Effect of common inorganic ions on aniline degradation in groundwater by activated persulfate with ferrous iron
Yan Zhao, Yongsheng Zhao, Qin Li, Rui Zhou and Xu Chen

ABSTRACT
Aniline is widespread in groundwater and of great toxicity. Advanced oxidation processes, such as the ferrous iron (Fe2+)−activated persulfate process, have been proven to be effective for organic pollutants. However, few studies have focused on the effects of coexisting ions on the degradation of aniline. In this study, the degradation efficiency of aniline and the effects of common inorganic ions (CO32−/CO2−, PO43−/CO3−, HCO3−/CO2−, SO42−/CO2−, NO3−/CO2−, Na+, K+, Mg2+, and Ca2+) on aniline degradation were examined. Under the optimum operating conditions, 86.33% aniline degradation (C0 = 11 mmol/L) was observed within 60 min. The effects of cations on aniline degradation were negligible. Anions decreased the removal efficiency of aniline because of the radicals generated by the reaction between sulfate radical or hydroxyl radical and these anions. As the concentrations of PO43−/C0, CO32−/C0, SO42−/C0, HCO3−/C0, and NO3−/C0 increased from 0 mmol/L to 5 mmol/L, the removal efficiency of aniline decreased to 19.72%, 24.56%, 66.76%, 68.76%, and 82.42%, respectively. The order of inhibitory effects was PO43−/C0 > CO32−/C0 >> SO42−/C0 > HCO3−/C0 > NO3−/C0.

KEY WORDS | aniline, ferrous ion, groundwater, inorganic ions, persulfate

INTRODUCTION
Aniline widely exists in wastewater discharged from chemical industries, such as polymer, antioxidant, pesticide, and dye industries (Matsushita et al. 2005). It comprises a benzene ring to which one amino group is attached. This structure causes it to become a carcinogen, gastrointestinal toxicant, and kidney toxicant (Anotai et al. 2011). Although many regulations restrict its discharge, it is still detected in groundwater, especially after a sudden industrial accident (Zhu et al. 2007).

Traditional remediation methods for aniline-contaminated water, including physical (Tanhaei et al. 2014), chemical (Gomes et al. 2008), and biological (Jin et al. 2012) methods, have certain limitations because of the feature of groundwater. Advanced oxidation processes (AOPs) have been developed for the treatment of organic contaminants (Wang & Xu 2012). AOPs utilize active radicals, such as −OH and SO4• produced by several physical chemical reactions, to degrade pollutants (Liang & Su 2009; Zheng et al. 2014). Although AOPs cannot thoroughly mineralize contaminants (Antoniou et al. 2010) due to the relatively low radical yields and the complex water matrix, the AOPs may degrade most of the organic pollutants. (Huang & Huang 2009, Sun et al. 2015) and decrease the secondary pollution (Chu et al. 2015).

In AOPs, sodium persulfate (Na2S2O8) can be chemically (by transition metal ions, such as Fe2+, Ag+, and Co2+) or thermally activated, and produces SO4• which is a stronger oxidant (E° = +2.6 v) than S2O82− (E° = +2.01 v) (Hussain et al. 2012). SO4• has a longer half-life than −OH (Liu et al. 2014), and could degrade organic pollutants over a wide pH range (Oh et al. 2009). The activated reactions are as follows:

\[ S_2O_8^{2−} + 2e^- \rightarrow 2SO_4^{2−} \]
S_{2}O_{8}^{2-} + \text{heat/UV} \rightarrow 2SO_{4}^{\bullet} \quad (2)

S_{2}O_{8}^{2-} + \text{Me}^{n+} \rightarrow SO_{4}^{\bullet} + \text{Me}^{(n-1)+} + SO_{4}^{2-} \quad (3)

Ferrous ion is one of the most common inorganic ions in groundwater. Fe^{2+}-activated persulfate processing requires lower activation energy (62.16 kJ/mol) than thermal activation (140.7 kJ/mol) to produce SO_{4}^{\bullet} (Zhang et al. 2014). Thus, Fe^{2+} is a promising activator agent (Wu et al. 2014).

S_{2}O_{8}^{2-} + Fe^{2+} \rightarrow SO_{4}^{\bullet} + Fe^{3+} + SO_{4}^{2-} \quad (4)

Nevertheless, the existence of common inorganic ions in groundwater may influence the efficiency of AOPs. Previous studies have shown that major anions can affect the effectiveness of Fenton advanced oxidation treatment. Siedlecka et al. (2007) reported that the addition of chloride or phosphate ions decreased the efficiency of Fenton treatment of methyl 2,4,6-trinitrophenol ether-contaminated water. Ratanatamskul et al. (2010) reported that inorganic ions, including chloride ions, dihydrogen phosphate ions, and nitrate ions, can decrease the removal of nitrobenzene by the fluidized-bed Fenton process. Wu et al. (2014) studied the system of persulfate activated by citric acid-chelated-ferrous ion, and observed that the trichloroethene (TCE) degradation rate decreased as the Cl\(^{-}\) and HCO\(_{3}\) anions increased. However, studies on the effects of coexisting ions on the remediation of aniline-contaminated groundwater by Fe\(^{2+}\)-activated persulfate are rare. Thus, this study aimed to explore the optimum reaction concentrations of Fe\(^{2+}\) and persulfate for efficient aniline degradation, and observe the influence of common groundwater ions on aniline degradation.

**MATERIALS AND METHODS**

**Chemicals**

Sodium persulfate, ferrous nitrate, sodium carbonate, sodium bicarbonate, sodium sulfate, sodium phosphate, sodium nitrate, sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aniline and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). All solutions were prepared with ultrapure water purified by a Milli-Q system.

**Batch oxidation experiments**

The experiments were conducted in cylindrical glass bottles in a shaking water bath at 20 °C, and pH was controlled at 7.0 by H\(_{2}\)SO\(_{4}\) (0.1 mol/L) and NaOH (0.1 mol/L). Appropriate volumes of stock aniline and ferrous ion solution were placed into the reactor, and then sodium persulfate solutions were added to initiate the reaction. The final solution volumes were set at 100 mL. Aliquots of 1,000 μL were collected at selected time intervals. Methyl alcohol (MA), a common scavenger (the reaction kinetic constant of MA and SO\(_{4}^{\bullet}\) or -OH are \(1.6–7.7 \times 10^7\) s\(^{-1}\) and \(1.2–2.8 \times 10^9\) s\(^{-1}\) (Liang et al. 2013)), were mixed with the samples to quench the reaction. The solutions were immediately passed through a 0.22 μm membrane filter (Oh et al. 2009; Liu et al. 2014) for aniline analysis.

Different species and dosages of inorganic salts were dissolved in ultrapure water and mixed with aniline solution to investigate the effect of coexisting ions. Groundwater was also applied in the oxidized system to demonstrate the influence of anions in groundwater. Experiments were conducted in duplicate or triplicate. The data points without error bars are the mean of duplicate experiments. The error bars in the bar chart represent ± one standard deviation from the mean of triplicate data.

**Analytical methods**

The concentration of residual aniline in the aqueous phase was measured using high performance liquid chromatography (HPLC) (Agilent 1200, USA) equipped with a C18 column (150 mmol/L × 4.6 mmol/L, 5 μm) and UV detector at \(\lambda = 262\) nm. The mobile phase was composed of acetonitrile and buffer salts (65/35, v/v) with a flow rate of 1.0 mL/min. pH was measured by a YSI pH100 multi-parameter tester (OH, USA).

**RESULTS AND DISCUSSION**

**Effect of initial concentration of Fe\(^{2+}\) and persulfate**

To determine effect of the Fe\(^{2+}\) dose on aniline oxidation, experiments were carried out at a fixed sodium persulfate...
concentration (4.4 mmol/L) at pH 7.0 and 20 °C. The results are shown in Figure 1(a). Without Fe²⁺, the degradation efficiency was only 19.05% over a 60 min reaction. With the addition of Fe²⁺ (1.1–3.3 mmol/L), the removal efficiency of aniline increased to 62.56–86.33%. The addition of more Fe²⁺ generated more SO₄²⁻ to oxidize more aniline. However, the amount of SO₄²⁻ did not increase further when the initial Fe²⁺ concentration reached 4.4 mmol/L (corresponding to a degradation ratio of 73.38%). When Fe²⁺ was added in excess, excess SO₄²⁻ species were yielded, which may be directly scavenged by the remaining Fe²⁺ rather than oxidize aniline (Liang et al. 2009).

\[
\text{SO}_4^- + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \\
 k_1 = 4.6 \times 10^9 \text{L/(mol s)} (5)
\]

In addition, aniline degradation mainly occurred in the first 2 min of reaction. These results demonstrated that the activation of S₂O₈²⁻ by Fe²⁺ was a fast process, i.e., SO₄²⁻ radical was generated instantly.

The effect of persulfate concentration was analyzed at 11 mmol/L aniline and 3.3 mmol/L Fe²⁺ at pH 7.0. The results are shown in Figure 1(b). Persulfate at 0, 2.2, 3.3, 4.4, and 5.5 mmol/L resulted in degradation efficiencies of 15.72, 80.68, 85.64, 86.33, and 82.76% in 60 min, respectively. When the persulfate concentration increased from 0–4.4 mmol/L, the removal efficiencies of aniline were enhanced to more than 65%. The highest degradation efficiency was 86.33% at 4.4 mmol/L persulfate. However, the aniline removal efficiency decreased when a higher concentration of persulfate (5.5 mmol/L) was applied. With excessive persulfate, a large quantity of SO₄²⁻ was produced within a short time and quenched by themselves (Xu & Li 2010). Excessive S₂O₈²⁻ also resulted in competition for SO₄²⁻ with the target contaminant (Lau et al. 2007).

\[
\text{SO}_4^- \cdot + \text{SO}_4^- \rightarrow \text{S}_2\text{O}_8^{2-} \\
k_2 = 4.0 \times 10^8 \text{L/(mol s)} (6)
\]

\[
\text{SO}_4^- \cdot + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^- \cdot \\
k_3 = 6.1 \times 10^5 \text{L/(mol s)} (7)
\]

Under the condition in this study, the optimum Fe²⁺ and PS concentrations were 3.3 and 4.4 mmol/L, respectively, and this condition was applied in subsequent experiments.

**Effect of different anions**

To determine the effect of anions on aniline degradation by Fe²⁺-activated persulfate, five types of anions (HCO₃⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, and PO₄³⁻) at different concentrations were added into the system. The results are shown in Figure 2. Figures 2(a)–2(d) indicate that HCO₃⁻, SO₄²⁻, CO₃²⁻, and PO₄³⁻ had negative effects on the degradation of aniline.
Figure 2(e) indicates that the influence of NO$_3^-$ on the degradation of aniline was not significant. As the anion concentration increased to 10 mmol/L, the degradation efficiencies of aniline decreased to 69.15, 59.83, 19.19, 17.32, and 82.47% for HCO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$, CO$_3^{2-}$, and NO$_3^-$, respectively. However, the removal efficiency of aniline was 86.33% without any added anions in the solution.

As shown in Figure 2(a), the degradation of aniline decreased with increasing CO$_3^{2-}$ concentration. The aniline removal efficiencies ranged from 66.36% to 17.32% at 1 to 10 mmol/L CO$_3^{2-}$, respectively. Previous studies reported that SO$_4^{2-}$ can react with H$_2$O and OH$^-$ to generate OH$^-$ at different pH levels (Liang et al. 2007). SO$_4^{2-}$ starts to convert into OH$^-$ quickly at the solution pH > 8.5. As the solution pH > 10.7, OH$^-$ will become the main radical in the reaction.
system (Dogliotti & Hayon 1967). The initial pH value was 11.4 in the reaction systems when we added 2 mmol/L CO$_3^{2-}$. Thus, ·OH was the major radical for aniline degradation. Radicals may be scavenged by the anions in solutions, and the formation of the corresponding anion radicals has also been demonstrated (Roshani & Karpet vel Leitner 2011). These corresponding anion radicals can oxidize organic compounds at different rates (Neta et al. 1988). Under this condition, CO$_3^{3-}$ is the radical quencher of ·OH (Buxton et al. 1988).

$$
\text{CO}_3^{2-} + \cdot \text{OH} \rightarrow \text{OH}^- + \text{CO}_3^{3-} \\
k_4 = 3.9 \times 10^8 \text{L/(mol s)}
$$

(8)

Figure 2(a) also shows the effect of different dosages of CO$_3^{2-}$ on aniline degradation. At low CO$_3^{2-}$ concentration, CO$_3^{3-}$ may compete with ·OH, which could lead to the decrease in the degradation efficiency of aniline because CO$_3^{3-}$ is a poorer oxidant than SO$_4^{2-}$ (Wu et al. 2014). When the concentration increased to 10 mmol/L, the anion was possibly converted into an insoluble compound with Fe$^{2+}$ in solution, which resulted in the reduction in Fe$^{2+}$ concentration. Given that Fe$^{2+}$ was applied to activate the persulfate to generate ·OH or SO$_4^{2-}$, lower utilization of Fe$^{2+}$ could reduce the quantity of radicals and then decrease the removal efficiency.

In reaction systems with PO$_4^{3-}$ (pH 11.6) and HCO$_3$ (pH 8.1), the degradation efficiencies of aniline decreased from 86.33% to 55.30% and 72.49%, respectively, at an anion concentration of 2 mmol/L. For solutions containing PO$_4^{3-}$ and HCO$_3$, the major radicals decomposing aniline were ·OH and SO$_4^{2-}$, respectively. Quenching of ·OH or SO$_4^{2-}$ occurred and generated free radicals with lower oxidizing ability than ·OH or SO$_4^{2-}$ (Neta et al. 1988).

$$
\text{PO}_4^{3-} + \cdot \text{OH} \rightarrow \text{OH}^- + \text{PO}_4^{2-} \\
k_5 = 1.0 \times 10^7 \text{L/(mol s)}
$$

(9)

$$
\text{HCO}_3^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{CO}_3^{3-} + \text{H}^+ \\
k_6 = 9.3 \times 10^6 \text{L/(mol s)}
$$

(10)

As shown in Figure 2(b), when the concentration of PO$_4^{3-}$ was low, such as 1 mmol/L, the degradation percentage of aniline decreased from 86.33 to 64.50%. At high PO$_4^{3-}$ concentration of 5 mmol/L, the removal efficiency of aniline was 19.72%. Besides the scavenging of ·OH and SO$_4^{2-}$, Fe$^{2+}$ and Fe$^{3+}$ may form an insoluble compound with PO$_4^{3-}$, such as FePO$_4$ and Fe$_3$(PO$_4$)$_2$, with respective solubility products (Ksp) of $4 \times 10^{-27}$ and $1 \times 10^{-36}$. The precipitation of Fe$^{2+}$ resulted in low utilization of Fe$^{2+}$ to activate persulfate and decreased the removal of aniline.

As shown in Figure 2(d), the degradation efficiency of aniline decreased from 72.49 to 59.83% as the concentration of SO$_4^{2-}$ increased from 1 to 10 mmol/L. The inhibitory effect of SO$_4^{2-}$ on aniline removal was slightly larger than that of HCO$_3$ and much smaller than those of CO$_3^{3-}$ and PO$_4^{3-}$. According to chemical equilibrium theory, the accumulation of reaction products inhibited the forward reaction. Based on Equation (4), the addition of SO$_4^{2-}$ inhibited the forward reaction between $\text{S}_2\text{O}_8^{2-}$ and Fe$^{2+}$ and reduced the generation of SO$_4^{2-}$. Thus, the additional SO$_4^{2-}$ inhibited aniline removal. SO$_4^{2-}$ could not react with SO$_4^{2-}$ or ·OH nor precipitate with Fe$^{2+}$. Therefore, the inhibitory effect of SO$_4^{2-}$ was smaller than that of CO$_3^{3-}$ and PO$_4^{3-}$. The effect of NO$_3$ on aniline degradation was not significant (Figure 2(e)). The removal efficiency of aniline was between 86.33 and 82.47% when the nitrate concentrations varied from 0 to 10 mmol/L. NO$_3$ did not form insoluble compounds with Fe$^{2+}$ or Fe$^{3+}$, and the reaction between Fe$^{2+}$ and persulfate was not suppressed. In addition, NO$_3$ did not react with SO$_4^{2-}$ or ·OH, so the removal efficiency of aniline was not inhibited.

In the Fe$^{2+}$-activated persulfate system, coexisting anions inhibited the removal of aniline. As shown in Figure 5, different anions affected aniline degradation at different degrees. The order of inhibitory effect was PO$_4^{3-} >$ CO$_3^{3-} >$ SO$_4^{2-} >$ HCO$_3$ > NO$_3$. The removal efficiencies of aniline were 68.76, 66.76, 19.72, 24.65, and 82.42% with HCO$_3$, SO$_4^{2-}$, PO$_4^{3-}$, CO$_3^{3-}$, and NO$_3$ at 5 mmol/L, respectively. Quenching of SO$_4^{2-}$ or ·OH by PO$_4^{3-}$, CO$_3^{3-}$, and HCO$_3$ generated radicals corresponding to these anions. These radicals had lower oxidizing ability than SO$_4^{2-}$ or ·OH, resulting in the decline of the aniline removal. Besides that, PO$_4^{3-}$ and CO$_3^{3-}$ could also form insoluble compounds with Fe$^{2+}$ (such as FeCO$_3$ and Fe$_3$(PO$_4$)$_2$) and lower the utilization of Fe$^{2+}$, which lower the generation
of $\text{SO}_4^{2-}$. Hence, $\text{CO}_3^{2-}$ and $\text{PO}_4^{3-}$ had larger inhibitory effects than $\text{SO}_4^{2-}$, $\text{HCO}_3^-$, and $\text{NO}_3^-$. According to chemical equilibrium theory, addition of $\text{SO}_4^{2-}$ inhibited the generation of $\text{SO}_4^{2-}$ and then decreased the removal of aniline in the system. $\text{NO}_3^-$ did not undergo the reactions mentioned above, so the inhibitory effect of $\text{NO}_3^-$ on the aniline removal was the smallest of all anions.

**Effect of different cations**

Four different types of cations ($\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, and $\text{Ca}^{2+}$) at two concentrations (10 and 50 mmol/L) were added in the reaction system. Figure 4 shows that these cations had no significant effects on aniline degradation. Although the concentration of added cations increased to 10 and 50 mmol/L, the removal efficiency of aniline deceased only less than 5%. This finding indicated that all these cations could not activate persulfate to produce the $\text{SO}_4^{2-}$, or inhibited the yields of $\text{SO}_4^{2-}$ and $\cdot\text{OH}$. These results were consistent with the findings of previous studies, which demonstrated that persulfate can be activated only by transition metal ions ($\text{Me}^{n+}$) to form $\text{SO}_4^\bullet$ (Wu et al. 2014).

**Aniline removal in groundwater**

Experiments were conducted to study the degradation of aniline in real groundwater and ultrapure water. Properties of the groundwater sample are: pH: 7.24; total dissolved solids (TDS): 830 mg/L; $\text{CO}_3^{2-}$: 0.2 mmol/L; $\text{HCO}_3^-$: 1.6 mmol/L; $\text{SO}_4^{2-}$: 1.74 mmol/L; $\text{Cl}^-$: 1.58 mmol/L; and $\text{NO}_3^-$: 0.62 mmol/L. Figure 5 shows the comparison of $\text{Fe}^{2+}$-activated persulfate oxidation of aniline in groundwater and ultrapure water at 20°C. It can be seen that aniline removal efficiency in groundwater was 53.05% within 60 min which was much lower than that in ultrapure water (86.33%). The anions existed in groundwater, such as $\text{CO}_3^{2-}$, $\text{HCO}_3^-$ and $\text{SO}_4^{2-}$, hindered the degradation of aniline in $\text{Fe}^{2+}$-activated persulfate system. When the concentrations of $\text{CO}_3^{2-}$, $\text{HCO}_3^-$ and $\text{SO}_4^{2-}$ were 1 mmol/L, 2 mmol/L and 2 mmol/L in ultrapure water, the aniline removal efficiency reduced tp 19.97, 13.85 and 17.18% respectively. Comparatively, although

![Image 3](https://iwaponline.com/ws/article-pdf/16/3/667/412601/ws016030667.pdf)

**Figure 3** | Effect of different anions on degradation of aniline at [Anions] = 5 mmol/L. [Aniline] = 11 mmol/L; [Persulfate] = 4.4 mmol/L; [Fe$^{2+}$] = 3.3 mmol/L.

![Image 4](https://iwaponline.com/ws/article-pdf/16/3/667/412601/ws016030667.pdf)

**Figure 4** | Effect of common cations on degradation of aniline. [Aniline] = 11 mmol/L; [Persulfate] = 4.4 mmol/L; [Fe$^{2+}$] = 3.3 mmol/L.

![Image 5](https://iwaponline.com/ws/article-pdf/16/3/667/412601/ws016030667.pdf)

**Figure 5** | Comparison of degradation of aniline in groundwater and ultrapure water. [Aniline] = 11 mmol/L; [Persulfate] = 4.4 mmol/L; [Fe$^{2+}$] = 3.3 mmol/L.
the concentration of each anion in groundwater was lower than that in the ultrapure water, the total concentration was higher, and the inhibition influence of the anions on aniline removal efficiency was enhanced to 33.28%.

CONCLUSIONS

Aniline degradation was investigated via Fe\(^{2+}\)-activated persulfate under different ion conditions. The major conclusions included the following. (1) In the aqueous solution system, the highest removal efficiency of aniline (C\(_0\) = 11 mmol/L) reached 83.66% within 60 min. The degradation efficiency decreased by further addition of either persulfate or Fe\(^{2+}\). (2) An inhibitory effect was found with the addition of CO\(_3\)\(^{2-}\), PO\(_4\)\(^{3-}\), SO\(_4\)\(^{2-}\), HCO\(_3\), and NO\(_3\). The order of the inhibition was PO\(_4\)\(^{3-}\) > CO\(_3\)\(^{2-}\) > SO\(_4\)\(^{2-}\) > HCO\(_3\) > NO\(_3\). The reasons included: (i) quenching of SO\(_4\)\(^{2-}\) or •OH by CO\(_3\)\(^{2-}\), PO\(_4\)\(^{3-}\), SO\(_4\)\(^{2-}\), and HCO\(_3\) generated free radicals with lower oxidizing ability than SO\(_4\)\(^{2-}\) and •OH, which decreased the removal efficiency of aniline; (ii) given that CO\(_3\)\(^{2-}\) and PO\(_4\)\(^{3-}\) could form insoluble compounds with Fe\(^{2+}\), which further decreased the aniline degradation efficiency; (iii) according to chemical equilibrium theory, addition of SO\(_4\)\(^{2-}\) may retard the generation of SO\(_4\)•, thereby reducing the removal of aniline; and (iv) the inhibition of NO\(_3\) on aniline removal was negligible. (3) Cations (Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) common in groundwater also had minimal and negligible effects on the degradation efficiency of aniline.

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