Efficient degradation of naproxen by persulfate activated with zero-valent iron: performance, kinetic and degradation pathways
Shuyu Dong, Xiaoxue Zhai, Ruobing Pi, Jinbao Wei, Yunpeng Wang and Xuhui Sun

ABSTRACT
Degradation of naproxen (NAP) by persulfate (PS) activated with zero-valent iron (ZVI) was investigated in our study. The NAP in aqueous solution was degraded effectively by the ZVI/PS system and the degradation exhibited a pseudo-first-order kinetics pattern. Both sulfate radical (SO₄²⁻) and hydroxyl radical (HO) participate in the NAP degradation. The second-order rate constants for NAP reacting with SO₄²⁻ and HO were (5.64 ± 0.73) × 10⁹ M⁻¹ s⁻¹ and (9.05 ± 0.51) × 10⁹ M⁻¹ s⁻¹, respectively. Influence of key parameters (initial pH, PS dosage, ZVI dosage, and NAP dosage) on NAP degradation were evaluated systematically. Based on the detected intermediates, the pathways of NAP degradation in ZVI/PS system was proposed. It was found that the presence of ammonia accelerated the corrosion of ZVI and thus promoted the release of Fe²⁺, which induced the increased generation of sulfate radicals from PS and promoted the degradation of NAP. Compared to its counterpart without ammonia, the degradation rates of NAP by ZVI/PS were increased to 3.6–17.5 folds and 1.2–2.2 folds under pH 7 and pH 9, respectively.

Key words | ammonia, degradation pathways, reactive species, ZVI/PS system

HIGHLIGHTS
● Naproxen (NAP) could be efficiently degraded by persulfate activated with zero-valent iron.
● The rate constants of NAP reacting with SO₄²⁻ and HO were determined.
● The possible oxidation pathways was elaborated for NAP degradation.
● Ammonia enhanced the degradation of NAP by accelerating the release of dissolved iron.

GRAPHICAL ABSTRACT

INTRODUCTION

Naproxen (NAP), a typical nonsteroidal anti-inflammatory drug (NSAID), was frequently detected in wastewater treatment plant effluents with concentration ranging from 25 ng L\(^{-1}\) to 33.9 μg L\(^{-1}\) (Kanakaraju et al. 2015). The toxicological study indicated that adverse impact on Vibrio fischeri was caused by NAP with an EC\(_{50}\) of 21.2 μg L\(^{-1}\) (Luo et al. 2018a). Moreover, long-term ingestion of NAP may increase the risk of heart attack in humans (Chi et al. 2019). Unfortunately, it is still a challenge for conventional water treatment to eliminate NAP efficiently at a short treatment period (Xu et al. 2019), and thus it is urgent to exploit appropriate approaches to degrade these contaminants in the aqueous environment.

In the past decade, advanced oxidation processes (AOPs) based on the sulfate radical (SO\(_4^\cdot\), \(E^0 = 2.5\)–3.1 V) were found to be excellent for degradation of refractory organic contaminants such as ranitidine, sulfamethoxazole, ibuprofen, ketoprofen, chloramphenicol, theophylline, etc. (Ghauch et al. 2017; Naim & Ghauch 2019; Li et al. 2019a, 2019b; Yan et al. 2019). Among these, transition metal ion activation has the superiorities of high efficiency and cost effectiveness (Rao et al. 2014; Chen et al. 2018). Iron is of special interest due to its abundance and environmentally friendly properties (Zhao et al. 2016). SO\(_4^\cdot\) can be efficiently generated from the reaction of Fe\(^{2+}\) with PS.

Unlike homogeneous Fe\(^{2+}\) activation, zero-valent iron (ZVI) could react as an alternative source of Fe\(^{2+}\) to gradually release Fe\(^{2+}\) (Equations (1)–(3)) (Girit et al. 2015; Zhao et al. 2016), causing minimal quenching of SO\(_4^\cdot\) induced by excessive Fe\(^{2+}\) (Equation (4)) (Ghauch et al. 2013; Wei et al. 2016). ZVI has been used as stand-alone material to eliminate pharmaceuticals from water such as diclofenac (Ghauch et al. 2010). However, the excess of iron sludge formation inspired researchers to use it as a sacrificial catalyst in AOPs as, for example, the degradation of carabamazepine in ZVI/H\(_2\)O\(_2\) systems, sulfamethoxazole in bimetalllics and trimetallics iron–PS based systems, or ranitidine using iron scrap multi-metallic systems (Ghauch et al. 2011; Ayoub & Ghauch 2014; Naim & Ghauch 2016). Moreover, Fe\(^{3+}\) could be recycled to produce Fe\(^{2+}\) on the surface of ZVI through Equation (5) (Hussain et al. 2012). Therefore, utilization efficiency of PS is enormously enhanced especially in oxic solutions where total organic carbon (TOC) removal was improved compared to anoxic conditions as reported earlier (Ghauch et al. 2013; Ayoub & Ghauch 2014). Recently, there has been interest in using the combination of ZVI/PS for refractory organics decontamination. Wei et al. (2016) examined the roles of key parameters in the ZVI/PS process. A study on fenitrothion (FNT) degradation in the ZVI/PS process revealed that the addition of ZVI increased the FNT degradation by PS (Liu et al. 2019). However, there were several defects in the reaction between Fe\(^{2+}\) and PS, particularly in the limits of a strict pH range as in the traditional Fenton-like system (Wu et al. 2015), which results in reduced removal efficiency of target pollutants.

\[
\begin{align*}
\text{Fe}^0 + \text{H}_2\text{O} + 0.5\text{O}_2 & \rightarrow \text{Fe}^{2+} + 2\text{OH}^- \quad \text{(oxic condition)} \\
\text{Fe}^0 + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2 \quad \text{(anoxic condition)} \\
\text{Fe}^0 + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} \\
\text{SO}_4^\cdot + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \\
\text{Fe}^0 + 2\text{Fe}^{3+} & \rightarrow 3\text{Fe}^{2+}
\end{align*}
\]

As far as we know, NAP has been investigated in thermally activated PS systems (Ghauch et al. 2015); however, there is no information about NAP degradation in the ZVI/PS system. The major purposes of this work were: (1) to elucidate the superiority and kinetics of ZVI/PS system on NAP degradation; (2) to make clear the primary reactive species contribution to NAP degradation and to determine the reaction rates between NAP and reactive species; (3) to explore the impacts of pivotal parameters, including initial pH, PS dosage, ZVI dosage, and NAP concentration on NAP degradation; (4) to propose the NAP degradation pathways by the detected intermediates analysis; and (5) to show an unexpected finding that better removal of NAP were achieved with adding ammonia in ZVI/PS system under neutral and basic conditions.
MATERIALS AND METHODS

Materials

All chemicals were of reagent grade without any further purification. The solutions were prepared using deionized (DI) water produced from a Milli-Q Academic water purification system and stored at 4 °C before being used. Except for NAP, all the stock solutions were prepared daily. NAP (purity >99.0%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and ZVI (purity >99%) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Approximately 50% of these ZVI particles had a diameter size less than 36.54 μm (shown in Figure S1, Supplementary Material). Methanol (high performance liquid chromatography (HPLC) grade) and all other chemicals used were purchased from Sinopharm Chemical Reagent Co. Ltd (Beijing, China).

Experimental procedure

Experiments were carried out in a 1-L glass beaker to investigate the degradation efficiency of NAP in the ZVI/PS process. For each run, 500 mL of prepared NAP (25 μM) solution was poured into the 1-L glass beakers and the initial solution pH (3.0–11.0) was adjusted using 0.1 M H2SO4 and/or NaOH. Experiments were initiated by adding the appropriate amount of ZVI (0.25–1.50 mM) and PS (0.1–0.5 mM) to the aforementioned solution. The temperature of experiments was maintained at 25 ± 1 °C. The solution was mixed uniformly by a mechanical stirrer, the rotate speed of agitation bar was kept at 300 rpm to ensure a complete mixing state. Samples were withdrawn at predetermined time intervals with 5.0 mL syringes and quickly filtered with 0.22 μm membrane. At the same time, 800 μL filtered sample was collected and 200 μL ethanol (EtOH) was injected into each sample to terminate the reaction.

The scavenging experiments with tertbutyl alcohol (TBA) and EtOH were conducted by adding desired alcohols into the reaction solution before the addition of PS. To disclose the potential effect of ammonia, NAP solution was mixed with NH4Cl (0–10 mM) first, and then the pH was adjusted to 7.0 and 9.0 using the procedures described above. All tests were repeated at least twice.

Analytical methods

The concentrations of benzoic acid (BA), nitrobenzene (NB), and NAP were measured with HPLC (Shimadzu LC-2010AHT, Kyoto, Japan), and the detailed parameters are shown in Text S1 (Supplementary Material). PS was quantified spectrophotometrically (Liang et al. 2008). The concentration of Fe²⁺ was quantified at 510 nm according to the 1,10-phenanthroline method and total iron was determined by atomic absorption spectroscopy (Shimadzu AA-7000, Kyoto, Japan). TOC was measured with a TOC analyzer (liqui TOC II, Elementar, Germany). The pH value was measured with a pH meter (Mettler Toledo Five Easy Plus pH Meter, Shanghai, China). The electron spin resonance (ESR) was carried out using a JES-FA 200 ESR spectrometer. The ESR experiments were performed under the following conditions: a center field of 335 mT, a sweep width of 10 mT, a microwave frequency of 9,425.572 MHz, a microwave attenuator of 30 dB, a microwave power of 0.998 mW, and a sweep time of 60 s. The intermediates of NAP were detected using ultra-performance liquid chromatography (UPLC)–quadrupole time-of-flight mass spectrometry (QTOF–MS)/mass spectrometry (MS) (AB SCIEX ExionLC AD UPLC coupled with AB SCIEX 5600 + Q-TOF, USA), with details shown in Text S2.

To determine the utilization efficiency of PS, the reaction stoichiometric efficiency (RSE) was used in previous articles (Ghauch et al. 2015, 2017; Amasha et al. 2018), which is defined as the ratio between the number of NAP degraded versus the number of PS consumed.

RESULTS AND DISCUSSION

Degradation of NAP in different systems

The results of NAP degradation in different systems can be seen in Figure 1. Neither ZVI nor PS alone had a notable effect on the NAP degradation with the extremely low NAP removal efficiency (<2%). In contrast, the ZVI/PS process showed high levels of removal efficiency (93.5%) for NAP. Similar results have also been observed in the ZVI/PS system for degradation of sulfamethoxazole (Ghauch et al. 2015; Ayoub & Ghauch 2014) and bentazon (Wei et al. 2016). As NAP was difficult to be degraded by only PS oxidation and ZVI, it could be concluded that SO4²⁻ and/or HO’ were the main reactive species in NAP degradation during the ZVI/PS process (Equations (6)–(9)) (Oh et al. 2010; Wu et al. 2014). However, NAP degradation in PS thermally activated system showed that SO4²⁻ were the dominant species responsible for NAP degradation. The structure of NAP has a naphtalenic ring favoring more electron transfer than hydrogen abstraction (Ghauch et al. 2015). The average % RSE calculated was close to 44.5%, which is
smaller than that obtained in thermally activated PS systems (Ghauch et al. 2015); however, it exceeded the RSE values in chemically activated systems (Amasha et al. 2018). The Fe^{2+}/PS system was also set up in this study. For comparison, the additional amount of Fe^{2+} was the total amount of Fe dissolved in the ZVI/PS system: 1.07 mg/L. As shown in Figure 1, NAP was promptly degraded in the ZVI/PS system: 1.07 mg/L. As shown in Figure 2(b), these results suggest that both SO_4^{2-} and HO’ almost react with scavengers rather than NAP. Although SO_4^{2-} was usually recognized as one of the dominant active species, it was controversial whether HO’ was one of the reactive species (Liang & Su 2009; Rastogi et al. 2009; Wang & Chu 2011; Ghauch et al. 2013). To test the role of HO’ in the ZVI/PS process, nitrobenzene (NB)

follows a pseudo-first-order kinetics model (Equation (10)):

\[
\ln\left(\frac{C_t}{C_0}\right) = -k_{obs} \times t
\]  

where \(C_0\) is the initial concentrations of NAP; \(C_t\) is the concentrations of NAP at reaction time \(t\), and \(k_{obs}\) is the degradation rate constant. In the inset of Figure 1, the degradation rate constant of NAP was determined to be 0.08418 min^{-1} under the certain experimental condition.

**Reactive species identification**

It has been demonstrated that reactive oxidants (i.e. SO_4^{2-}, HO’) could be produced in the decomposition of PS induced by catalysts (Zou et al. 2013; Li et al. 2016). EtOH with α-H is a suitable quencher for both SO_4^{2-} (\(k = 2.5 \times 10^7\) M^{-1} s^{-1}) and HO’ (\(k = 9.7 \times 10^8\) M^{-1} s^{-1}), while TBA without α-H is an effective scavenger for HO’ (\(k = 6.0 \times 10^8\) M^{-1} s^{-1}) but not for SO_4^{2-} (\(k = 8.0 \times 10^5\) M^{-1} s^{-1}) (Buxton et al. 1988; Neta et al. 1988). Based on these properties, EtOH and TBA, were used to differentiate the role of active species in NAP degradation.

In order to inhibit the oxidation adequately, the radical scavengers were added to obtain a concentration of 0.25 M: scavengers/PS/NAP (10000/10/1). The results taken from the scavenging experiments are shown in Figure 2(a). It is obvious that either TBA or EtOH presented strong inhibiting impact on NAP degradation at pH 5.0 and the addition of 0.25 M EtOH almost completely inhibited NAP degradation. When TBA and EtOH were added, the value of \(k_{obs}\) decreased from 0.10475 min^{-1} to 0.03952 min^{-1} and 0.00386 min^{-1}, respectively, indicating that both SO_4^{2-} and HO’ are the primary reactive species facilitating NAP degradation (as shown in Table 1). In addition, Figure S2 and Table 1 show that the addition of TBA and EtOH exerted negative effect on the NAP degradation under both pH 7.0 and pH 9.0 conditions. These results demonstrated that both SO_4^{2-} and HO’ are responsible for the removal of NAP in the ZVI/PS system. However, there was no difference in PS decomposition between the results with and without scavengers (Figure 2(b)). These results suggest that both SO_4^{2-} and HO’ almost react with scavengers rather than NAP. Although SO_4^{2-} was usually recognized as one of the dominant active species, it was controversial whether HO’ was one of the reactive species (Liang & Su 2009; Rastogi et al. 2009; Wang & Chu 2011; Ghauch et al. 2013). To test the role of HO’ in the ZVI/PS process, nitrobenzene (NB)}
was selected as the probe for efficient reactivity toward •OH \((k = 3.9 \times 10^9 \text{ M}^{-1} \text{s}^{-1})\) (Neta et al. 1988) but insignificant toward \(\text{SO}_4^{2-}\) \((k \leq 1.0 \times 10^6 \text{ M}^{-1} \text{s}^{-1})\) (Buxton et al. 1988). As depicted in Figure S3, approximately 70% of NB was oxidized within 30 min, while NB oxidation was inhibited with the presence of TBA (10 mM). The findings further verify that \(\text{HO}^+\) was also one of the dominant active species in the ZVI/PS system.

ESR technology was conducted to detect \(\text{SO}_4^{2-}\) and \(\text{HO}^+\) directly. DMPO was employed as the spin-trapping agent, and recent studies reported that \(\text{SO}_4^{2-}\) and \(\text{HO}^+\) can be identified through the detected signal of DMPO–\(\text{SO}_4\) adducts and DMPO–\(\text{HO}\) adducts, respectively (Zou et al. 2014; Li et al. 2019b). As shown in Figure 3, a specific four-peak spectrum with intensity ratios of 1:2:2:1 was detected, and the special hyperfine coupling constants of \(a(\text{N}) = 1.50 \text{ mT}\) and \(a(\text{H}) = 1.49 \text{ mT}\) were consistent with DMPO–OH adducts (Zou et al. 2013; Li et al. 2019b), indicating that \(\text{HO}^+\) was generated. The ESR spectra at pH 5.0 showed the signal of DMPO–OH adducts with higher intensity than at pH 3.0. The typical spectrum of DMPO–\(\text{SO}_4\) adducts was not found. The results might suggest that DMPO–\(\text{SO}_4\) adducts had been converted to DMPO–\(\text{HO}\) adducts by nucleophilic substitution (Zou et al. 2013; He et al. 2020).

### Reaction rate constants of NAP with \(\text{SO}_4^{2-}\) and \(\text{HO}^+\)

A competition kinetic method was utilized to measure the reaction rate constants of NAP with \(\text{SO}_4^{2-}\) and \(\text{HO}^+\). The

<table>
<thead>
<tr>
<th>pH</th>
<th>kobs (\times 10^2 \text{ (min}^{-1})) with addition of</th>
<th>Contribution to NAP degradation of</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>104.75, 3.86, 39.52</td>
<td>60.8%, 39.2%</td>
</tr>
<tr>
<td>7.0</td>
<td>8.36, 1.29, 5.03</td>
<td>28.9%, 71.1%</td>
</tr>
<tr>
<td>9.0</td>
<td>7.08, 0.82, 3.03</td>
<td>51.6%, 48.4%</td>
</tr>
</tbody>
</table>

Figure 2 | Effect of different radical scavengers on (a) NAP degradation and (b) PS decomposition. Experimental conditions: \([\text{NAP}]_0 = 25 \mu\text{M}, [\text{PS}]_0 = 0.25 \text{mM}, [\text{TBA}]_0 = 0.25 \text{M}, [\text{EtOH}]_0 = 0.25 \text{M}, T = 298.15 \text{K}, \text{initial pH} = 5.0.\)

Figure 3 | ESR spectra with the existence of DMPO in the ZVI/PS system. Experimental conditions: \([\text{PS}]_0 = 5.0 \text{mM}, [\text{ZVI}]_0 = 3.0 \text{g/L}, [\text{DMPO}]_0 = 100 \text{mM}, T = 298.15 \text{K}.\)
reaction rate constants between BA with HO\(^-\) (5.9 \times 10^9 \text{ M}^{-1} \text{s}^{-1}) and SO\(_4\)\(^{-}\) (1.2 \times 10^9 \text{ M}^{-1} \text{s}^{-1}) were determined (Wang et al. 2019), thus BA was selected as the reference. Because the contribution of direct oxidation by oxidants can be ignored (Figure S4), the reaction rate constant for NAP reacting with SO\(_4\)\(^{-}\) can be calculated using Equation (11) (see Text S3 for details):

\[
\ln \frac{[\text{NAP}]_0}{[\text{NAP}]_t} = \frac{k_{\text{SO}_4^{-}/\text{NAP}}}{k_{\text{SO}_4^{-}/\text{BA}}} \ln \frac{[\text{BA}]_0}{[\text{BA}]_t}
\]  

(11)

The plot of \(\ln([\text{NAP}]_0/[\text{NAP}]_t)\) versus \(\ln([\text{BA}]_0/[\text{BA}]_t)\) drew a straight line with zero intercept. As seen from Figure 4(a), the value of the slope was 4.70 \pm 0.61, thus the reaction rate constant of SO\(_4\)\(^{-}\) with NAP was calculated as \((5.64 \pm 0.73) \times 10^9 \text{ M}^{-1} \text{s}^{-1}\). Applying the same means, the value of the slope was 1.54 \pm 0.09 (Figure 4(b)), and the rate constant of NAP with HO\(^-\) was calculated to be \((9.09 \pm 0.53) \times 10^9 \text{ M}^{-1} \text{s}^{-1}\).

**Effects of parameters on NAP degradation**

**Effect of initial pH**

The impacts of different initial pH (3.0, 5.0, 7.0, 9.0, 11.0) on the ZVI/PS degradation of NAP were evaluated and the experimental results are shown in Figure 5(a) and 5(b). At initial solution pH \(\leq 5.0\), the ZVI/PS process can effectively degrade NAP within 30 min. In particular, \(k_{\text{obs}}\) at initial pH 3.0 was the largest (0.27155 min\(^{-1}\)). The \(k_{\text{obs}}\) of NAP removal markedly decreased from 0.08418 to 0.00815 min\(^{-1}\) with pH increasing from 5.0 to 7.0, then indistinctively decreased to 0.00691 min\(^{-1}\) at pH 9.0; however, the NAP degradation was marginal at pH 11.0 (\(k_{\text{obs}} = 0.00201 \text{ min}^{-1}\)), indicating that the ZVI/PS process cannot degrade NAP in strong alkaline condition. The results suggest the following. (1) Acidic conditions favor the formation and maintenance of Fe\(^{2+}\) (Figure S5) and Fe\(^{2+}\) plays a major role in the production of SO\(_4\)\(^{-}\) (Equation (7)). The pitting corrosion of ZVI decreased under neutral conditions (Ghauch et al. 2013), and the passivation on the ZVI surface was accelerated in alkaline solution, and thus hindered the further release of Fe\(^{2+}\), which results in less reactive oxygen species generated. (2) SO\(_4\)\(^{-}\) tended to be converted to HO\(^-\) (Equations (8) and (9)), and the oxidation–reduction potential of HO\(^-\) is significantly decreased to 1.8 V under alkaline conditions (Li et al. 2018a). HO\(^-\)-induced oxidation was unselective and previous reports showed that SO\(_4\)\(^{-}\) can oxidize organic pollutants that cannot be oxidized by HO\(^-\) (Monteagudo et al. 2016). Moreover, SO\(_4^2\) could accumulate during the treatment and the gradually increased SO\(_4^2\) could impede the HO\(^-\)-driven oxidation reported by Wei et al. (2016). (3) The speciation of NAP will vary with solution pH. With a pKa value of 4.15, its proportion was calculated and results are shown in Figure S6. When the solution pH is over the pKa, the fraction
Figure 5 | Effect of (a) and (b) initial pH, (c) and (d) PS dosage, (e) and (f) ZVI dosage, and (g) and (h) NAP concentration on NAP degradation. Experimental conditions: (a) [NAP]₀ = 25 μM, [PS]₀ = 0.25 mM, [ZVI]₀ = 0.5 mM; (c) [NAP]₀ = 25 μM, [ZVI]₀ = 0.5 mM, initial pH = 5.0; (e) [NAP]₀ = 25 μM, [PS]₀ = 0.25 mM, initial pH = 5.0; (g) [PS]₀ = 0.2 mM, [ZVI]₀ = 0.5 mM, initial pH = 5.0.
of the deprotonated form increases. The reaction rate constant of SO$_4^{2-}$ with deprotonated organic contaminants may be lower due to electric repulsion (Rickman & Mezyk 2010; Gu et al. 2019; Wang et al. 2019).

**Effect of ZVI dosage**

Different ZVI dosages (0.1–0.5 mM) on the NAP removal rate was examined and the results are shown in Figure 5(c) and 5(d). The removal rate of NAP increased with an increase of ZVI dosage. Figure 5(d) exhibits a linear relationship between $k_{obs}$ and ZVI dosage ($R^2 = 0.99$). The value of $k_{obs}$ increased from 0.02844 min$^{-1}$ to 0.17915 min$^{-1}$ as the ZVI dosage increased from 0.1 mM to 0.5 mM. The degradation of NAP was distinctly improved by increasing the ZVI dosage because more reactive species were generated in the case of higher oxidants, which is in accordance with other reports (Rao et al. 2014; Chen et al. 2018). However, the PS deplection occurred in the ZVI/PS process, and only approximately 20% of PS was consumed (Figure S7). The maximum % RSE (82.5%) obtained was at [PS]$_0$ = 0.1 mM, which is higher than that obtained in thermally activated PS systems (Ghauch et al. 2015; Amasha et al. 2018). As [PS]$_0$ increased from 0.1 mM to 0.5 mM, the RSE decreased from 82.5% to 24.0%, probably due to both Fe$^{2+}$ and PS acting as scavengers of the sulfate radical (Equations (4) and (12)) and the recombination between two sulfate radicals (Equation (13)) (Amasha et al. 2018; Gu et al. 2019).

$$
\text{SO}_2^{2-} + \text{SO}_4^{2-} \rightarrow \text{SO}_2\text{O}_8^{-} + \text{SO}_4^{2-} \quad k = 6.1 \times 10^5 \text{M}^{-1} \text{s}^{-1} \quad (12)
$$

$$
\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{-} \quad k = 4 \times 10^8 \text{M}^{-1} \text{s}^{-1} \quad (13)
$$

**Effect of PS dosage**

Different PS dosages (0.1–0.5 mM) on the NAP removal rate was examined and the results are shown in Figure 5(c) and 5(d). The removal rate of NAP increased with an increase of PS dosage. Figure 5(d) exhibits a linear relationship between $k_{obs}$ and PS dosage ($R^2 = 0.99$). The value of $k_{obs}$ increased from 0.02844 min$^{-1}$ to 0.17915 min$^{-1}$ as the PS dosage increased from 0.1 mM to 0.5 mM. The degradation of NAP was distinctly improved by increasing the PS dosage because more reactive species were generated in the case of higher oxidants, which is in accordance with other reports (Rao et al. 2014; Chen et al. 2018). However, the PS deplection occurred in the ZVI/PS process, and only approximately 20% of PS was consumed (Figure S7). The maximum % RSE (82.5%) obtained was at [PS]$_0$ = 0.1 mM, which is higher than that obtained in thermally activated PS systems (Ghauch et al. 2015; Amasha et al. 2018). As [PS]$_0$ increased from 0.1 mM to 0.5 mM, the RSE decreased from 82.5% to 24.0%, probably due to both Fe$^{2+}$ and PS acting as scavengers of the sulfate radical (Equations (4) and (12)) and the recombination between two sulfate radicals (Equation (13)) (Amasha et al. 2018; Gu et al. 2019).

$$
\text{Fe}^0 + \text{H}^+ + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + \text{Fe}^{2+} \quad (14)
$$

$$
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+} + \text{HO}^* \quad (15)
$$

**Effect of NAP dosage**

Figure 5(g) and 5(h) show the impact of different NAP dosage (5–25 μM) on NAP degradation in the ZVI/PS system. As NAP dosage was increased from 5 μM to 25 μM, the $k_{obs}$ within 30 min gradually decreased from 0.19671 min$^{-1}$ to 0.07324 min$^{-1}$ (Figure 5(h)), consistent with studies concerning other organic contaminants (Wang & Zhou 2016; Wei et al. 2016; Zhu et al. 2019). Theoritically, the overall yields of generated reactive species could be relatively fixed once the PS and ZVI dosages were fixed. With increasing concentration of NAP, the molar ratio of NAP to reactive species increased, causing a reduction in NAP degradation at a specific reaction time.

**Degradation intermediates and degradation pathway of NAP**

The NAP mineralization during the ZVI/PS system was also examined and the results are plotted in Figure S9. As the PS concentration (0.1–0.5 mM) increased, the TOC removal efficiency also increased, which was in accordance with other reports (Ayoub & Ghauch 2014; Ghauch et al. 2015, 2017; Amasha et al. 2018). The highest removal efficiency of TOC could reach 29.12% in the experiment. In contrast to the higher level of NAP removal (Figure 5(c)), most of the NAP was only degraded to intermediates. In order to further understanding the degradation pathways of NAP in the ZVI/PS system, UPLC–QTOF–MS/MS was used to identify the intermediates. All the detected intermediates are listed in Table 2. The MS/MS spectra of nine degradation products are presented in Figures S10–S18.

It has been investigated that both SO$_4^{2-}$ and HO$^*$ were responsible for the destruction of NAP in this study. SO$_4^{2-}$ shares similar reaction mechanisms, including hydrogen...
The structure of NAP, it may be attacked by SO$_4$$^-$$^-$
ions (Dulova et al. 2017; Luo et al. 2018b). According to
the structure of NAP, it may be attacked by SO$_4$$^-$$^-$ and/or
HO$^-$ with an addition on the aromatic ring or by hydrogen
abstraction and hydroxyl addition with HO$^-$, while single
electron transfer is more prevailing in SO$_4$$^-$$^-$-driven reac-
tions (Dulova et al. 2017; Luo et al. 2018b). According to
the structure of NAP, it may be attacked by SO$_4$$^-$$^-$ and/or
HO$^-$ with an addition on the aromatic ring or by hydrogen
attraction on the saturated $\alpha$-carbon (Waldemer et al. 2007;
Chi et al. 2019ab). Based on the identified oxidation pro-
ducts, the possible degradation pathways of NAP in the
ZVI/PS system are proposed in Figure 6. For pathway I,
OP-246 was identified as a hydroxylated product, which
was formed by HO$^-$ attacking the methyl position (Luo
et al. 2018a; Ray et al. 2018). OP-184 may be formed by
the dehydration and decarboxylation of OP-246 (Jallouli
et al. 2016; Chi et al. 2019a; Xu et al. 2019). Additionally,
the NAP molecule is ionized on the naphthalene ring
upon electron abstraction by SO$_4$$^-$$^-$ (Ghauch et al. 2015;
Chi et al. 2019a). The ionized NAP molecule can be trans-
formed to OP-184 followed by decarboxylation, which was
consistent with several studies (Marotta et al. 2015; Kan-
karaju et al. 2015; Coria et al. 2016; Chi et al. 2019a; Tu
et al. 2019). The unsaturated carbon in the OP-184 molecu-
lar structure is easily attacked by SO$_4$$^-$$^-$ and HO$^-$, which
makes it further oxidized to OP-200 (Chi et al. 2019a,
2019b; Xu et al. 2019). In pathway II, SO$_4$$^-$$^-$/HO$^-$ attack
the methyl position of the naphthalene ring to break the
C–C$_{\text{carboxyl}}$ bond, which leads to the decarboxylation
of NAP to form OP-186 (Jallouli et al. 2016; Tu et al. 2019;
Jung et al. 2020). OP-186 can transform to OP-202 with
hydrogen extraction reaction and hydroxylation (Jallouli
et al. 2016; Tu et al. 2019). In the presence of dissolved
oxygen, OP-186 can further form the alkyperoxide derive-
tive OP-218 (Kanakaraju et al. 2015; Jallouli et al. 2016; Tu
et al. 2019). During the production of OP-200 from OP-
218, the hydrogen atom on the C atom in the C–O bond
in OP-218 moves toward distal oxygen and then dehydrates
to form a ketone derivative OP-200 (Tu et al. 2019). In path-
way III, OP-214 was produced by eliminating the hydroxyl
group (–OH) from the carboxyl group (–COOH) of NAP
(Ray et al. 2018). During formation of fragment OP-202
from OP-214, the carbonyl group is also eliminated fol-
lowed by hydroxylation (Ray et al. 2018). OP-202
undergoes a hydrogen extraction reaction and a free radical
coupling reaction to form a secondary glycol derivative and
then produces OP-200 through its intramolecular dehy-
dration condensation reaction (Arany et al. 2013; Jallouli
et al. 2016; Tu et al. 2019). Moreover, in OP-202, the clea-
vage of the C–C bond to the naphthalene ring attacked
by SO$_4$$^-$$^-$/HO$^-$ causes the formation of OP-158 (Méndez-
Arriaga et al. 2008; Kanakaraju et al. 2013). For pathway IV,
OP-216 was possibly formed by the attack of SO$_4$$^-$$^-$
and/or HO$^-$ on the methoxyl group on the naphthalene
ring, and this is followed by demethoxylation, which was
consistent with previous research (Méndez-Arriaga et al.
2008; Chin et al. 2014; Chi et al. 2019a, 2019b).

<table>
<thead>
<tr>
<th>Oxidation products</th>
<th>[M + H]$^+$ (m/z)</th>
<th>Molecular formula</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAP</td>
<td>231</td>
<td>C$<em>{14}$H$</em>{14}$O$_3$</td>
<td><img src="image1" alt="NAP structure" /></td>
</tr>
<tr>
<td>OP-246</td>
<td>247</td>
<td>C$<em>{13}$H$</em>{14}$O$_4$</td>
<td><img src="image2" alt="OP-246 structure" /></td>
</tr>
<tr>
<td>OP-214</td>
<td>215</td>
<td>C$<em>{14}$H$</em>{14}$O$_2$</td>
<td><img src="image3" alt="OP-214 structure" /></td>
</tr>
<tr>
<td>OP-186</td>
<td>187</td>
<td>C$<em>{13}$H$</em>{14}$O</td>
<td><img src="image4" alt="OP-186 structure" /></td>
</tr>
<tr>
<td>OP-202</td>
<td>203</td>
<td>C$<em>{13}$H$</em>{14}$O$_2$</td>
<td><img src="image5" alt="OP-202 structure" /></td>
</tr>
<tr>
<td>OP-184</td>
<td>185</td>
<td>C$<em>{13}$H$</em>{13}$O$_3$</td>
<td><img src="image6" alt="OP-184 structure" /></td>
</tr>
<tr>
<td>OP-158</td>
<td>159</td>
<td>C$<em>{11}$H$</em>{16}$O</td>
<td><img src="image7" alt="OP-158 structure" /></td>
</tr>
<tr>
<td>OP-216</td>
<td>217</td>
<td>C$<em>{13}$H$</em>{13}$O$_3$</td>
<td><img src="image8" alt="OP-216 structure" /></td>
</tr>
<tr>
<td>OP-200</td>
<td>201</td>
<td>C$<em>{13}$H$</em>{13}$O$_2$</td>
<td><img src="image9" alt="OP-200 structure" /></td>
</tr>
<tr>
<td>OP-218</td>
<td>219</td>
<td>C$<em>{13}$H$</em>{14}$O$_3$</td>
<td><img src="image10" alt="OP-218 structure" /></td>
</tr>
</tbody>
</table>
Figure 6 | Proposed degradation pathways of NAP in ZVI/PS system.
In this work, the effect of chloride on the degradation of NAP was marginal (data not shown), and therefore ammonia is defined as the total of \( \text{NH}_3 + \text{NH}_4^+ \) in solutions. The results of NAP degradation during the ZVI/PS process with different dosages of ammonia at pH 7.0 are plotted in Figure 7. With the increase of ammonia dosages, the removal efficiency of NAP increased. The value of \( k_{\text{obs}} \) in the absence of ammonia was 0.00815 min\(^{-1}\), while the value of \( k_{\text{obs}} \) varied linearly from 0.02976 min\(^{-1}\) to 0.14276 min\(^{-1}\) with increasing concentration of ammonia (the inset of Figure 7). Next, experiments were also conducted at pH 9.0 and a similar enhanced impact of ammonia on NAP degradation is presented in Figure S19. When the pH was increased from 7.0 to 9.0, the promotion effect of ammonia on NAP degradation was weakened, which might be interpreted as the equilibrium of ammonia (Equation (16)). The favorable effect of ammonia for NAP oxidation in ZVI/PS could be explained by high production of \( \text{Fe}^{2+} \) in the case of ammonia. Passivation films that formed and covered the surface of ZVI can be destructed by depassivators (Ansaf et al. 2016; Ling et al. 2018). In addition, \( \text{NH}_4\text{Cl} \) has shown a promising ability to activate the hydrogen ion, thus it is a good anti-passivation corrosive chemical for many kinds of metal (Forse et al. 1995; Baranwal & Venkatesh 2017; Li et al. 2018b; Baranwal & Rajaraman 2019).

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \quad \text{pK}_a = 9.4
\]  

(16)

CONCLUSIONS

In this paper, the degradation of NAP by ZVI-activated PS was surveyed in detail. The ZVI/PS system performs better at degrading NAP than the \( \text{Fe}^{2+}/\text{PS} \) system, and the NAP degradation by the ZVI/PS system showed a pseudo-first-order kinetics pattern. The degradation of NAP was mainly attributable to \( \text{SO}_4^{2-} \) and \( \text{HO}^+ \) using radical scavenging experiments and ESR study. The second-order rate constants for NAP with \( \text{SO}_4^{2-} \) and \( \text{HO}^+ \) were estimated to be \((5.64 \pm 0.73) \times 10^8 \text{ M}^{-1} \text{s}^{-1}\) and \((9.05 \pm 0.51) \times 10^8 \text{ M}^{-1} \text{s}^{-1}\), respectively. NAP oxidation rate increased with an increase in PS dosage and ZVI concentration, but it decreased with increasing solution pH and NAP concentration. The oxidation products of NAP were detected and the pathways of NAP degradation were analyzed. The addition of ammonia into the ZVI/PS system could significantly improve the removal efficiency of NAP under neutral and basic conditions. This work proves that ZVI is an efficient and convenient PS activator and thus the ZVI/PS technique can be introduced to eliminate refractory pollutants in the aqueous environment. In order to use ZVI/PS technology for wastewater application, for example hospital and pharmaceutical industries effluents, further research is needed into the cost of implementing ZVI/PS on a larger scale at the source of pollution.

Work in this direction is currently in progress in our laboratory.

Figure 7 | Effect of ammonia on the ZVI/PS oxidation of NAP. Experimental conditions: \([\text{NAP}]_0 = 25 \mu\text{M}, [\text{PS}]_0 = 0.25 \text{mM}, [\text{ZVI}]_0 = 0.5 \text{mM}, \text{initial pH} = 7.0, T = 298.15 \text{K}.

Ammonial-enhanced oxidation of NAP under neutral and basic conditions

In order to test the impact of ammonia on PS activation by ZVI, the change of dissolved total iron (\( \text{Fe}_{\text{tot}} \)) with different ammonia dosages was plotted in Figure S20. Apparently, ammonia could enhance the corrosion of ZVI. Once the ammonia was applied, more dissolved iron was observed after 30 min treatment. At pH of 7.0, for example, with ammonia added, the generation of \( \text{Fe}_{\text{tot}} \) increased from 0.51 mg L\(^{-1}\) at 0 mM to 1.563 mg L\(^{-1}\) at 10 mM. The enhanced production of \( \text{Fe}^{2+} \) generated more \( \text{SO}_4^{2-} \) and \( \text{HO}^+ \) and thus increased the degradation of NAP. Previous publications also observed that the dissolution rate of carbon steel increased with increasing \( \text{NH}_4\text{Cl} \) concentration and the dissolved species was detected as \( \text{Fe}^{2+} \) (Baranwal & Venkatesh 2017; Baranwal & Rajaraman 2019). The results also indicated the promising role of ammonia in NAP removal in the system due to faster and more \( \text{Fe}^{2+} \) being generated.

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \quad \text{pK}_a = 9.4
\]
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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/wst.2020.263.

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