Effect of solution matrix and pH in Z-nZVI-catalyzed percarbonate system on the generation of reactive oxygen species and degradation of 1,1,1-trichloroethane

Muhammad Danish, Xiaogang Gu, Shuguang Lu, Usman Farooq, Ayyaz Ahmad, Muhammad Naqvi, Xiang Zhang, Xiaori Fu and Yunfei Xue

ABSTRACT

This study primarily focuses on evaluating the effects of solution matrix and pH for the generation of reactive oxygen species (ROSs) in a Z-nZVI-catalyzed sodium percarbonate (SPC) system to degrade 1,1,1-trichloroethane (1,1,1-TCA) in the absence and presence of a reducing agent (RA), i.e. hydroxylamine. Degradation of 1,1,1-TCA was 49.5% and 95% in the absence and presence of RA. Probe tests confirmed the generation of major hydroxyl radicals (OH•) and minor superoxide species (O2•-), and scavenger tests verified the key role of OH• and less of O2•- radicals. Degradation of 1,1,1-TCA decreased significantly in the presence of Cl– and HCO3–, while NO3– and SO42– had negligible effects in the absence of RA. Addition of RA significantly enhanced 1,1,1-TCA degradation by generating more OH• and O2•- radicals in the presence of anions. Degradation of 1,1,1-TCA increased in the acidic range (1–5), while an inhibitive trend from neutral to basic (7–9) was observed. In contrast, a significant increase in 1,1,1-TCA degradation was observed with the addition of RA at all pH values (1–9). In conclusion, the anions and pH significantly influenced the generation and intensity of ROSs and 1,1,1-TCA was effectively degraded in the Z-nZVI-catalyzed SPC system in the presence of RA.

Key words | groundwater remediation, hydroxylamine, nano-scale composite, reactive oxygen species, sodium percarbonate, solution matrix

INTRODUCTION

Chlorinated organic solvents (COSs) present in contaminated groundwater are of major environmental and public health concern due to their extensive usage in degreasing, mechanical or electronic cleaning industries. Frequently detected COSs in contaminated sites are 1,1,1-TCA, trichloroethylene (TCE) and tetrachloroethylene (PCE). Degradation of such pollutants has become a global problem, even after tremendous efforts towards remediation (Wu et al. 2014). In-situ chemical oxidation (ISCO) is an effective technique for the remediation of groundwater and soils compared with other conventional methods such as phytoremediation, bioremediation, and pump and treat. Catalytic decomposition of H2O2 by Fe2+ to generate hydroxyl radicals (OH•) is commonly used to degrade COSs non-selectively due to its higher redox potential of 2.70 V and its solubility but the formation of ferric hydroxide limits its applicability to a narrow pH range of 2.5–3.5 (Ahmad et al. 2015; Danish et al. 2016a, 2016b). Therefore, heterogeneous Fenton-like systems have been investigated to minimize the above-mentioned drawbacks.

Recently, sodium percarbonate (SPC) took its place as a safe alternative to the Fenton reagent in ISCO. SPC is considered more stable than liquid H2O2 in comparison with its transportation, storage and handling properties. The
activation of SPC produces OH* radicals from H2O2 through redox reactions which have higher oxidation potential than SPC itself (Danish et al. 2016a, 2016b). The OH* radicals readily decompose the hazardous contaminants in the aqueous solution whereas other reactive oxygen species (ROSs) like O2^- are also produced in the system (Danish et al. 2016c). The reactivity of SPC with COSs has also been confirmed in a wider pH range in our previous studies (Danish et al. 2017a, 2017b). SPC decomposes into products non-toxic to microorganisms making it suitable for further bioremediation.

A very high dosage of Fe^{3+} is required to produce OH* radicals and it is very difficult to regenerate Fe^{2+} when it is converted into Fe^{3+}. Zero valent iron (ZVI) has been used as an alternative to Fe^{2+} due to its exceptional advantages over using iron salt as an Fe^{2+} resource (Xu et al. 2014; Ahmad et al. 2015). ZVI contributes in the activation of SPC and regeneration of Fe^{2+} from Fe^{3+} complexes. The high surface area of nano zero valent iron (nZVI) makes it more attractive and a suitable alternative to micro-size ZVI due to its high reactivity and efficiency. The nZVI tends to aggregate and has low stability which makes it less reactive. This aggregation can be minimized using support material such as carbon nanotubes, graphene and zeolite to overcome the aggregation problem by their unique properties (He et al. 2012; Ahmad et al. 2015). Therefore, we synthesized the nZVI-loaded natural zeolite composite (Z-nZVI) and further confirmed the higher reactivity and no aggregation of nZVI particles on the natural zeolite surface.

Various types of ROSs like OH*, O2^-, HO2 and HO2 are generated in Fenton and Fenton-like processes and OH* is considered the most active among all ROSs. For example, Danish et al. (2017a, 2017b) found that OH* and O2^- were generated in SPC systems in which OH* contributed significantly in the oxidation of tetrachloroethene. Zhang et al. (2015) also credited the generation of OH* and O2^- for the degradation of TCE in SPC systems. In addition, some reducing agents (RAs) such as hydroxylamine, ascorbic acid, oxalic acid and hydrazine may also promote the transformation of Fe^{3+} to Fe^{2+}, further elevating the generation of ROSs. Therefore, it is possible that simultaneous reactions (redox) may occur in the Z-nZVI-catalyzed percarbonate (SPC) process in the absence or presence of RA, which needs the identification of ROS by chemical probe tests and scavenger tests to verify the role of ROSs.

The anions (Cl^-, HCO3-, NO3 and SO4^2-) are always present in groundwater in a complex matrix that affects the composition and reactivity between target contaminants and oxidants. These anions in groundwater behave differently in the systems. For example, Xu et al. (2014) found that HCO3 has increased the intensity of O2^- but decreased the intensity of OH*. While Cl^- severely decreased the intensity of both OH* and O2^- radicals. Liang et al. (2006) reported that HCO3 has accelerative and NO3 has inhibitory effects on 1,1,1-TCA degradation, whereas Cl^- and SO4^2- have negligible effects. Similarly, Wu et al. (2014) reported that 1,1,1-TCA degradation increased in the presence of HCO3 and decreased in the presence of NO3 whereas Cl^- and SO4^2- had almost negligible effects (Wu et al. 2014).

In order to completely understand the mechanism and role of ROSs generated in the Z-nZVI-catalyzed SPC system and the effects of solution matrix and pH on contaminant degradation, the following objectives were addressed in the absence and presence of RA: (1) identify the role of the ROSs in 1,1,1-TCA degradation using probe chemical compound probes, (2) assess the effect of scavengers on ROS generation using scavenger tests, (3) investigate the effects of various groundwater anions, such as Cl^-, HCO3-, NO3 and SO4^2- on the performance of 1,1,1-TCA degradation, and (4) elucidate the influence of the initial solution pH on 1,1,1-TCA degradation.

MATERIALS AND METHODS

Materials/chemicals

Analytical-grade 1,1,1-TCA (>99%) was purchased from Aaladdin Reagent Co. Ltd (Shanghai, China). Methanol (CH3OH, >99.9%), carbon tetrachloride (CT, CCl4, >99.5%), sodium bicarbonate (NaHCO3, >99.5%), sodium chloride (NaCl, >99.5%), sodium nitrate (NaNO3, >99.0%), n-hexane (C6H14, >97%), ferrous sulfate heptahydrate (FeSO47H2O, >99.5%) and sodium sulfate (Na2SO4, >99.0%) were acquired from Shanghai Ling Feng Reagent Co. Ltd (Shanghai, China). Hydroxylamine hydrochloride (NH2OH-HCl, >99.0%), tert-butyl alcohol (TBA,
(CH₃)₃COH, >99.0%), nitrobenzene (NB, >99.0%), trichloromethane (CHCl₃, >99.0%), sodium borohydride (>99.5%), SPC (>98%), and aluminosilicates (natural zeolite) were purchased from Shanghai Jingchun Reagent Co. Ltd (Shanghai, China). Milli-Q water (Classic DI, ELGA, Marlow, UK) was used to prepare all aqueous solutions.

**Preparation of the Z-nZVI composite**

Zeolite-supported nano zero valent iron (Z-nZVI) was prepared using the wet ion exchange method (Chen et al. 2014) in a nitrogen environment. Natural zeolite (0.5 g) and ferrous sulfate heptahydrate (1.0 g) were mixed in ultrapure water (250 mL) in a three-neck flask. Nitric acid (1.0 M) was used to maintain the initial solution pH at 4 to inhibit the oxidation of Fe²⁺ and the mixture was treated with ultrasound for 10 minutes. The mixture was stirred vigorously at room temperature for another half hour. Sodium borohydride (1.0 M) was added dropwise into the mixture for the reduction of Fe²⁺. Black solid particles were separated from the solution using a vacuum filtration flask. Impurities were removed by washing the particles thrice with ethanol and water and it was further vacuum-dried.

$$\text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{Fe}^0 + 2\text{B(OH)}_3^- + 7\text{H}_2$$  (1)

**Experimental procedures**

A stock solution of 1,1,1-TCA (0.15 mM) was prepared by addition of the pure non-aqueous phase liquid plus deionized water with continuous stirring for 60 min in darkness. A cylindrical glass reactor (250 mL, inner diameter and height of reactor were 6.0 cm and 9.0 cm) with two openings at the top was used, one for dosing and the other for sampling purposes. A temperature bath (DC Ningbo, China) was attached to circulate the water through the jacket of the reactor to keep the temperature at a constant value of 20 ± 0.5 °C. Predetermined amounts of Z-nZVI and SPC were added sequentially into the reactors along with 1,1,1-TCA after addition of the anions and other regents. A magnetic stirrer was inserted into the reactor to ensure homogenous mixing. Initial and final pHs of the solutions were recorded periodically with a pH meter. Samples (1.0 mL) were taken at a specific interval of time from the reactor to the headspace vials containing 1.0 mL of n-hexane. Gas chromatography (GC) was used to analyze the degradation of contaminants immediately. All experiments were performed in duplicate and the mean values are reported. Identification of ROSs was done using probe chemical compound tests. Similar methodology was implemented for probe tests except for the replacement of 1,1,1-TCA with nitrobenzene (NB, OH• probe) or carbon tetrachloride (CT, O₂•⁻ probe) (Danish et al. 2016a, 2016b).

**Analytical methods**

One millilitre of each aqueous sample of 1,1,1-TCA, NB or CT was added with n-hexane (1.0 mL), and the vials were placed in a vortex stirrer for 3 min before separation for 5 min. A gas chromatograph (Agilent 7890A, Palo Alto, CA, USA) furnished with an auto-sampler (Agilent 7693), a DB-VRX column (length 60 m, i.d. 250 μm and thickness 1.4 μm) and an electron capture detector were used to analyze the chemical concentration. The temperatures of injector, detector and oven were 240, 260 and 75 °C respectively. One microlitre of the sample was inoculated into the GC for analysis at a split ratio of 20:1. CT analyses were also performed like the 1,1,1-TCA analysis method with only the modification of the oven temperature at 100 °C. Analyses of NB samples were conducted with a flame ionization detector furnished with an HP 5 column (length 30 m, i.d. 250 μm and thickness 0.25 μm). The temperatures of the injector, detector and oven were 240, 260 and 75 °C, respectively. The amount of NB samples injected was 1.0 μL, with a split ratio of 5:1. A pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland) was used to determine the pH of the solutions.

**RESULTS AND DISCUSSION**

**Identification of ROSs in the Z-nZVI-catalyzed SPC system in the absence and presence of RA**

The performance of the degradation of 1,1,1-TCA (0.15 mM) in the Z-nZVI (100 mg/L) catalyzed SPC (15 mM) system...
can be seen in Figure 1 in the absence and presence of RA (5 mM). Control experiments were also conducted and showed very minor loss due to volatilization. The degradation of 1,1,1-TCA was 49.5% and 95.8% in the absence and presence of RA. It is suggested that Fe$^{2+}$ released from the Z-nZVI decomposed SPC and produced sufficient OH$^*$ radicals for the degradation of 1,1,1-TCA in the presence of RA.

In this study, NB was selected as an oxidative probe due to its high reactivity with OH$^*$ ($k_{OH^*} = 3.9 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) and CT as a reductive probe for O$_2^{*-}$ ($k_e = 1.6 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$). The degradation of NB and CT can be seen in Figure 2. Figure 2(a) shows the degradation kinetics of both probe compounds; 56% of NB and 39% of CT were degraded in the same interval of time in the Z-nZVI-catalyzed SPC system in the absence of RA. The addition of 1,1,1-TCA in the NB and CT experiments was also studied to investigate the intensity of both radicals, suggesting that much less decrease in the degradation of NB was observed, which might be due to the weak competition of 1,1,1-TCA with NB for the OH$^*$ radicals in the system. By contrast, a significant decrease in CT degradation was observed with the addition of 1,1,1-TCA, which might be due to (i) the greater affinity of O$_2^{*-}$ radicals for 1,1,1-TCA degradation and (ii) the participation of O$_2^{*-}$ radicals in the decomposition of SPC in the presence of chloride ions released from 1,1,1-TCA.

The addition of RA significantly increased NB and CT degradation from 56% to 96% and from 39% to 74% respectively, as shown in Figure 2(b).

The addition of 1,1,1-TCA in the presence of RA for the NB and CT degradation experiments showed minor differences. The significant degradation of NB even in the presence of 1,1,1-TCA indicated that the addition of RA efficiently generated OH$^*$ radicals (Chen et al. 2014). The chemical equations showing the catalytic decomposition of SPC, RA and reduction of ferric to ferrous are shown here.
in Equations (2)–(10):

$$\text{Fe}^{3+} + \text{NH}_2\text{OH} \rightarrow \text{NH}_2\text{O}^+ + \text{Fe}^{2+} + \text{H}^+$$  \hspace{1cm} (2)

$$2\text{NH}_2\text{O}^+ \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$$ \hspace{1cm} (3)

$$\text{Fe}^{3+} + \text{NH}_2\text{O}^+ \rightarrow \text{NHO} + \text{Fe}^{2+} + \text{H}^+$$ \hspace{1cm} (4)

$$2\text{NHO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$$ \hspace{1cm} (5)

$$\text{Fe}^{3+} + 2\text{H}_2\text{O} + \text{NH}_2\text{O}^+ \rightarrow \text{NO}_3^- + \text{Fe}^{2+} + 6\text{H}^+$$ \hspace{1cm} (6)

$$\text{NO}_3^- + \text{NH}_2\text{OH} + \text{OH}^- \rightarrow \text{NO}^- + \text{NO}_2^- + 2\text{H}_2\text{O}$$ \hspace{1cm} (7)

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + 2\text{OH}^*$$ \hspace{1cm} (8)

$$\text{Fe}^{5+} + 2\text{OH}^* \rightarrow \text{Fe}^{2+} + \text{O}_2^- + 2\text{H}^+$$ \hspace{1cm} (9)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^* + \text{OH}^-$$ \hspace{1cm} (10)

The CT degradation trend was also similar to NB, which might be due to the hindrance of the propagating reactions between $\text{O}_2^-$ and chloride ions released from 1,1,1-TCA (Ahmad et al. 2015). It is reported that $\text{OH}^*$ has a low reactivity with highly oxidized contaminants like hexachloroethane (Zhang et al. 2015). However, our results indicated the significant potential of the Z-nZVI-catalyzed SPC system in the presence of RA to degrade a highly oxidized contaminant like 1,1,1-TCA, which offers an efficient method for in-situ remediation.

**Scavenger tests in the Z-nZVI-catalyzed SPC system in the absence and presence of RA**

Scavenger tests were conducted to ensure the identification and contribution of ROSs for 1,1,1-TCA degradation. It has been found in the literature that TBA reacts rapidly with OH* ($k_{\text{OH}^*} = 5.2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$) and that chloroform (CF) reacts slowly with OH* ($k_{\text{OH}^*} = 7 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$), whereas CF reacts more rapidly with $\text{O}_2^-$ ($k_c = 5 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$) (Teel & Watts 2002; Danish et al. 2016a, 2016b). Therefore, the TBA was selected as OH* scavenger and CF as $\text{O}_2^-$ scavenger. Both the concentrations of TBA and CF were set at 10 mM, which was high enough compared with the initial concentration of 1,1,1-TCA (0.15 mM). The degradation of 1,1,1-TCA indicated a significant scavenging effect with TBA addition to 29% in the absence of RA as shown in Figure 3(a), while the 1,1,1-TCA degradation rate was 45.8% in the presence of RA as shown in Figure 3(c). A significant decrease in 1,1,1-TCA degradation in the presence of RA further elucidated the intensity and generation of OH* in the Z-nZVI-catalyzed SPC system. The degradation of 1,1,1-TCA with the addition of CF decreased to 30.4% in the absence of RA as shown in Figure 3(b), while in the presence of RA it reached 61.7% as shown in Figure 3(d). The addition of CF significantly decreased 1,1,1-TCA degradation, which also verified the contribution of $\text{O}_2^-$ in the Z-nZVI-catalyzed SPC system. It is suggested that both OH* and $\text{O}_2^-$ radicals were responsible for 1,1,1-TCA degradation, in which OH* contributed more than $\text{O}_2^-$ in the system.

**Effect of solution matrix on 1,1,1-TCA removal in the Z-nZVI-catalyzed SPC system in the absence and presence of RA**

The degradation of contaminants is affected by the anions present in the groundwater. They might have a significant effect on the strength of ROSs (Zhang et al. 2015). With the increasing concentrations of Cl anions from 0 to 1.0, 10 and 100 mM, 1,1,1-TCA degradation decreased to 48.3%, 46% and 34.7%, respectively, as shown in Figure 4(a). Cl anions have a low reactivity with highly oxidized contaminants like hexachloroethane (Zhang et al. 2015). However, our results indicated the significant potential of the Z-nZVI-catalyzed SPC system in the presence of RA to degrade a highly oxidized contaminant like 1,1,1-TCA, which offers an efficient method for in-situ remediation.

Cl anions reacted with OH* to produce Cl$_2^*$, which is less reactive and also has a scavenging effect on OH*. The intermediate compounds such as chloro complexes of Fe$^{3+}$...
ions were produced due to the complex reactions between Cl$^-$ and Fe$^{2+}$ that can inhibit the generation of Fe$^{2+}$. The higher concentration of Cl$^-$ anions (100 mM) inhibited 1,1,1-TCA degradation due to the aggressive behavior of Cl$^-$ with passivating oxides to form strong complexes on the surface of the iron as shown in Equations (11)–(14) (Bennedsen et al. 2012):

$$\text{Cl}^- + \text{OH}^- \rightarrow \text{ClOH}^- \quad k = 4.3 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \quad (11)$$

$$\text{ClOH}^- + \text{H}^+ \rightarrow \text{HClOH} \quad k = 3.0 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \quad (12)$$

$$\text{HClOH} \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad k = 5.0 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \quad (13)$$

$$\text{HClOH} + \text{Cl}^- \rightarrow \text{Cl}_2^- + \text{H}_2\text{O} \quad k = 8.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \quad (14)$$

The degradation of 1,1,1-TCA decreased to 41% and 31% with 1.0 and 10 mM HCO$_3^-$ whereas a minor increase was achieved from 31% to 34.7% with 100 mM as shown in Figure 4(b). The addition of RA with HCO$_3^-$ (1.0 to 10 mM) decreased the degradation to 69% and 58%, but
in the case of 100 mM of HCO$_3^-$ anions, it was up to 64%, as shown in Figure 5(b). The HCO$_3^-$ anions behave as scavengers for hydroxyl radicals due to which destruction of the most of the organic contaminants is scavenged (Grebel et al. 2010; Chen et al. 2011), but the addition of RA enhanced 1,1,1-TCA degradation from 30% to 58% with 10 mM HCO$_3^-$. The addition of RA, along with HCO$_3^-$, led towards the acidic range and decreased the buffering capacity of the aqueous solution. The decrease in 1,1,1-TCA degradation might be due to the scavenging effect of HCO$_3^-$ and the increase in pH of the aqueous solution, which generated HCO$_3^-$ and CO$_3^{2-}$ in the aqueous solution through Equations (15)–(17):

$$
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{HCO}_3^{2-} + \text{HO}^- \\
k = 8.5 \times 10^6 \text{M}^{-1} \text{s}^{-1} \tag{15}
$$

$$
\text{CO}_3^{2-} + \text{OH}^- \rightarrow \text{CO}_3^{3-} + \text{HO}^- \\
k = 4.2 \times 10^8 \text{M}^{-1} \text{s}^{-1} \tag{16}
$$

$$
\text{HCO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HCO}_3^{2-} + \text{H}_2\text{O} \tag{17}
$$
Due to the rise in pH, the dissolution of SPC and the release of H$_2$O$_2$ were inhibited, and the precipitation of Fe$^{2+}$ was promoted. Richardson et al. (2000) reported that at neutral pH, there is a rapid equilibrium formation of peroxymonocarbonate ions (HCO$_3$) from HCO$_3$ anions and H$_2$O$_2$; thus, HCO$_3$ increases the 1,1,1-TCA degradation process at higher concentrations because it is a potent oxidant in aqueous solution.

A minute inhibitive effect on the degradation of 1,1,1-TCA was observed after the addition of NO$_3$ (1.0, 10 and 100 mM) in the absence and presence of RA as shown in Figures 4(c) and 5(c). This might be due to the presence of solvated electrons in the Z-nZVI-catalyzed SPC system. Similarly, no considerable inhibitive effect was observed on 1,1,1-TCA degradation when SO$_4^{2-}$ anions (1.0, 10 and 100 mM) were added to the system in the absence of RA as shown in Figure 4(d), as well as with the addition of RA but with increased 1,1,1-TCA degradation as shown in Figure 5(d). However, our results are not consistent with the previous results of De Laat & Le (2005) who demonstrated that efficiency of Fe$^{3+}$/H$_2$O$_2$ oxidation significantly decreased in the presence of SO$_4^{2-}$. It might be possible that addition of SO$_4^{2-}$ decreased the formation of Fe$^{3+}$ peroxo-complexes and H$_2$O$_2$ did not form any complex.
with Fe$^{3+}$/sulfato complexes since the rate of decomposition of H$_2$O$_2$ significantly decreased. On the other hand, dissolution of SPC offers more benefits in H$_2$O$_2$ decomposition. Hence, the effect of SO$_4^{2-}$ on the decomposition of H$_2$O$_2$ is negligible in the Z-nZVI-catalyzed SPC system.

**Effect of the solution pH in the Z-nZVI-catalyzed SPC system in the absence and presence of RA**

The solution pH plays very important role in generating the various kinds of ROSs. The degradation of 1,1,1-TCA decreased to 87%, 84.3%, 80%, 58.3% and 37.3% with an increasing trend of pHs (1.0, 3.0, 5.0, 7.0 and 9.0) as shown in Figure 6(a).

The addition of RA significantly improved 1,1,1-TCA degradation performance to 98.2%, 95.2%, 85%, 70.7% and 51.8% respectively even with an increasing trend of pH (1–9), as shown in Figure 6(b). The above results confirmed the superiority of our system in the presence of RA over other Fenton reagents due to its effectiveness over a wider range of pH. Fe$^{2+}$ is significantly soluble over a wider range of pH (1–9) (Stefánsson 2011) compared with ferric oxyhydroxides that are formed due to the precipitation of Fe$^{3+}$ at higher pH values. In this study, no buffering

![Figure 6](https://iwaponline.com/ws/article-pdf/17/6/1568/205184/ws017061568.pdf)
agents were added to maintain the pH of the reaction during the experiments. The final pH of the solution was 4.1 when the initial pH of the solution was adjusted to 7, whereas the final pH at the end of the reaction was 7.6 when the initial pH was 9 in the presence of RA. This decrease in the pH of the solution may be responsible for the reduced precipitation of Fe(OH)₃ and increased generation of OH⁻, which ultimately contributed to degrade the 1,1,1-TCA rapidly. The NB and CT probe tests were also conducted at various pHs (1–9) to investigate its effect on the generation and intensity of ROSs as shown in Figure 6(c) and 6(d). At the pH values of 7 and 9, NB degradation decreased significantly as compared with other tested pH values which might be due to the reactions between carbonate and hydroxyl radicals. A very minute difference at the pHs of 1–3 for NB degradation was observed. CT degradation was also inhibited in the basic pH region, which might be due to the consumption of O₂⁻ radicals for SPC degradation and its conversion to hydrogen peroxide, whereas, CT degradation increased in the basic pH region. This increase in generation and intensity of O₂⁻ radicals is consistent with literature findings (Teel et al. 2001).

CONCLUSIONS

The Z-nZVI-catalyzed SPC system in the absence and presence of RA was used to investigate the effect of anions and pH for the generation and intensity of ROSs to degrade 1,1,1-TCA. Probe and scavenger tests confirmed the main contribution of OH⁻ and minor contribution of O₂⁻ for 1,1,1-TCA degradation. The solution matrix investigation indicated the scavenging effect of Cl⁻ in the absence of RA, whereas a significant decrease in scavenging effect was observed in the presence of RA. HCO₃⁻ anions showed a severe inhibitive effect in the absence of RA, whereas a minute scavenging effect was observed in the presence of RA. Negligible effect was observed in the cases of NO₃⁻ and SO₄²⁻ in the absence and presence of RA. The above results showed great advantages of RA in defending the negative effect caused by solution matrix and solution pH in COS contaminated groundwater remediation using a Z-nZVI-catalyzed SPC system.

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