Degradation of chloramphenicol by persulfate activated by Fe^{2+} and zerovalent iron

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HIGHLIGHTS

- The removal efficiencies for CAP in water by PS activated by Fe^{2+} and ZVI were studied.
- CAP was effectively removed by the ZVI–PS system at a broad pH range of 3–10.
- CAP removal was significantly influenced by operational parameters.
- The ZVI–PS system shows potential prospects in wastewater or even concentrated wastewater treatment.
- An oxidation pathway was proposed for CAP removal by the ZVI–PS system.

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ABSTRACT

This study evaluated the removal of chloramphenicol (CAP) by persulfate (PS) activated by Fe^{2+} and zerovalent iron (ZVI). Results showed that the Fe^{2+} –PS system ineffectively degraded CAP. However, CAP oxidation accelerated as the number of Fe^{2+} portions added increased. Comparing with Fe^{2+} , up to 96.1% of CAP was degraded when ZVI was employed as an alternative source of Fe^{2+} . The ZVI–PS system was effective in a broader initial pH range from 3 to 10, and low pH promoted CAP degradation. In addition, the results of scavenging tests suggested that $\text{HO}^\bullet$, $\text{SO}_4^{\bullet-}$ and $\text{O}_2^{\bullet-}$ contributed to the overall degradation performance, but $\text{HO}^\bullet$ predominated at all pH levels used. The rate of CAP removal slightly increased upon the addition of 1 mM Cl^- , but adding Cl^- at concentrations higher than 1 mM apparently inhibited CAP degradation. HCO_3^- , NO_3^- , NO_2^- , H_2PO_4^- , HPO_4^{2-} , and HA significantly inhibited CAP decomposition. Up to 92.8%, 94.7%, and 75.7% of CAP were removed from the filtrate, permeate, and retentate phases of wastewater, respectively. This result indicated that the ZVI–PS system can significantly remove CAP from wastewater and even concentrated wastewater. The intermediate products during oxidation were identified, and the degradation pathways of CAP were tentatively proposed.

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1. Introduction

Antibiotics are widely used in large quantities to treat bacterial diseases in both humans and animals. However, antibiotics have attracted increasing attention in recent years because of their adverse effects on human health and aquatic ecosystems [1]. Chloramphenicol (CAP) is an antibiotic commonly used in veterinary clinics since the 1950s. CAP causes numerous serious side effects, such as aplastic anemia. Thus, CAP has been banned by many countries for use in food-producing animals in the European Union and the United States of America in the 1990s.

However, CAP is still widely used in many low-income countries because of its low cost, steady antibacterial effectiveness, and high availability [2]. In addition, CAP remains ubiquitous in various aquatic environments because of the poor removal efficiencies of conventional treatment technologies, such as activated sludge [3]. The presence of CAP in aquatic environments may threaten the ecosystem even at trace levels [4]. Therefore, the development of innovative technologies that can effectively remove CAP in wastewater treatment is important.

Several works have proposed advanced oxidation processes (AOPs) that are based on the generation of hydroxyl radical ($\text{HO}^\bullet$) and other free radicals to remove CAP from aqueous solutions. These processes include Fenton [5], photo-Fenton [6], ionizing radiation treatment [7], and UV/ H_2O_2 [8]. Recent studies have

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proven $\text{SO}_4^{\cdot-}$ -based AOPs to be effective in degrading recalcitrant organic pollutants. Sulfate radical ($\text{SO}_4^{\cdot-}$) is a strong oxidant with a redox potential of 2.5 V and is more selective for oxidation than $\text{HO}^{\cdot}$ [9–10]. Persulfate (PS) is a common source of $\text{SO}_4^{\cdot-}$ through activation processes that involve heat, UV, base, or transition metals.

We have recently investigated CAP degradation by using a thermally activated PS process in a batch system [11]. We observed that CAP can be completely degraded after 160 min at 70 °C and that the optimal PS-to-CAP mole ratio is 20:1. However, thermally activated PS oxidation is undesirable in practical applications because of its high energy consumption. Transition metals can activate PS to generate $\text{SO}_4^{\cdot-}$ at ambient temperature. Fe^{2+} is a widely studied transition metal because of its relative nontoxicity, low cost, and effectiveness (Eq. (1)). However, excess Fe^{2+} can scavenge $\text{SO}_4^{\cdot-}$ and thus reduce the concentration of $\text{SO}_4^{\cdot-}$ through Eq. (2). In addition, Fe^{3+} precipitates as hydroxide at neutral pH; as a result, the treatment efficiency dramatically decreases with increasing pH:

Zerovalent iron (ZVI) has been attempted as an alternative activator [12]. It can not only serve as a releasing source of dissolved Fe^{2+} in oxygenated or deoxygenated water (Eqs. (3) and (4)), but also can release Fe^{2+} by PS through direct electron transfer (Eq. (5)) [16]. Meanwhile, ZVI can recycle Fe^{3+} to Fe^{2+} , as shown in Eq. (6), and thus reduce the precipitation of iron hydroxides during the oxidation. In addition, the use of ZVI also avoids the introduction of other counter anions (e.g., SO_4^- , Cl^- , or NO_3^-) by ferrous salts to the system. In 2008, Liang et al [13] firstly reported the use of ZVI as a source for Fe^{2+} activated PS oxidation of trichloroethylene (TCE). The catalytic properties of ZVI for the degradation of 2,4-dinitrotoluene [14], spent caustic [15] and sulfamethoxazole [16] in the presence of PS were also tested. They concluded that ZVI can control the rate of $\text{SO}_4^{\cdot-}$ by smoothly and continuously releasing Fe^{2+} to activate PS, thereby enhancing the reaction efficiency:

The effects of Fe^{2+} -PS and ZVI-PS systems on CAP degradation remain unknown to date. In this study, we systematically evaluated the oxidative degradation of CAP by using these two systems. The performance of the two processes to improve CAP degradation was evaluated on the basis of various operational parameters, such as activator dosage, oxidant dosage, initial solution pH, Fe^{2+} addition mode, dissolved oxygen (DO), various inorganic ions, humic acid (HA), and water matrix. The oxidation intermediates of CAP in the ZVI-PS system were identified, and pathways of CAP degradation were proposed.

2. Materials and methods

2.1. Materials

Unless otherwise stated, all chemicals in the study were at least analytical grade, and all solvents were high performance liquid chromatography (HPLC) grade. CAP was purchased from J&K

(China). Methanol (MeOH) and CH_2Cl_2 were supplied by CNW Technologies GmbH (Germany). HA was purchased from Jufeng Chemical Technology Co. (China) and contained total acidic group (133.2 mg g^{-1}), carboxyl group (130.4 mg g^{-1}), phenolic hydroxyl group (2.5 mg g^{-1}), H_2O (4.2–5.2%), chloride (<0.05%) and sulfate (<0.05%). Other reagents used in this study such as PS, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, ZVI, KI, NaH_2PO_4 , Na_2HPO_4 , NaOH, NaNO_3 , NaCl, NaHCO_3 , NaNO_2 , H_2SO_4 , tartaric acid (TA), citric acid (CA), L-malic acid (L-MA), ethylene diamine tetraacetic acid (EDTA), ethanol (EtOH), tert-butyl alcohol (TBA) and hydroxylamine hydrochloride were obtained from Sinopharm (Shanghai, China). The ZVI (purity $\geq 98\%$) contained Cu ($\leq 0.005\%$), Sulfuric acid insoluble matter ($\leq 0.1\%$) and water soluble ($\leq 0.03\%$). The iron particles were approximately 80–100 μm in diameter, with a Brunauer–Emmett–Teller (BET) surface area $3.1829 \text{ m}^2 \text{ g}^{-1}$ and an adsorption average pore width (4V/A by BET) 50.6130 Å. All chemicals were used without further purification. Deionized distilled water was used throughout the experiments. Stock solutions of all chemicals were freshly prepared.

2.2. Wastewater collection and colloidal isolation

Wastewater samples were collected from the effluent of a beef cattle operation. The samples were coarsely filtered on 1 μm glass filters to obtain the filtrate phase, and then further filtered through cross flow ultrafiltration (CFUF) to obtain the permeates (soluble phase) and the retentates (concentrated colloidal phase) [17,18]. The CFUF system was composed by a Millipore 1 kDa regenerated cellulose Pellicon 2 PLAC ultrafiltration membrane and a ratio of the volume of the initial sample to the retentate volume of 25 was used. Therefore, in the present study, filtrates are defined as below 1 μm , permeates are below 1 kDa, and retentates are defined as particles ranging from 1 kDa to 1 μm . Details about the samples are listed in Table 1.

2.3. Experimental procedures

All degradation tests were performed in 250 mL glass conical flasks with 100 mL of simulated CAP-contaminated solution at ambient temperature ($25 \pm 2^\circ\text{C}$) (Fig. S1). The flasks were open to the atmosphere and a magnetic stirrer provided a rapid and constant stirring (200 rpm) was used to maintain the solution well mixed. The solutions were added to each reactor starting with the CAP solution and the PS solution if needed. All reactions were initiated by adding the desired dosages of activators (soluble FeSO_4 or ZVI) without controlling the initial pH, except for the tests that considered the effects of initial pH, which was adjusted by adding 0.1 M NaOH or H_2SO_4 . At designated time intervals, 2 mL sample was collected from each reactor, immediately filtered through a 0.22 μm filter. Subsequently, 1 mL filtrate was stored in a vial pre-filled with 0.2 mL EtOH to quench the reaction before HPLC analysis. NaNO_2 was used as the quenching agent for total organic carbon (TOC) analysis. The other procedures for solution preparation and measurements were similar to those in the batch experiments.

2.4. Analytical methods

The CAP concentration in aqueous samples was measured with HPLC (Ultimate 3000, Dionex, USA) equipped with an XDB-C18 analytical HPLC 5 μm (4.6 mm $\times$ 150 mm) reversed-phase column and a variable UV-Vis wavelength detector with a detection wavelength of 252 nm. The column temperature was 30 °C, and the injection volume was 20 μL . The mobile phase was a mixture of methanol–water solution (v/v = 60:40) at a flow rate of 0.8 mL min^{-1} .

Table 1

Basic physical and chemical characteristics of different water matrices.

Water matrix	Particulate size	DOC (mg L ⁻¹)	pH	Cl ⁻ (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	UV ₂₅₄	<i>k</i> _{obs} (min ⁻¹)	Half-life (min)	<i>R</i> ²
Control	0	0.07	6.79	0	42.7	0.005	0.059	11.689	0.933
Wastewater	Filtrate	<1 μm	9.56	7.11	116.7	0.125	0.037	18.633	0.972
	Permeate	<1 kDa	4.51	7.11	114.9	0.088	0.041	16.743	0.958
	Retentate	1 kDa–1 μm	115.61	7.11	118.1	0.368	0.013	53.319	0.870

The reaction solution (50 mL) was extracted by CH₂Cl₂ (5 mL), and the oxidation intermediates in the extract were then identified by a gas chromatography-mass spectrometer (GC-MS, 7890A/5975C, Agilent, USA) equipped with a HP-5MS polysiloxane polymer column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. The following column temperature was adopted: start at 100 °C (1 min); 100–260 °C (15 °C min⁻¹); 260–280 °C (3 °C min⁻¹) and 280 °C (2 min). The injector and interface temperature were set at 300 and 280 °C, respectively. Full scan mode (*m/z* = 50–600) was used.

The concentration of residual PS was spectrophotometrically determined [19]. The amount of Fe²⁺ was spectrophotometrically determined at a wavelength of 510 nm after adding 1,10-phenanthroline to form a colored complex. Total dissolved iron (TDI) was measured when Fe³⁺ was reduced to Fe²⁺ by adding hydroxylamine hydrochloride. TOC in aqueous solutions were analyzed by TOC analyzer (TOC-L CPH, Shimadzu, Japan).

3. Results and discussions

3.1. Degradation of CAP by the Fe²⁺–PS system

3.1.1. Effect of initial Fe²⁺ dosage, initial pH values and chelating agents

Fe²⁺ alone and PS alone did not lead to a significant CAP decomposition (<2%) within 80 min (Fig. S2). In the Fe²⁺–PS system, the rate of CAP removal was fast at the initial 2 min stage, and then much slower (Fig. S3a). The rates of CAP and PS oxidation slowed down after 2 min because the amount of Fe²⁺ was almost depleted at this stage (Fig. S3b); this result indicated that the added Fe²⁺ was rapidly consumed and cannot continuously and sustainably activate PS. CAP degradation was accelerated as the Fe²⁺ concentration increased from 0.05 mM to 0.5 mM. However, further increasing Fe²⁺ concentration from 0.5 mM to 1 mM did not considerably improve CAP degradation (Fig. S3a). Varying the initial pH did not considerably change CAP degradation (Fig. S4a), and for each test, the pH value decreased to 3 in two minutes even when initial pH was adjusted at 10 (Fig. S4b). In the present study, the presence of chelating agents negatively affected the oxidation of CAP (Fig. S5). The inhibition of CAP degradation by the chelating agents can be attributed to the strong complexation of Fe²⁺ with chelating agents and the competition with target contaminants for reactive radicals [20–22].

3.1.2. Effect of multiple addition of Fe²⁺

The Fe²⁺–PS system was ineffective in degrading CAP; in particular, it removed only less than 35% of CAP within 45 min. As discussed above, the retardation stage is likely caused by the rapid depletion of Fe²⁺. Therefore, maintaining suitable quantities of free Fe²⁺ during the reaction is essential to slow down the generation of SO₄⁻. Tests were conducted to evaluate the form of multiple addition of Fe²⁺ and efficiently remove CAP. The same amount of Fe²⁺ (0.1 mmol) was equally divided into *n* portions (*n* = 1, 5, 10 and 20). These portions were sequentially added with equal time intervals into the reaction solution. As shown in Fig. 1, the degradation of CAP accelerated as the number of Fe²⁺ portions added increased.

Up to 77.2%, 88.9%, and 90.1% of CAP were removed with the sequential addition of Fe²⁺ for *n* = 5, 10 and 20, respectively, whereas only 31.6% of CAP was removed with the single injection of Fe²⁺. This result suggested that Fe²⁺ exhaustion was the principal reason for the retardation stage in the Fe²⁺–PS system. The rapid addition of Fe²⁺ might lead to the elimination of significant amounts of SO₄⁻ generated by Fe²⁺ through Eq. (2). As a result, CAP degradation dramatically decreased after the complete depletion of Fe²⁺ at the retardation stage [23]. By contrast, multiple additions of Fe²⁺ can reduce the concentration of Fe²⁺ in the solution. Thus, more SO₄⁻ can be captured by CAP [24].

3.2. Degradation of CAP the ZVI–PS system

3.2.1. Effect of initial ZVI dosage

ZVI alone did not lead to a significant CAP decomposition (<2%) within 80 min (Fig. S2). The effect of initial ZVI dosage on CAP degradation by the ZVI–PS system is shown in Fig. 2 and Table 2. The degradation rate was heavily influenced by the dosage of ZVI at a fixed PS dosage. The pseudo-first-order reaction rate constant (*k*_{obs}) was increased from 0.018 to 0.063 min⁻¹ when the dosage of ZVI was increased from 0.05 mM to 2 mM but gradually decreased to 0.059 and 0.046 min⁻¹ when the dosage was further increased to 2 mM and 3 mM, respectively. Within 80 min, the CAP removal efficiencies were 68.9%, 81.7%, 91.7%, 96.1%, 95.9%, 89.3% and 68.9% at ZVI dosage 0.125, 0.25, 0.5, 1, 2 and 4 mM, respectively. We hypothesized that ZVI at a relatively high dosage provides excess Fe²⁺ that might scavenge the produced SO₄⁻, resulting in decreased degradation efficiency [25].

3.2.2. Effect of initial PS dosage

The effect of initial PS dosage on CAP degradation by the ZVI–PS system is shown in Table 2 and Fig. 3a. The observed rate constant of CAP degradation increased from 0.014 to 0.063 min⁻¹ when the

Fig. 1. CAP degradation using Fe²⁺–PS system under different Fe²⁺ addition times. Conditions: [CAP]₀ = 0.05 mM; [PS]₀ = 1 mM; [pH]₀ = 5.4; [Fe²⁺]_{total} = 0.1 mmol.

Fig. 2. Effect of initial ZVI dosage on CAP degradation in ZVI-PS system. Conditions: $[CAP]_0 = 0.05$ mM; $[ZVI]_0 = 0.125$ –4 mM; $[PS]_0 = 1$ mM; $[pH]_0 = 5.4$.

dosage of PS went up from 0.25 to 1 mM, but was gradually decreased to 0.052 and 0.055 min^{-1} when the dosage further increased to 1.5 and 3 mM, respectively. CAP degradation efficiency increased and peaked at 96.1% when the PS dosage was increased to 1 mM. However, PS dosage exceeding 1 mM in the ZVI-PS system reduced the CAP removal efficiency of the system because of the consumption of SO_4^- generated by excess PS [26]. Therefore, the optimum ZVI and PS dosages were 1 mM and 1 mM in the present study, respectively. As shown in Fig. 3b, soluble Fe^{2+} can be slowly and continuously produced from the corrosion of ZVI in the presence of PS, which allowed the highly efficient decomposition of CAP in the ZVI-PS system. PS and ZVI were gradually consumed throughout the reaction because of the slow release of Fe^{2+} from the self-corrosion of ZVI [13].

3.2.3. Effect of initial pH

The effect of initial pH on CAP degradation by the ZVI-PS system is shown in Fig. 4. The ZVI-PS system effectively removed CAP at a broad pH range of 3.0–10.0, at which more than 90% of CAP was degraded within 80 min. Although the CAP degradation efficiency under various pH values did not significantly differ, the acidic pH was more favorable than neutral and alkaline pH. For instance, the performance was initially retarded at pH 10.0. Similar results were observed in the degradation of p-chloroaniline [27] and acetaminophen [25] in aqueous solutions by using the ZVI-PS system.

The decomposition of PS (Eqs. (7) and (8)) and the production of carboxyl acids [28] rapidly decreased the solution pH. For different initial pH values, with the progress of the reaction, pH would

Table 2
Pseudo-first-order rate constant for oxidation of CAP in ZVI-PS system.

Concentration (mM)			k_{obs} (min^{-1})	Half-life (min)	R^2
$[CAP]_0$	$[ZVI]_0$	$[PS]_0$			
0.05	0.125	1	0.018	39.383	0.996
0.05	0.25	1	0.027	25.390	0.995
0.05	0.5	1	0.039	17.728	0.986
0.05	1	1	0.063	10.950	0.964
0.05	2	1	0.059	11.689	0.933
0.05	4	1	0.046	15.003	0.848
0.05	1	0.25	0.014	48.135	0.973
0.05	1	0.5	0.024	29.124	0.962
0.05	1	1.5	0.052	13.381	0.947
0.05	1	3	0.055	12.512	0.949

Fig. 3. (a) Effect of initial PS dosage on CAP degradation in ZVI-PS system. Conditions: $[CAP]_0 = 0.05$ mM; $[ZVI]_0 = 1$ mM; $[pH]_0 = 5.4$; $[PS]_0 = 0.25$ –3 mM; (b) time course of PS, Fe^{2+} and TDI during CAP degradation reaction. Conditions: $[CAP]_0 = 0.05$ mM; $[ZVI]_0 = 1$ mM; $[pH]_0 = 5.4$; $[PS]_0 = 1$ mM.

Fig. 4. CAP degradation using ZVI-PS system under different initial pH value. Conditions: $[CAP]_0 = 0.05$ mM; $[PS]_0 = 1$ mM; $[pH]_0 = 3$ –10; $[ZVI]_0 = 1$ mM.

decrease to nearly the same value (2.9–3.5) except for the differences within the initial 35 min (Fig. S6a). As shown in Fig. S6b and c, the concentration of Fe^{2+} and the total iron species (Fe^{2+}

and Fe^{3+}) produced in the system were greatly influenced by the initial pH. Low initial pH favored the corrosion of ZVI and the generation of soluble Fe^{2+} to produce SO_4^- for CAP oxidation. By contrast, the amount of soluble Fe^{2+} was limited at a high initial pH (e.g., only 0.025–0.050 mM within the first 35 min at initial pH 10.0). In addition, the amount of soluble Fe^{2+} decreased at pH higher than 4.0 because of the formation of Fe^{2+} complexes that hinder the further activation of PS [29]:

3.2.4. Identification of the reactive species

Tests using ethanol (EtOH) and tert-butyl alcohol (TBA) were performed to identify which radical (SO_4^- or $\text{HO}^\cdot$) is principally involved during CAP removal at different pH levels. EtOH is an effective quenching agent for both $\text{HO}^\cdot$ and SO_4^- ($k_{\text{HO}^\cdot} = 1.2\text{--}2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{SO}_4^-} = 1.6\text{--}7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). TBA is a strong scavenger for $\text{HO}^\cdot$, and it reacts slowly with SO_4^- ($k_{\text{HO}^\cdot} = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{SO}_4^-} = 4\text{--}9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [30]. In this part, excessive amount of EtOH and TBA were added into the reaction solution at a scavenger/PS molar ratio of 10:1, 60:1 and 300:1, respectively. Table 3 shows the results obtained for the removal of CAP without and with scavengers for the ZVI–PS system. It appeared that both EtOH and TBA can significantly inhibit the degradation of CAP. Which indicated that both $\text{HO}^\cdot$ and SO_4^- were two major oxidizing species in the ZVI–PS system. The CAP degradation efficiencies were almost the same in the presence of different amounts of EtOH (10, 60 and 300 mM). Therefore, 10 mM EtOH or 10 mM TBA was enough to quench $\text{HO}^\cdot$ in ZVI–PS system. At initial pH values 3 and 5, significant drop in oxidation efficiency was observed at high TBA dosage (60 and 300 mM), which might be attributed to the higher concentration of SO_4^- under acidic conditions [11,16].

It is well reported that O_2^- was generated in Fe_3O_4 -PS and MnO_2 -PS system [31–32], and it may also be generated in ZVI–PS system. Dissolved oxygen can readily accept electron from ZVI to generate reactive oxidants such as $\text{HO}^\cdot$ and O_2^- [32]. In order to confirm the contribution of DO, control experiments for the removal of CAP were done under N_2 -saturated, and atmosphere-insulation conditions. As shown in Fig. 5a, higher concentration of DO concentration in the reaction solution favored the degradation of CAP, which might attributed to the more O_2^- radicals were generated in the presence of higher DO [32]. Furthermore, DO that quickly favored the oxidation of ZVI into Fe^{2+} promoting therefore the production of SO_4^- [33]. The DO dropped gradually to nearly zero in the atmosphere-insulation

ZVI–PS system, which suggested oxygen could take part in the oxidation process (Fig. 5b). To sum up, radicals quenching experiments clearly identified the generation of the reactive oxygen species in ZVI–PS system, namely SO_4^- , $\text{HO}^\cdot$ and O_2^- . Moreover, though the reactions are relatively complex, the inhibition effects of EtOH were stronger than that of TBA and N_2 which indicated that $\text{HO}^\cdot$ might play a more important role. Han et al investigated the PS oxidation of aniline activated by several chelating agents mediated Fe^{2+} (initial pH = 3.0), and the results indicated that both

Fig. 5. (a) Effect of DO on the degradation of CAP by ZVI–PS. (b) DO change profiles. Conditions: $[\text{CAP}]_0 = 0.05 \text{ mM}$; $[\text{PS}]_0 = 1 \text{ mM}$; $[\text{ZVI}]_0 = 1 \text{ mM}$.

Table 3

The degradation efficiency of CAP with and without scavengers in ZVI–PS system.

Initial pH	Reaction time (min)	Degradation efficiency (%)						
		No addition	TBA = 10 mM	TBA = 60 mM	TBA = 300 mM	EtOH = 10 mM	EtOH = 60 mM	EtOH = 300 mM
3	35	90.9	46.7	41.7	40.9	18.1	17.4	15.9
	80	95.1	58.8	50.9	49.1	26.5	26.7	26.7
5	35	84.5	42.0	40.4	41.2	12.9	12.6	12.2
	80	94.3	57.7	49.3	47.1	24.2	23.4	23.3
7	35	89.5	40.7	40.4	39.6	12.4	12.1	12
	80	93.4	47.5	47.5	46.4	20.4	22.9	25.3
8.5	35	82.8	40.1	36.3	33.3	10.2	8.7	7.3
	80	93.2	46.1	46.2	45.6	24.3	24.6	24.5
10	35	84.0	32.2	34.2	29.4	10.0	10.9	5.3
	80	92.5	45.1	46.3	45.7	22.1	22.5	22.6

Table 4

Pseudo-first-order rate constant for oxidation of CAP in the presence of various substances.

Coexisting substance	Concentration	k_{obs} (min ⁻¹)	Half-life (min)	R^2	Initial pH	Final pH
Control	0 mM	0.063	10.950	0.964	5.4	3.11
Cl ⁻	1 mM	0.066	10.486	0.925	5.4	3.09
	10 mM	0.032	21.935	0.912	5.4	3.12
	100 mM	0.006	119.508	0.973	5.4	3.13
	500 mM	0.004	182.407	0.832	5.5	3.15
HCO ₃ ⁻	1 mM	0.004	192.541	0.939	7.3	6.2
	10 mM	0.001	693.147	0.839	8.3	8.1
	100 mM	0.000	6931.472	0.084	8.4	8.4
NO ₃ ⁻	1 mM	0.038	18.289	0.929	5.4	3.12
	10 mM	0.031	22.652	0.957	5.4	3.12
	100 mM	0.013	51.727	0.903	5.4	3.13
NO ₂ ⁻	1 mM	0.006	111.798	0.850	5.4	3.12
	10 mM	0.003	239.016	0.826	5.4	3.13
HPO ₄ ²⁻	1 mM	0.002	315.067	0.986	7.2	7.0
	10 mM	0.000	2310.491	0.531	8.0	7.8
H ₂ PO ₄ ⁻	1 mM	0.021	33.648	0.974	6.0	5.5
	10 mM	0.007	103.455	0.860	5.7	5.3
HA	1 mg L ⁻¹	0.036	19.362	0.953	6.3	3.17
	5 mg L ⁻¹	0.039	17.911	0.811	6.3	3.26
	15 mg L ⁻¹	0.042	16.662	0.963	6.3	3.40
	45 mg L ⁻¹	0.022	32.090	0.924	6.5	3.67

SO₄⁻ and HO[•] contributed to the overall degradation performance, but HO[•] was the dominant oxidative species. Lei et al. [34] and Wu et al. [35] also obtained similar results for Acid Orange 7 treatment in Fe²⁺-PS-ascorbic acid system (initial pH = 3) and trichloroethylene treatment in Fe²⁺-PS-CA system, respectively.

3.2.5. Effect of co-existing inorganic ions

The effect of co-existing inorganic ions on CAP degradation by the ZVI-PS system is shown in Table 4, Fig. 6 and Fig. S7. CAP removal is extremely sensitive to the inorganic ions present in the solution of the ZVI-PS system. The Cl⁻ in the ZVI-PS system exhibited dual effects (favorable or adverse) on CAP degradation (Fig. 6a). The removal rate of CAP was slightly accelerated by the addition of a low Cl⁻ content (1 mM) but was gradually inhibited by the addition of a high Cl⁻ content. Both SO₄⁻ and HO[•] can oxidize Cl⁻ to less reactive chlorine species, which can also participate in CAP oxidation (Eqs. (9)–(12)). In the present study, [Cl₂⁻]/[Cl⁻] > 10 was expected because the concentration of the added Cl⁻ ions were higher than 0.1 mM and pH lower than 9 [36–37]. Excess SO₄⁻ in the absence of Cl⁻ may be scavenged through the cannibalization of SO₄⁻ by Eqs. (13) and (14) [38]:

At a low concentration of Cl⁻, excess SO₄⁻ reacts with Cl⁻ to form Cl₂⁻. Thus, the faster degradation of CAP may be partly attributed to the oxidation by Cl₂⁻. However, at a high concentration of

Fig. 6. The effect of co-existing inorganic ions on CAP degradation performance using ZVI-PS system: (a) Cl⁻, (b) HCO₃⁻. Conditions: [CAP]₀ = 0.05 mM; [PS]₀ = 1 mM; [ZVI]₀ = 1 mM.

Cl⁻, excess SO₄⁻ or HO[•] was consumed by Cl⁻, and the concentration of Cl₂⁻ rapidly increased with increasing Cl⁻ dosage. Hence, the degradation efficiency was reduced [37]. We also observed that the dual effects of Cl⁻ in CAP decomposition in the PS-heat system were concentration-dependent.

As shown in Fig. 6b, CAP oxidation was remarkably slow in the presence of HCO₃⁻, and the removal rate of CAP decreased with increasing HCO₃⁻ concentration. This result might be attributed to the competition for SO₄⁻ and HO[•] of HCO₃⁻ and the pH buffer action of the H₂CO₃/HCO₃⁻ system [39]. The reaction rate of SO₄⁻ recombination (Eq. (11)) is approximately two or three times higher than that of HCO₃⁻ or CO₃²⁻ generation (Eqs. (15)–(18)). Therefore, the contribution of HCO₃⁻ to CAP degradation might be negligible [37]:

The addition of phosphate species (H₂PO₄⁻ and HPO₄²⁻) significantly inhibited CAP degradation (Fig. S7a and b). Iron ions, including Fe²⁺ and Fe³⁺, remove phosphate from wastewater by chemical

Fig. 7. Oxidative removal of CAP in wastewaters using ZVI-PS system. Conditions: $[CAP]_0 = 0.05$ mM; $[PS]_0 = 1$ mM; $[ZVI]_0 = 1$ mM.

precipitation. Therefore, iron ions can rapidly form different complexes with phosphate species and decrease the available soluble Fe^{2+} for PS activation [16,28,40]. In addition, iron-phosphate complexes might rapidly cover the surface of ZVI, preventing PS access and therefore complicating iron corrosion. This phenomenon might be another reason for the inhibition of CAP degradation [19].

The addition of NO_2^- significantly decreased the removal efficiency even at a low ionic strength (i.e., 1 mM) (Fig. S7c). This finding can be attributed to the fact that NO_2^- is a strong scavenger for both $SO_4^{\cdot-}$ and $HO^{\cdot}$. The presence of NO_3^- also negatively influenced the removal of CAP by ZVI-PS (Fig. S7d). The removal efficiency decreased with increasing NO_3^- concentrations. A previous study showed that NO_3^- can react with ZVI to form NO_2^- and NH_3 by obtaining electrons from ZVI surfaces [41]. Hence, the generated Fe^{2+} would be oxidized to Fe^{3+} more quickly in the presence than in the absence of NO_3^- . In addition, the reaction between NO_3^- and ZVI is a corrosive process and leaves a film on the surface of ZVI that hinders further reactions with PS [42].

3.2.6. Effect of HA

The effect of HA on CAP degradation by the ZVI-PS system is shown in Fig. S8. Adding HA negatively influenced the removal efficiency of CAP. The inhibitory effect was enhanced with increasing

HA dosage. HA can compete with organic pollutants to react with reactive species and lower the degradation rates. In addition, the hydrophobic layer formed by HA is adsorbed onto the surface of ZVI [43]. Furthermore, the complexes or colloids between HA and the generated iron ions may inhibit the corrosion of ZVI. Consequently, $SO_4^{\cdot-}$ forms at a slow rate, and the degradation efficiency of the ZVI-PS system declines [43,44].

3.2.7. Oxidative removal of CAP in wastewaters

The oxidative removal of CAP in wastewaters by the ZVI-PS system is shown in Table 1 and Fig. 7. As discussed above, complex environmental matrices limit the efficiency of the ZVI-PS system. Previous studies suggested that colloids can act as a significant sink for antibiotics [1]. Moreover, the interaction of antibiotics with colloids affects the compound activity, and the effect is markedly affected by the colloidal composition [1,17]. However, to the best of our knowledge, the present study is the first to report the effect of wastewater colloids on CAP removal by the ZVI-PS system. Tests were conducted by using the filtrate, permeate, and retentate phases of wastewater to validate the capabilities of the system for CAP removal. The removal rates were slower in wastewater than in deionized water because the amount of organic matter was higher in wastewater than in deionized water. Coexisting constituents such as HCO_3^- and phosphate species in wastewater can also affect the removal efficiency. Compared with the filtrate and permeate, the retentate had lower removal rate and higher dissolved organic carbon content. Up to 92.8%, 94.7%, and 75.7% of CAP were removed from the filtrate, permeate, and retentate within 80 min, respectively. Considering that the CAP in the retentate can be effectively eliminated by the ZVI-PS system in the present work, we hypothesized that the ZVI-PS system can be effective in applications with concentrated wastewater containing a considerable organic load.

3.3. CAP degradation pathways in the ZVI-PS system

In the present study, seven major intermediate products were identified in the ZVI-PS system. The results of GC-MS based on comparison with the NIST data library revealed that intermediates formed during CAP degradation. The proposed reaction pathway for CAP removal by the ZVI-PS system is illustrated in Fig. 8. The sequence is initiated by the dehydration of CAP to yield III. Csay et al. [7] observed that reactive radicals preferentially attack the two asymmetric centers (C1 and C2) of CAP or VII. In the present work, the former led to the formation of III, which was further

Fig. 8. Expanded reaction pathway supposed in this study.

Fig. 9. Evolution profiles of intermediates using ZVI-PS system. Conditions: $[CAP]_0 = 1 \text{ mM}$; $[PS]_0 = 20 \text{ mM}$; $[ZVI]_0 = 20 \text{ mM}$.

transformed into IV. The latter resulted in VI and V with the loss of II, and I originated from the reduction of compound II via dehalogenation because of the low bond energy of C–Cl. The evolution profiles of the intermediates are organized and shown in Fig. 9. The yields of III and VII were the first and the second highest intermediates in the ZVI-PS system. After 80 min, the amounts of III were still appreciably high, whereas those of the other intermediates were relatively low. The TOC removal during ZVI-PS oxidation of CAP is presented in Fig. S9, and the TOC removal ratio after 80 min oxidation was 52%.

4. Conclusions

Fe^{2+} and ZVI were used to activate PS for CAP degradation. When activated by Fe^{2+} , CAP degradation was rapid but quickly slowed down. Changing the pH did not considerably influence CAP degradation, and the presence of chelating agents negatively affected oxidation efficiency. By contrast, the sequential addition of Fe^{2+} further enhanced CAP degradation. CAP oxidation efficiency reached 90.1% after 20 injections of Fe^{2+} . ZVI-activated PS facilitated a steady and efficient degradation of CAP. The optimum molar ratio of CAP/ZVI/PS was 1:20:20. The ZVI-PS system was effective for the CAP removal over a broad pH range of 3.0–10.0, and the acidic pH was more favorable for CAP degradation than neutral and alkaline. Scavenging tests suggested that $HO^\cdot$, $SO_4^{\cdot-}$ and $O_2^{\cdot-}$ contributed to the overall degradation performance, but $HO^\cdot$ predominated at all pH levels used. HCO_3^- , NO_3^- , NO_2^- , $H_2PO_4^-$, HPO_4^{2-} , and HA demonstrated adverse effects on CAP oxidation. Adding a low Cl^- concentration facilitated CAP degradation, but adding a high Cl^- concentration apparently inhibited this process. Up to 92.8%, 94.7%, and 75.7% of CAP were removed from the filtrate, permeate, and retentate phases of wastewater within 80 min, respectively. Therefore, the ZVI-PS system could be considered as a promising treatment method for decreasing the load of CAP in concentrated wastewater containing a considerable organic load. Seven intermediates were identified during CAP oxidation by the ZVI-PS system, and pathways of CAP degradation were proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.05.055>.

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