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ORIGINAL PAPER

Zero-valent iron/persulfate(Fe^0/PS) oxidation acetaminophen in water

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Abstract Zero-valent iron (Fe^0), as an alternative iron source, was evaluated to activate persulfate (PS) to degrade acetaminophen (APAP), a representative pharmaceutically active compound in water. Effects of key factors in the so-called Fe^0/PS process, including Fe^0 dosage, initial pH, temperatures and chelating agents, were studied. Under all the conditions tested, the APAP degradation followed a pseudo-first-order kinetics pattern. The degradation efficiency of APAP was highest when the Fe^0 to PS molar ratio increased to 1:1, and the degradation rate constant and removal were 23.19×10^{-3} min^{-1} and 93.19 %, respectively. Comparing with Fe^{2+}, Fe^0 served as an alternative iron source that can gradually release Fe^{2+} into water, thereby consistently activating PS to produce sulfate radicals. The Fe^0/PS system was effective in a broader pH range from 3 to 8.5. Heat could facilitate production of sulfate radicals and enhance the APAP degradation in the Fe^0/PS system. High reaction temperature also improved the Fe^{2+}/PS oxidation of APAP. Finally, sodium citrate (a chelating agent) at an appropriate concentration could improve the APAP degradation rate in the Fe^{2+}/PS and Fe^0/PS system. The optimal molar ratio of Fe^0 to citrate depended on solution pH. Our results demonstrated that Fe^0 was an alternative iron source to activate PS to degrade APAP in water.

Keywords Affecting factors · pH · Sodium citrate · Sulfate radicals · Temperature

Introduction

Over the past few decades, advanced oxidation processes (AOPs), such as O_3, UV/H_2O_2, UV/O_3, Fe^{2+}/H_2O_2 and UV/O_3/H_2O_2, have been intensively demonstrated to be highly effective and practically feasible for the removal of persistent organic pollutants in water. These AOPs utilize hydroxyl radicals (HO·) as a principal oxidizing agent to degrade a broad spectrum of organic pollutants with extremely high second-order rate (10^7–10^{10} $M\ s^{-1}$) (Matta et al. 2011). Recently, emerging AOPs employing sulfate radicals ($SO_4^{\cdot-}$) as the major oxidant have been increasingly paid to great attention. Sulfate radical-induced AOPs (SR-AOPs) have become an alternative for traditional hydroxyl radical AOPs (HR-AOPs). $SO_4^{\cdot-}$ are also a strong oxidant with a redox potential of 2.5–3.1 V, similar to HO· with a redox potential of 1.8–2.7 V (Guan et al. 2011). Compared with HO·, they have a longer half life and higher selectivity for the oxidation of target organic compounds (Sun et al. 2009; Anoniou et al. 2010). $SO_4^{\cdot-}$ can be produced from activation of persulfate (PS) salts by different methods, such as heat (Eq. 1) (Johnson et al. 2008; Mora et al. 2009), transition metals (Eq. 2) (Anipsitakis and Dionysiou 2004; Tan et al. 2012a, b), ultraviolet light (Eq. 3) (Antoniou et al. 2010; Criquet and Vel Leitner 2009) and ultrasonic irradiation (Eq. 4) (Neppolian et al. 2010; Gayathri et al. 2010).

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$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\cdot -} \quad (1)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + M^{(n+1)+} \quad (2)$$

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\cdot -} \quad (3)$$

$$S_2O_8^{2-} + \text{US} \rightarrow SO_4^{\cdot -} + SO_4^{2-} \quad (4)$$

Many transition metals such as Co(II) and Ag(I) can efficiently activate PS to generate $SO_4^{\cdot -}$ (Nfodzo and Choi 2011). However, the adverse effect of cobalt on human health and the high cost of silver have significantly limited their application in water treatment. Therefore, there is a demand to develop a new catalyst to activate $SO_4^{\cdot -}$. With a low cost, little toxicity and commercial availability, iron salts are widely used in water treatment. For example, Fenton reagents (Fe^{2+}/H_2O_2) or Fenton-like reagents (Fe^{3+}/H_2O_2) are an operation-simple, environmental friendly, and viable option to yield HO·. However, Fenton or Fenton-like processes are only effective at an acidic condition, but much less active at a neutral or alkaline condition under which iron salts are almost insoluble. In a similar manner, Fe^{2+} and PS or Fe^{3+} and PS can generate $SO_4^{\cdot -}$ to remove organic pollutants. Although they typically perform well at a low pH, their treatment efficiencies dramatically drop with a pH increase. The degradation efficiency significantly decreased with an increase in solution pH during Fe^{2+}/PS oxidation of lindane (Cao et al. 2008). Fe^{2+}-activated $SO_4^{\cdot -}$ oxidation process could also completely degrade polychlorinated biphenyls (PCBs) at pH 3, but less than 50 % oxidation efficiency was achieved at pH 5 and 9 (Rastogi et al. 2009a, b). To address this pH issue, zero-valent iron (ZVI) has been attempted as an alternative iron source. The catalytic properties of iron power for the oxidation of 4-chlorophenol have been tested in the presence of hydrogen peroxide (Lucking et al. 1998). They concluded that iron powder could continuously release ferrous ions to activate H_2O_2 through Fenton chemistry. In addition, Fe^0 was more effective than Fe^{2+} as activating agent and potentially more suitable for environmental applications (Oh et al. 2010).

The objective of this study was to evaluate Fe^0 as an alternative catalyst to activate PS and degrade acetaminophen (APAP, also known as paracetamol), a representative pharmaceutically active compound in water. APAP is a broadly used analgesic, antipyretic drug that relieves fever, headache, and minor aches (Lin et al. 2010). In 2000, it was ranked as one of the top three drugs prescribed in the United Kingdom (Zhang et al. 2008). The performance of the Fe^0/PS process to improve the degradation of APAP was evaluated through the examination of various operational parameters, including Fe^0 dosage, initial solution pH and temperature. In addition, sodium citrate was chosen as the representative chelating agent to evaluate its effect on the Fe^0/PS and Fe^{2+}/PS system, respectively. The experiments were conducted at the State Key Laboratory of Pollution Control Reuse, Tongji University, Shanghai (March 2012).

Materials and methods

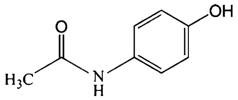
Chemicals

All the chemicals were of analytical grade, except as noted. APAP (≥99 %) was purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Its basic physicochemical properties are listed in Table 1. High performance liquid chromatography (HPLC) graded acetonitrile and methanol supplied by Sigma-Aldrich Chemical Co., Ltd. (USA). PS (≥99.5 %), Fe^0 (≥98 %), sodium citrate, $FeSO_4{\cdot}4H_2O$, $Fe_2(SO_4)_3$, $NaNO_2$, NaOH and H_2SO_4 obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 0.1 M H_2SO_4 and NaOH were used for solution pH adjustment. All the solutions were prepared using deionized water (18 MΩ cm) from a Milli-Q water purification system. The pH value of solution was measured using a pH meter (PHS-3G, Leici Corp., China).

Experimental procedures

All the tests were performed in 250 mL glass vessels with 200 mL simulated APAP-contaminated water. The

Table 1 Selected physicochemical properties of APAP

Chemicals formula	Chemical structure	Molecular weight (g mol^{-1})	Water solubility (g mL^{-1}, 20 °C)	log K_{ow}	pK_a
$C_8H_9NO_2$		151.17	14,000	0.46	9.38

vessels were installed on magnetic stirrer that provided a rapid and constant stirring, thereby ensuring a completely mixed state. In the tests to study the effect of temperature, the vessels were installed in a water bath apparatus (SHZ-B, Shanghai Yuejin Medical Instruments Co., Ltd.) that provided a desirable reaction temperature. To prevent any photo-induced degradation, all the reactors were wrapped with tinfoil. At designated time intervals (0, 5, 10, 20, 30, 60, 90, 120 and 180 min), 2 mL sample was collected from each replicate vessel and immediately filtered through a 0.22-μm membrane. Subsequently, 0.5 mL filtrate was stored in a vial pre-filled with 0.5 mL methanol to quench the oxidation induced by any residual oxidant. To exclude the influence of methanol during total organic carbon (TOC) analysis, $NaNO_2$ was used as the quenching agent. All the experiments were carried out in duplicate to ensure accurate data acquisition and interpretation.

Analytical methods

APAP in water was measured by a reversed-phase HPLC (Waters 2010, USA) equipped with a UV–vis detector (Waters 2489) at $\lambda = 242$ nm using Symmetry C18 column (4.6 mm × 250 mm, 5 μm, Waters, USA). The injection volume of each sample was 20 μL and the column temperature was maintained 30 °C. The mobile phase used for elution was a mixture of Milli-Q deionized water and acetonitrile (v:v = 85 %:15 %) at a flow rate of 1 mL min^{-1}. TOC was measured using a TOC analyzer (TOC-L, CPH CN200, Shimadzu, Japan).

Results and discussion

Effect of initial Fe^0 dosage

For the purpose of investigating the effect of Fe^0 dosage on the degradation of APAP, a series of comparative experiments were conducted by adding different amount of Fe^0, while APAP to PS molar ratio was fixed at 1:1. As can be seen in Fig. 1, the APAP degradation strictly followed pseudo-first-order kinetics for any particular Fe^0 dosage in 90 min. Of interest, the degradation rate was heavily influenced by the molar ratio of Fe^0 to PS at a fixed PS dosage. The pseudo-first-order reaction rate constant was increased from 2.15 to 23.19×10^{-3} min^{-1} when the molar ratio of Fe^0 to PS went up from 0.25 to 1, but was gradually decreased to 15.23×10^{-3} min^{-1} when the molar ratio further increased to 2.5. As shown in the insert of Fig. 1, within 180 min, the APAP removal efficiencies were 28.95, 64.36, 93.19 and 79.31 % at Fe^0: PS = 0.25:1, 0.5:1, 1:1 and 2.5:1, respectively. Too high Fe^0 dosage likely provided too much Fe^{2+} that might scavenge $SO_4^{\cdot -}$ produced in the Fe^0/PS system (Eq. 5), thereby reducing the overall degradation rate and efficiency.

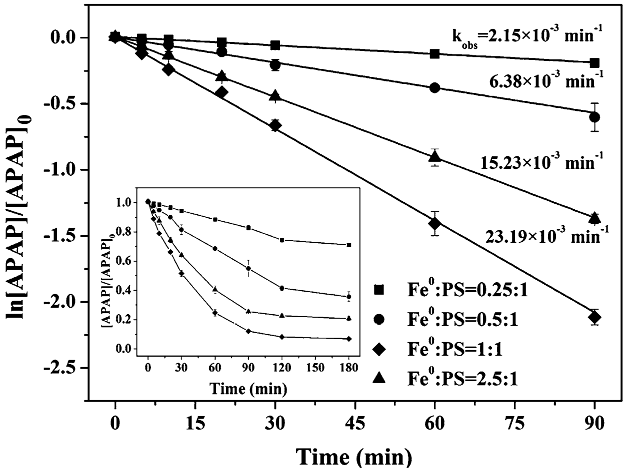


Fig. 1 Effect of initial Fe^0 dosage on APAP degradation in the Fe^0/PS system. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; [Fe^0] = 0.1–1 mM; room temperature; no pH adjustment

$$Fe^{2+} + SO_4^{\cdot -} \rightarrow Fe^{3+} + SO_4^{2-} \tag{5}$$

It is reported that Fe^{2+} is one of the strongest species that can catalyze PS to generate $SO_4^{\cdot -}$ which can significantly improve the efficiency of the pollutant degradation (Anipsitakis and Dionysiou 2004). The previous studies showed that Fe^0 can apply as the source of Fe^{2+} in acid media in Fenton reactions (Zhao et al. 2010). In this study, the combination of Fe^0 and $SO_4^{\cdot -}$ is also highly effective for APAP degradation in water. With the increase of the Fe^0 dosage, the amount of $SO_4^{\cdot -}$ in Fe^0/PS system increases, consequently leading to the increase of the degradation rate. However, too high Fe^0 dosage could not achieve the high APAP degradation efficiency, because excess Fe^{2+} present rapidly activated all the PS and then act as the scavenger of $SO_4^{\cdot -}$, accounting for the decrease in the rate of APAP oxidation.

Therefore, the optimum Fe^0 to PS molar ratio was 1:1 in this study. The finding is consistent with previous studies that the optimal Fe^0 to PS molar ratio was found to be 1:1, and complete oxidation of polyvinyl alcohol (PVA) was obtained by Fe^0 activated PS in 120 min (Oh et al. 2009). This optimum molar ratio of Fe^0 to PS would be used in the following experiments.

Comparison of Fe^0/PS, PS and Fe^0 alone for APAP degradation

To further understand the role of each component in the Fe^0/PS system, APAP was treated by Fe^0/PS, PS and Fe^0 alone, respectively. As shown in Fig. 2, PS itself could not degrade any APAP within 180 min at room temperature, indicating that PS was not adequately strong to effectively decompose APAP. The results were in agreement with the observations of Hussain et al. (2012) who used PS to destroy *p*-chloroaniline in aqueous solution. In the presence of Fe^0, only 14.27 % of APAP was degraded from water with the same reaction time. The reduction reaction of Fe^0 itself led to the degradation of APAP, but the degradation was not significant. However, when Fe^0 and PS were used together at a molar ratio of 1:1, more than 91.5 % APAP was removed within 180 min, thus suggesting a synesthetic effect after combination of Fe^0 and PS. The added Fe^0 was expected to contribute to Fe^{2+} that could activate PS to yield extremely active $SO_4^{\cdot-}$ through Eq. (6).

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + 2SO_4^{2-} + SO_4^{\cdot-} \quad (6)$$

There are four possible ways to generate Fe^{2+} from Fe^0 in the Fe^0/PS system: (1) initially, Fe^0 is corroded by H^+ under acidic conditions (Eq. 7); (2) direct electron transfer from Fe^0 to PS occurs through a pathway similar to the Haber–Weiss mechanism in a Fenton-like system (Eq. 8) (Zhao et al. 2010): Fe^0 (a redox potential of −0.44 V) may act as a reducing agent and it can induce reductive decomposition of PS (a redox potential of +2.01 V); (3) Fe^0 in water is corroded under either aerobic or anaerobic conditions (Eqs. 9–10) (Zhou et al. 2008); and (4) after Fe^{2+} is oxidized to Fe^{3+} accompanied with production of $SO_4^{\cdot-}$ and Fe^{3+} may be reduced by residual Fe^0 to Fe^{2+}, as shown in Eq. (11). The slow release and the fast recovery of Fe^{2+} both make the highly efficient decomposition of APAP in the Fe^0/PS system.

$$Fe^0 + H^+ \rightarrow Fe^{2+} + H_2 \text{ (Acidic condition)} \quad (7)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (8)$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow Fe^{2+} + 4OH^- \quad (9)$$

$$2Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (10)$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (11)$$

Effects of different iron sources

Existing forms of iron in aqueous solution seriously affected the formation of $SO_4^{\cdot-}$. The comparison of APAP degradation was explored by conducting experiments using three iron-based catalysts: Fe^{3+}, Fe^{2+} and Fe^0 in this study. As presented in Fig. 3, compared with Fe^{3+}/PS and Fe^{2+}/PS system, Fe^0/PS system has the best performance in degradation of APAP. The removal of APAP can reach 92.94 % in the Fe^0/PS system within 180 min. However, the removal of APAP in the Fe^{3+}/PS and the Fe^{2+}/PS system was only 14.73 and 40.16 % in the same time period, respectively.

Of interest, within the first 5 min, the Fe^{2+}/PS system apparently achieved the highest APAP degradation rate. Immediately after that, the degradation was significantly slowed down. The unique APAP two-phase degradation patterns in the Fe^{2+}/PS system are ascribed to a rapid consumption of Fe^{2+} at the beginning stage. Once Fe^{2+} added into the PS solution, high concentrations of Fe^{2+}

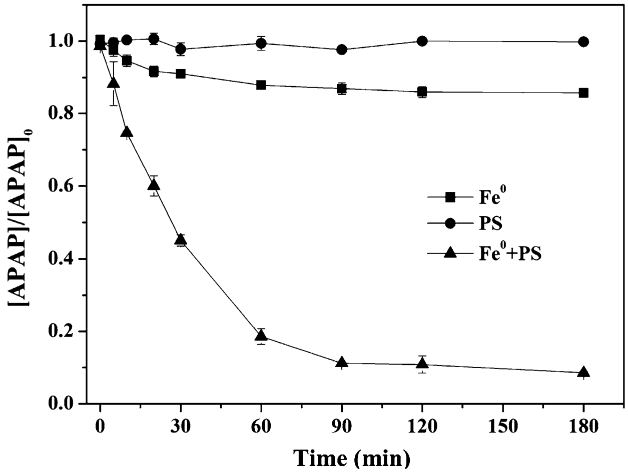


Fig. 2 Comparison of APAP degradation by Fe^0/PS, PS and Fe^0 alone. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; [Fe^0] = 0.4 mM; room temperature; no pH adjustment

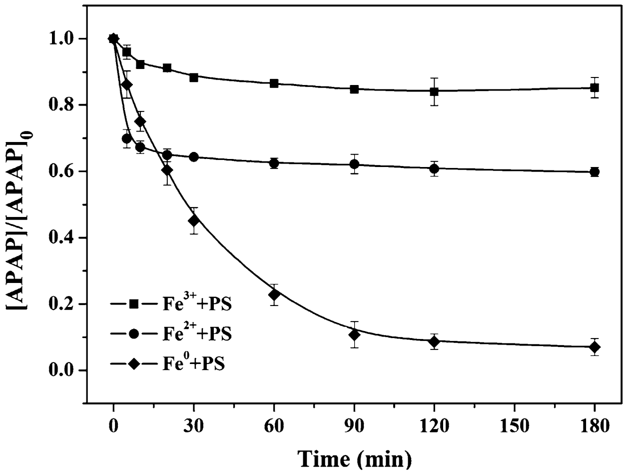


Fig. 3 The comparison of APAP degradation by three iron-based catalysts activated persulfate. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; [Fe^{3+}] = [Fe^{2+}] = [Fe^0] = 0.4 mM; room temperature; no pH adjustment

and PS violently reacted to rapidly produce a high concentration of $SO_4^{\cdot -}$ that accomplished a significantly high APAP degradation rate and led to 30 % degradation of APAP. The reaction of Fe^{2+} and PS has a low activation energy of 14.8 kJ mol^{-1} (Romero et al. 2010). Meanwhile, part of $SO_4^{\cdot -}$ was likely to be wasted due to the scavenging induced by Fe^{2+} (Eq. 5). Because Fe^{2+} substantially existed in the solution at the initial phase, the fraction of scavenged $SO_4^{\cdot -}$ was expected to be relatively high. After the rapid oxidation stage, most Fe^{3+} which generated by Fe^{2+} was difficult to reduced back, so that the yield of $SO_4^{\cdot -}$ dramatically dropped. Therefore, the APAP degradation in the follow-on phase was almost marginal. The phenomenon occurred in the Fe^{3+}/PS system was similar to the second stage of the Fe^{2+}/PS system, and the corresponding removal of APAP was insignificant. In contrast, Fe^0 as a Fe^{2+} alternative source had a few advantages over ferrous and ferric salts. Fe^0 could gradually release Fe^{2+} into water, and ensured consistent production of $SO_4^{\cdot -}$. The yield of Fe^{2+} during the entire Fe^0/PS reaction was much less than that at the beginning phase of the Fe^{2+}/PS system, thus minimizing the waster of $SO_4^{\cdot -}$ scavenged by a high concentration of Fe^{2+} (Eq. 5). More importantly, Fe^0 could reduce Fe^{3+} back to Fe^{2+} (Eq. 11), and increased the reuse efficiency of iron as a PS activator. In addition, metal iron is less expensive and can reduce total dissolved solids (TDS) and electrical conductivity (EC), different from ferrous and ferric salts that generally increase TDS and EC after treatment.

Effect of initial pH

To observe the effect of pH on the degradation of APAP, experiments were carried out at different pH from 1.5 to 10. The effect of pH on the Fe^0/PS oxidation of APAP is shown in Fig. 4. As shown, the Fe^0/PS was effective for the APAP degradation over a broad pH range of 3–8.5, at which more than 90 % of APAP was removed within 180 min. Although the APAP removal efficiency under different pH (3–8.5) over 180 min were close, their degradation rates were significantly different. All the degradation well followed pseudo-first-kinetics patterns within the first 60 min. The observed rate constant of APAP degradation decreased from 71.04×10^{-3}, 33.08×10^{-3}, 21.49×10^{-3} to 16.13×10^{-3} min^{-1} with the increasing pH from 3, 5.5, 7 to 8.5. Generally, an acid condition facilitates the formation rate of Fe^{2+} (Eq. 7) that generates more $SO_4^{\cdot -}$ in the Fe^0/PS system. This finding is in agreement with a previous study (Zhao et al. 2010) that a low pH (pH 3) favored the degradation of 4-chlorophenol in the Fe^0/PS system.

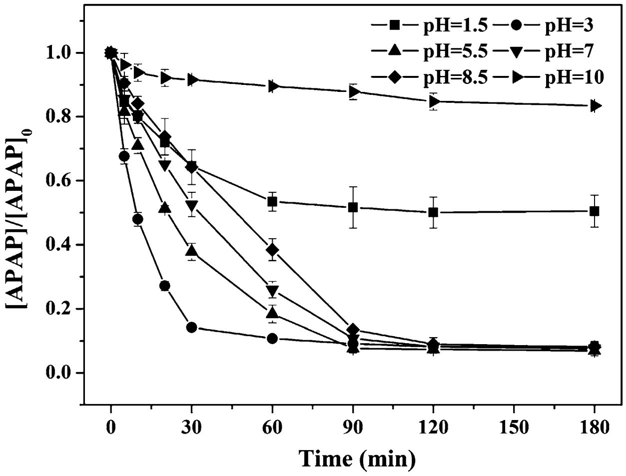


Fig. 4 Effect of initial pH on APAP degradation in the Fe^0/PS system. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; $[Fe^0]$ = 0.4 mM; room temperature

Conversely, the APAP degradation was poor at an extreme acidic or alkaline condition. Only 49.51 % of APAP was degraded at pH 1.5 within 180 min. Although the rapid transformation of Fe^0 to Fe^{2+} by H^+ (Eq. (7), as well as the acid-catalyzation (Eqs. 12, 13) could accelerate the formation of $SO_4^{\cdot -}$, too many $SO_4^{\cdot -}$ in the Fe^0/PS system enhanced scavenging of $SO_4^{\cdot -}$ by itself (Eq. 14) and $S_2O_8^{2-}$ (Eq. 15), thereby significantly slow down the APAP degradation (Buxton et al. 1999). On the other side, only 16.57 % APAP was degraded at pH 10 within 180 min. This finding is because Fe^{2+} and Fe^{3+} are almost insoluble at such a high pH, so that the iron ions rapidly form precipitates and escape from the reaction system. In addition, the presence of $SO_4^{\cdot -}$ could result in radical interconversion reactions and produce hydroxyl radicals (Eqs. 16, 17) (Liang et al. 2007a, b). The generated HO· could be readily scavenged by SO_4^{2-} that was abundant in the Fe^0/PS system.

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (12)$$

$$HS_2O_8^- \rightarrow H^+ + SO_4^{\cdot -} + SO_4^{2-} \quad (13)$$

$$SO_4^{\cdot -} + SO_4^{\cdot -} \rightarrow S_2O_8^{2-} \quad (14)$$

$$SO_4^{\cdot -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\cdot} \quad (15)$$

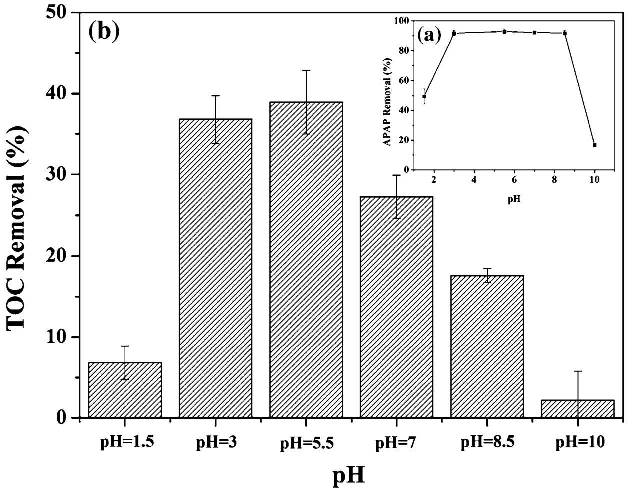


Fig. 5 **a** Removal of APAP in the Fe^0/PS system at different pH. **b** Mineralization of APAP in the Fe^0/PS system at different pH. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; $[Fe^0]$ = 0.4 mM; room temperature

$$\text{Alkaline pH}: \quad SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \tag{16}$$

$$\text{All pHs}: \quad SO_4^{\cdot -} + H_2O \rightarrow SO_4^{2-} + OH^{\cdot} + H^+ \tag{17}$$

Figure 5 presents the TOC removal at different pH during Fe^0/PS oxidation of APAP. Overall, the mineralization degree was not high. The highest mineralization was observed at pH 3 and 5.5, at which 36.81 and 38.92 % of TOC were removed, respectively. To achieve complete mineralization of APAP, Fe^0/PS system should combine with the other process, such as biological treatment.

It is reported that $SO_4^{\cdot -}$ are the predominant species in the oxidation system and both of them are present at near neutral pH (Criquet and Vel Leitner 2009). As the pH exceeds 10.5, the reaction of $SO_4^{\cdot -}$ with HO· becomes very significant (Eq. 18), which means HO· is dominant species in oxidant system. $SO_4^{\cdot -}$ have a longer half life than HO· mainly due to their preference for electron transfer reactions while HO· can participate in a variety of reactions with equal preference (Liang et al. 2004a, b). The high oxidation efficiency of the $SO_4^{\cdot -}$, in combination with the slow rate of consumption of precursor oxidants, makes SR-AOPs very useful for the degradation of recalcitrant organic contaminants. Anipsitakis and Dionysiou (2003) applied the Fenton system and the Co^{2+}/peroxymonosulfate (Co^{2+}/PMS) system for removing 2,4-dichlorophenol and compared the TOC removal. They found that the Fenton Reagent at pH 3.0 can achieve TOC removal of 55 %, and the Co^{2+}/PMS at neutral pH mineralized almost 90 % of the initial organic loading. Xu and Li (2010) also demonstrated that the Fe^{2+}/PS system could degrade azo dye orange G in aqueous solutions to a higher degree than the Fenton's reagent, which was beneficial to the mineralization of azo dyes.

$$SO_4^{\cdot -} + OH^- \rightarrow HO^{\cdot} + SO_4^{2-} \quad k = 6.5 \times 10^7\,M^{-1}\,s^{-1} \tag{18}$$

Effect of temperature

To elucidate the effect of temperature on the degradation of APAP in the Fe^0/PS system, four temperatures, namely 35, 50, 65 and 75 °C, were investigated in this study. Effect of temperature on PS and Fe^0/PS oxidation of APAP are shown in Fig. 6. Kinetics and thermodynamics parameters for the both degradation processes are summarized in Table 2. For either oxidation process, the APAP degradation followed the pseudo-first-order kinetics patterns. It is noted that heat energy can also be an effect way to activate PS and produce $SO_4^{\cdot -}$. At 35 °C, no APAP oxidation occurred using PS alone. When the temperature was increased to 50 °C, 11.12 % APAP was degraded within 90 min, indicating that a minimum temperature (between 35 and 50 °C in this study) was required to initiate the PS activation. As the temperature further went up, the degradation rate of APAP increased. This finding implied that the reactions involved with production of $SO_4^{\cdot -}$ were endothermic. Within 90 min, 54.73 and 94.15 % of APAP were degraded at 65 and 80 °C, respectively. With the temperature increase, PS consumption is corresponding increased, which means more $SO_4^{\cdot -}$ generated in the system.

In contrast, the presence of Fe^0 appeared to facilitate the production of $SO_4^{\cdot -}$. For any particular temperature, the Fe^0/PS system could achieve a higher APAP degradation rate than the PS alone. For example, the Fe^0/PS at 80 °C could degrade almost all the APAP only within 30 min, with a degradation rate almost six times as the one achieved by PS alone under identical conditions. Of note, the Fe^0/PS system did not require a minimum temperature to produce $SO_4^{\cdot -}$. At 35 °C under which PS could not be activated in this study, approximately 95 % APAP was degraded by the Fe^0/PS system within 180 min.

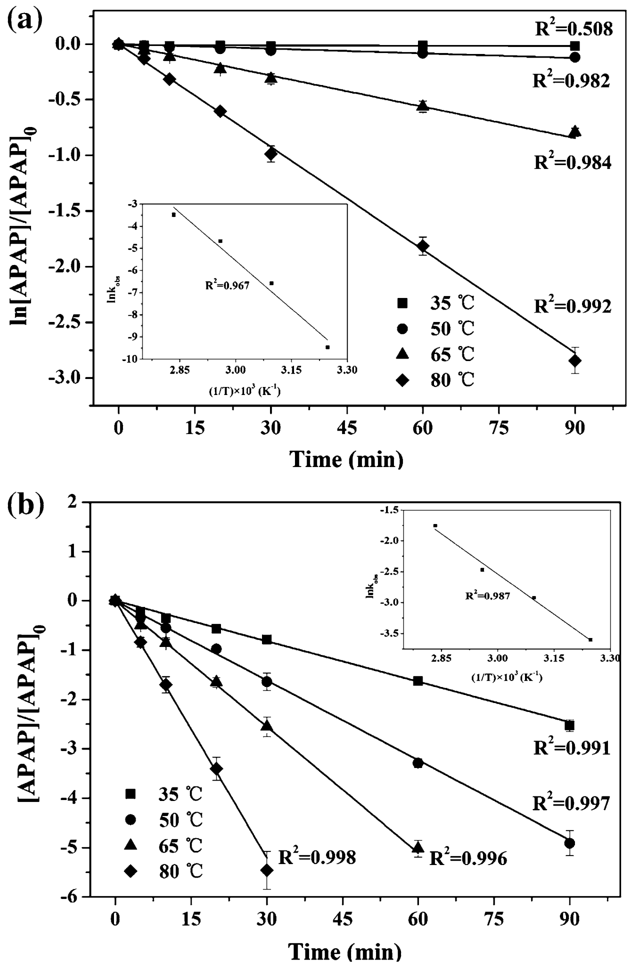


Fig. 6 Effect of temperature on persulfate and Fe^0/persulfate oxidation of APAP. **a** Effect of temperature on persulfate oxidation of APAP; **b** Effect of temperature on the degradation of APAP in Fe^0/PS system. The insert of the figure is Arrhenius plot – $\ln k_{obs}$ vs. $(1/T) \times 10^3$. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; [Fe^0] = 0.4 mM; no pH adjustment

The temperature dependency of the kinetic constants was further evaluated using the Arrhenius equation (Eq. 18), as shown in the inserts of Fig. 6.

$$\ln k_{obs} = \ln A - E_a/RT, \tag{19}$$

where A is the pre-exponential factor (s^{-1}), E_a is the apparent activation energy ($kJ\ mol^{-1}$), R is the universal gas constant (8.314×10^{-3} kJ·(mol K)$^{-1}$), and T is absolute temperature (K). As seen in Table 2, the activation energies for heat-activated PS and heat-activated Fe^0/PS were estimated to be 120.4 and 36.1 kJ mol^{-1}, respectively. The calculated activation energy for heat-activated PS was close to those reported for thermally activated PS oxidation of trichloroethylene (108 kJ mol^{-1}) (Waldemer et al. 2007), bisoprolol (119.8 kJ mol^{-1}) (Ghauch and Tuqan 2012), and *cis*-dichloroethylene (144 kJ·mol^{-1}) (Liang et al. 2007a, b). The activation energy for diuron degradation by heat-activated PS was 228.8 kJ mol^{-1}, indicating that APAP was easier to remove than diuron in heat-activated PS system (Tan et al. 2012a, b). However, the activation energy was significantly decreased to 36.1 kJ·mol^{-1} after introduction of Fe^0. It further proves that Fe^0 can improve the production of $SO_4^{\cdot-}$, indicating that the synergistic activation of PS by heat and Fe^0 could improve the degradation of APAP in the Fe^0/PS system as the temperature increased (Oh et al. 2009).

Effect of citrate dosage

Appropriate chelating agent such as citrate, humate, and *N*-(2-hydroxyethyl)iminodiacetic acid has been used to enhance Fe^{2+}/PS oxidation of certain pollutant (Choi and Lee 2012), because the chelating agent can increase Fe^{2+} solubility at neutral pH and follows for activation of PS to occur over a broader pH range. The effect of citrate on Fe^{2+}/PS and Fe^0/PS oxidation of APAP is shown in Figs. 7 and 8, respectively. In this study, sodium citrate was selected as chelating agent because it is an environmentally friendly and readily biodegradable multidentate organic complexing agent (Li et al. 2005).

Five different molar concentrations of sodium citrate were used to test the effect of citric acid concentrations on the degradation of APAP using Fe^{2+}/PS system. As shown in Fig. 7, without sodium citrate addition in the Fe^{2+}/PS system, 39.21 % APAP was removed within 180 min. When the Fe^{2+} to PS molar ratio increased to 1:1, the

Table 2 The calculated parameters in the Fe^0/PS system under different temperatures

	Heat-activated PS				Heat-activated Fe^0/PS			
	35 °C	50 °C	65 °C	80 °C	35 °C	50 °C	65 °C	80 °C
$k_{obs} \times 10^{-3}$ (s^{-1})	0	1.39	9.40	30.82	27.32	53.84	85.08	173.50
R^2	0.508	0.982	0.984	0.992	0.991	0.997	0.996	0.998
Half life (min)	1471.2	8.31	1.23	0.37	0.42	0.21	0.136	0.067
E_a (kJ·mol^{-1})	120.4				36.1			
A (s^{-1})	$2.40e^{37}$				$1.64e^{10}$			

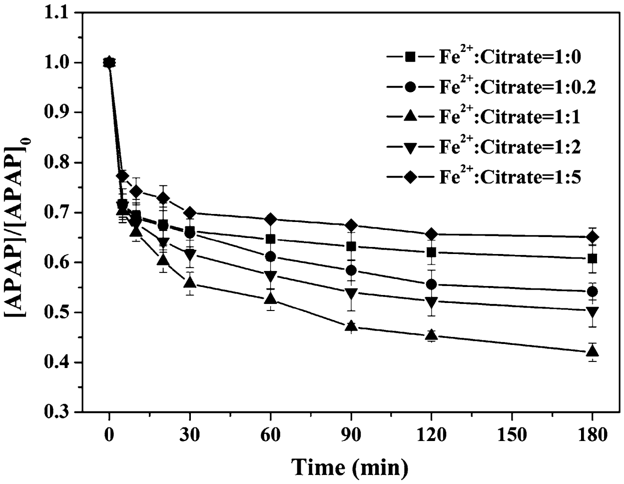


Fig. 7 Effect of citrate dosage on the degradation of APAP in the Fe^{2+}/PS system. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; [Fe^{2+}] = 0.4 mM; pH 7

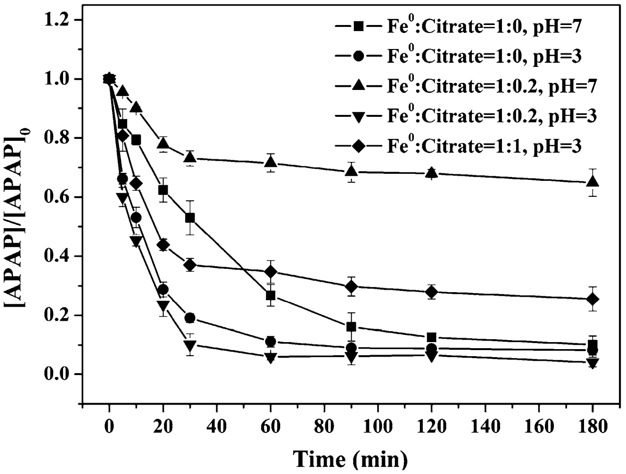


Fig. 8 Effect of citrate dosage on the degradation of APAP in the Fe^0/PS system. Experimental conditions: [APAP] = 0.066 mM; [PS] = 0.4 mM; [Fe^0] = 0.4 mM

APAP degradation efficiency increased and reached a maximum of 57.98 %. However, when the dosage of sodium citrate further increased, sodium citrate can compete with APAP for $SO_4^{\cdot-}$ attack and reduce its degradation efficiency. Since ferric citrate complexes have higher stability constants than ferrous citrate complexes, there is a possibility of unavailability of iron in the Fe^{3+}/PS system for activation of the PS at high concentration of citrate (Verma et al. 1997). Improved degradation of TCE by PS was observed when ferrous citrate was used as catalyst in place of ferrous iron only (Liang et al. 2004a, b). In the presence of excess ligand, possible formation of bulky hexa-coordinated complexes of iron hinders the accessibility of iron center for peroxide attachment, which results in decreased degradation efficiency. The removal efficiency of 4-chlorophenol also decreased at pH 3 when the Fe^{2+} to citrate molar ratio exceeded 1:0.2 (Rastogi et al. 2009a, b).

Three different molar concentrations of sodium citrate were used to investigate the effect of citric acid concentrations on the degradation of APAP in the Fe^0/PS system. As presented in Fig. 8, without sodium citrate addition, 89.88 % of APAP was removed in the Fe^0/PS system under neutral pH conditions. Different with the Fe^{2+}/PS system, adding a small amount of sodium citrate led to the significant reduction of the removal efficiency of APAP in the Fe^0/PS system. Due to slow generation rate of $SO_4^{\cdot-}$ under neutral pH conditions, the strong competition of $SO_4^{\cdot-}$ between sodium citrate and APAP reduced the available free radicals, which resulted in the remarkable decrease in APAP degradation efficiency. However, the same phenomenon in the Fe^{2+}/PS system was observed in the Fe^0/PS system at pH 3. In the presence of sodium citrate, a slight increase in degradation efficiency was observed up to a Fe^0:citrate molar ratio of 1:0.2, after which the increase in citrate concentration led to a remarkable decrease in removal efficiency. Acid conditions can accelerate the formation rate of Fe^{2+}, which generated more $SO_4^{\cdot-}$ in the Fe^0/PS system.

Conclusion

In this study, we evaluated Fe^0 as an alternative iron source to activate PS and degrade APAP in water. Fe^0 can gradually release Fe^{2+} that subsequently activates PS and produces $SO_4^{\cdot-}$ to degrade APAP. Compared with Fe^{2+} salt that is traditionally used as a PS activator, Fe^0 minimizes the $SO_4^{\cdot-}$ scavenging by Fe^{2+} and also improves the iron reuse efficiency by reduction of Fe^{3+} to Fe^{2+}. The performance of Fe^0/PS is heavily affected by Fe^0 dosage, pH, temperature, and presence of complexing agents. APAP could be completely degraded by Fe^0/PS under appropriate conditions. Our results demonstrate that Fe^0 is an effective alternative activator for PS to control water pollution caused by pharmaceuticals such as APAP.

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