by UV−PAA in the presence of TBA (conditions: $[BA]_0 = 40.0 \ \mu M$, $[PAA]_0 = 200.0 \ \mu M$, $[TBA]_0 = 10.0$ mM, initial pH = 6.0, Supporting Information Figure S2B). The UV−PAA system generates $CH_3C(O)OO^\bullet$, $CH_3C(O)O^\bullet$, and $^\bullet OH$ radicals, and adding 10.0 mM TBA efficiently scavenges $^\bullet OH$ and may lower the $CH_3C(O)OO^\bullet$ concentration.[15,27] The significant degradation of BA by UV−PAA−TBA along with the minimal removal of BA by PAA−Fe(III)−PICA further confirms that the major reactive species are Fe(IV)/Fe(V), rather than $CH_3C(O)OO^\bullet$ radicals.

The potential formation of $^\bullet OH$ in the PAA−Fe(III)−PICA system should be considered as well owing to the presence of H_2O_2 (eqs 4−6)

$$H_2O_2 + Fe(III)-PICA \rightarrow H(O)O-Fe(III)-PICA + H^+ \tag{4}$$

$$H(O)O-Fe(III)-PICA \rightarrow Fe(II)-PICA + HO_2^\bullet \tag{5}$$

$$H_2O_2 + Fe(II)-PICA \rightarrow Fe(III)-PICA + {}^\bullet OH + OH^- \tag{6}$$

However, the minimal impact of TBA (50.0 mM) on MPs' removal (Figure 4A−C) confirmed that there was little contribution of $^\bullet OH$ to the degradation of MPs in the PAA−Fe(III)−PICA system.

Additionally, other reactions to be considered are described in eqs 7−15, which may generate certain secondary radicals.

$$CH_3C(O)OOH + CH_3C(O)O^\bullet$$
$$\rightarrow CH_3C(O)OO^\bullet + CH_3C(O)OH \tag{7}$$

$$CH_3C(O)OOH + {}^\bullet OH \rightarrow CH_3C(O)OO^\bullet + H_2O \tag{8}$$

$$CH_3C(O)OOH + {}^\bullet OH \rightarrow HO_2^\bullet + CH_3C(O)OH \tag{9}$$

$$CH_3C(O)O^\bullet \rightarrow {}^\bullet CH_3 + CO_2 \tag{10}$$

$${}^\bullet CH_3 + O_2 \rightarrow CH_3OO^\bullet \tag{11}$$

$$CH_3C(O)O^\bullet + CH_3C(O)O^\bullet \rightarrow (CH_3C(O)O)_2 \tag{12}$$

$$CH_3C(O)OO^\bullet \rightarrow HO_2^\bullet + CH_2CO \tag{13}$$

$$H_2O_2 + CH_3C(O)OO^\bullet \rightarrow HO_2^\bullet + CH_3C(O)OOH \tag{14}$$

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \tag{15}$$
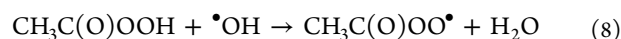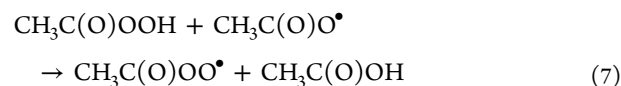
However, the secondary radicals, such as $HO_2^\bullet/O_2^{\bullet-}$, $^\bullet CH_3$, and $CH_3OO^\bullet$, should have minor contributions to MPs' degradation because of low reactivities ($k_{HO_2^\bullet/MPs} \approx 0-10^8 \ M^{-1} \ s^{-1}$,[69] $k_{CH_3OO^\bullet/MPs} \approx 10^5-10^7 \ M^{-1} \ s^{-1}$)[70] and the rapid reaction with O_2 ($k_{^\bullet CH_3/O_2} = 4.1 \times 10^9 \ M^{-1} \ s^{-1}$).[71]

The generation of Fe(II) in the PAA−Fe(III)−PICA system was investigated by determining the cumulative Fe(II) concentration (conditions: $[PAA]_0 = 500.0 \ \mu M$, $[Fe(III)]_0 = 50.0 \ \mu M$, $[PICA]_0 = 125.0 \ \mu M$, $[ferrozine]_0 = 300.0 \ \mu M$, initial pH = 5.0, Supporting Information Figure S3A). Note that Fe(II) can be formed via eq 3 and/or eq 5 in the PAA−Fe(III)−PICA system. The cumulative Fe(II) concentration was only about 1.3 μM within 10 min in PAA−Fe(III)−PICA, and there was no significant difference in the cumulative Fe(II) concentration between the PAA−Fe(III)−PICA and the H_2O_2−Fe(III)−PICA systems ($[H_2O_2]_0 = 200.0 \ \mu M$, which was close to the background concentration in the 500.0 μM PAA solution). These results indicate that Fe(II) formation by the reaction of Fe(III)−PICA with PAA (eq 3) is minimal, which is different from the H_2O_2−Fe(III)−PICA system (eq 5), showing the significant formation of Fe(II) as reported previously.[51]

Decay of PAA and H_2O_2 was also monitored in the PAA−Fe(III)−PICA system (conditions: $[PAA]_0 = 500.0 \ \mu M$, $[Fe(III)]_0 = 50.0 \ \mu M$, $[PICA]_0 = 125.0 \ \mu M$, initial pH = 5.0, Supporting Information Figure S3B). The PAA loss was about 20% in 10 min, which was greater than the Fe(III) concentration. This suggests that PAA can be additionally consumed by $^\bullet OH$ and/or Fe(IV)/Fe(V), which can compete with the MPs. Meanwhile, H_2O_2 loss in the PAA−Fe(III)−PICA system was minimal (only <1%), confirming that the reaction of PAA with Fe(III)−PICA significantly outperforms H_2O_2.

Abatement of the MPs by PAA−Fe(III)−PICA. The degradation of additional four MPs (CBZ, TMP, DCF, and BPA) and MB, NPX, and SMX by PAA−Fe(III)−PICA was evaluated at pH 7.0 (conditions: $[MPs]_0 = 15.0 \ \mu M$, $[PAA]_0 = $
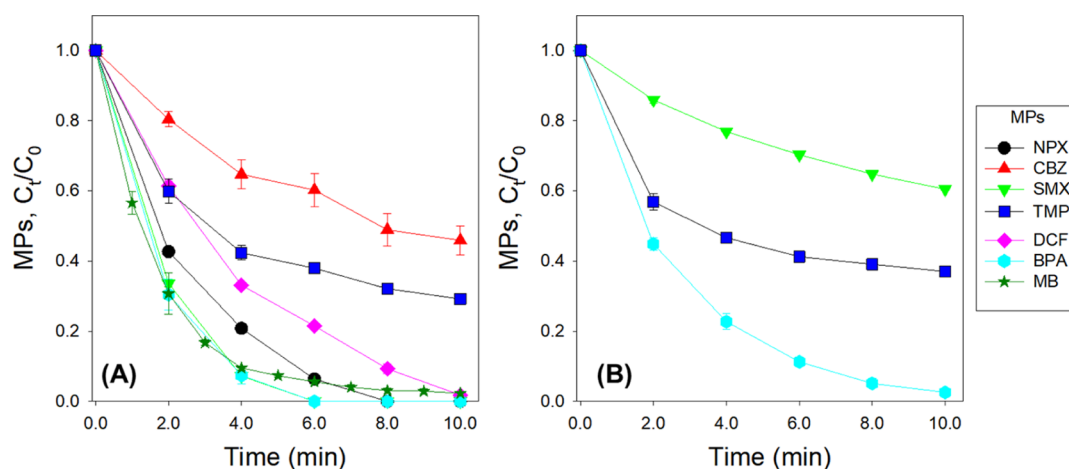
Figure 5. Degradation of MPs in reagent water (A) and tertiary effluent from a WWTP (B) by the PAA−Fe(III)−PICA oxidation process (experimental conditions: $[MP]_0 = 15.0\ \mu M$, $[PAA]_0 = 500.0\ \mu M$, $[Fe(III)]_0 = 50.0\ \mu M$, $[PICA]_0 = 125.0\ \mu M$, initial pH = 7.03 ± 0.02 for (A), pH 6.51 ± 0.06 for (B), T = 25 ± 1 °C). MPs: MB-methylene blue, NPX: naproxen, SMX: sulfamethoxazole, CBZ: carbamazepine, TMP: trimethoprim, DCF: diclofenac, and BPA : bisphenol-A.

$500.0\ \mu M$, $[Fe(III)]_0 = 50.0\ \mu M$, $[PICA]_0 = 125.0\ \mu M$, initial pH = 7.0, Figure 5A, Supporting Information Tables S5 and S6). Based on the $k_{initial}$ values and $[MP]_{removal,\%}$ at 10 min, the removal efficiency was in the order SMX ∼ BPA ∼ MB ∼ NPX > DCF > TMP > CBZ. The rate constants for the reaction of high-valent iron species with MPs are scarcely reported, but it is known that Fe(IV) can react with aromatic compounds, such as phenol, nitrophenols, and nitrobenzene, with a rate constant of ∼$10^4\ M^{-1}\ s^{-1}$.[72] Moreover, it has been reported that compounds containing aniline, phenolic, and amine groups have relatively high reactivity with high-valent iron species.[73,74] Luo et al.[75] also reported the rapid oxidation of amine-containing compounds by Fe(IV) at pH 9.0 with the estimated rate constants of 7.9×10^4, 8.3×10^4, and $1.3\ M^{-1}s^{-1}$ for SMX, TMP, and CBZ, respectively. The results in this study also showed slower degradation of CBZ and relatively faster degradation of SMX, DCF, TMP, BPA, and MB containing phenol, aniline, and/or amine moieties.

Additional experiments with NPX, TMP, and BPA in tertiary wastewater effluent showed >40% of MPs' removal by PAA−Fe(III)−PICA (Figure 5B). Note that the solution pH of tertiary wastewater effluent was 6.51, and the concentration of NH_3−N was about 0.5 mg·L^{-1}, that of total-P was 0.03 mg·L^{-1}, and that of TOC was 6.0 mg·L^{-1}.

Oxidation Products. The OPs of three compounds (MB, NPX, and SMX) in the PAA−Fe(III)−PICA system were identified by LC-HRMS. Supporting Information Table S7 and Figures S4−S9 show the retention time, accurate masses, ion fragments, evolution of the products with time, and proposed structures of the products. Overall, the hydrated products of three compounds were detected, which could be formed via electron transfer by high-valent iron species.[16,52,76] The products of MB included OP-M228 and OP-M270 (the demethylated products), OP-M256 (formed via methyl cleavage from the dimethylamino groups), and OP-M300 (the hydroxylated product). The detected products of NPX were OP-N201, OP-N215, and OP-N233 (formed by demethylation and/or subsequent hydroxylation), and OP-N185 (generated by decarboxylation and the subsequent β-elimination reaction). Similar products of MB and NPX have also been found in the PAA−Fe(II) system, which was previously reported to generate high-valent iron species.[16] The

products of SMX included OP-S270, OP-284, OP-300 (formed via the hydroxylation of the benzene ring and/or aniline ring oxidation), and OP-S99 (formed by the S−N bond cleavage). It was also reported that the S−N bond cleavage, hydroxylation, and aniline ring oxidation pathways of SMX are predominant in the systems generating high-valent iron species.[75,77]

Environmental Significance and Implications. This study demonstrated that, compared to other common CAs, PICA in combination with PAA−Fe(III) can significantly enhance MP degradation by providing the benefits of extending the working pH to a higher pH range, increasing the catalytic ability of Fe(III) toward PAA and maintaining reaction effectiveness in real water matrices. While only PAA−Fe(III) is unable to degrade MPs at higher pH, the PAA−Fe(III)−PICA system is a promising advanced oxidation process to degrade a range of MPs with different properties. The reaction of PAA with Fe(III)−PICA complex out-performed the coexistent H_2O_2, leading to faster MPs' degradation compared to H_2O_2−Fe(III)−PICA. The in-depth evaluation confirmed that the major reactive species contributing to MPs' degradation by PAA−Fe(III)−PICA were selective high-valent iron species [i.e., Fe(IV) and/or Fe(V)], rather than radicals, which would be less susceptible to water matrix's scavenging effects owing to their higher selectivity.

Compared to toxic and nonbiodegradable aminopolycarboxylic acid-type CAs (e.g., EDTA), PICA is biodegradable and has relatively less adverse environmental consequences.[51,78] Meanwhile, Fe(III) is ubiquitous and environmentally benign in natural aquatic and soil environments. Thus, the PAA−Fe(III)−PICA oxidation process is worth of further exploring as an advanced oxidation technology that can rapidly remove MPs in a circumneutral pH range and environmental matrices. Further research should assess the optimal conditions for practical application, taking into account the effects of anions on the complex formation between Fe(III) and PICA in environmental waters, as well as PICA toxicity and biodegradation..

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c08311.

Chemicals and reagents; analytical methods; chemical properties of micropollutants and probe compounds; chemical properties of chelating agents; initial reaction rate constants ($k_{initial}$) of degradation of MB by PAA–Fe(III)–CAs at the initial pH 5.0 and 22 °C; initial reaction rate constants ($k_{initial}$) of degradation of MB by PAA–Fe(III)–PICA at the initial pH 5.0 and 22 °C; initial reaction rate constants ($k_{initial}$) of degradation of MB, NPX, and SMX by PAA–Fe(III)–PICA at the initial pH 3.0–7.0 and 22 °C; initial reaction rate constants ($k_{initial}$) of degradation of additional four MPs (BPA, DCF, TMP, and CBZ) by PAA–Fe(III)–PICA at the initial pH 7.0 and 22 °C; effect of pre-equilibration of Fe(III)–PICA–MB prior to the addition of PAA and MB removal by Fe(III) precipitates; degradation of BA by PAA–Fe(III)–PICA and UV–PAA; cumulative Fe(II) concentration in PAA–Fe(III)–PICA or H_2O_2–Fe(III)–PICA systems and decay of PAA or H_2O_2 in PAA–Fe(III)–PICA system; reaction products of MB in the PAA–Fe(III)–PICA system at different reaction times; reaction products of NPX in the PAA–Fe(III)–PICA system at different reaction times; reaction products of SMX in the PAA–Fe(III)–PICA system at different reaction times; measured MS spectra of MB and the reaction products; measured MS spectra of NPX and the reaction products; and measured MS spectra of SMX and the reaction products (PDF)

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Notes

The authors declare no competing financial interest.

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