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Role of reactive oxygen species and effect of solution matrix in trichloroethylene degradation from aqueous solution by zeolite-supported nano iron as percarbonate activator

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Abstract The role of reactive oxygen species (ROSs) and effect of solution matrix have been investigated for the degradation of trichloroethylene (TCE). Zeolite-supported nano iron (Z-nZVI) was synthesized as an activator to catalyze sodium percarbonate (SPC) with or without hydroxylamine, i.e. as reducing agent (RA). The probe tests confirmed the generation of OH$^.$ and O$_2^-$$^.$ in the Z-nZVI activated SPC system in absence of the RA, while the presence of RA significantly increased the generation of OH$^.$ and O$_2^-$$^.$ radicals. Scavenger tests demonstrated that OH$^.$ was the main ROS responsible for TCE degradation, whereas O$_2^-$$^.$ also participated in TCE degradation. From the solution matrix perspective, the experimental results confirmed significant scavenging effects of Cl$^-$ (1.0, 10.0, and 100 mmol L^{-1}) and HCO$_3^-$ (1.0 and 10.0 mmol L^{-1}), whereas the scavenging effects were fairly impeded at 100 mmol L^{-1} concentration of HCO$_3^-$. On the other hand, a considerable decline in scavenging effect was observed in the presence of RA in tested Cl$^-$ and HCO$_3^-$ concentration ranges. In addition, negligible scavenging effects of NO$_3^-$ and SO$_4^{2-}$ anions were found in all tested concentrations. The effect of initial solution pH on catalytic activity indicated a significant increase in the TCE degradation in the presence of RA even at higher pH value of 9. The results

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indicated that the Z-nZVI activated SPC system in presence of RA can effectively degrade chlorinated organic solvents, but it is important to consider the intensive existence of anions in groundwater.

Keywords Trichloroethylene (TCE) · Solution matrix · Reactive oxygen species (ROSs) · Zeolite supported nano iron particles (Z-nZVI) · Groundwater remediation
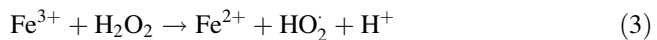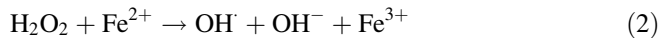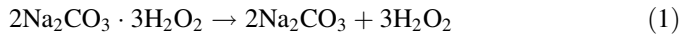
Introduction

Chlorinated organic solvents (COSs) have been widely used on a broad spectrum in various applications [1]. The random disposal of such wastes into the environment is one of the reasons for various environmental and public health issues since most of COSs are carcinogenic and toxic. Trichloroethylene (TCE) is considered a hazardous organic contaminant due to its large usage as COS; therefore, it is selected as widespread target contaminant due to its severe effects on human health in terms of teratogenicity, mutagenicity, and carcinogenicity [2].

In situ chemical oxidation (ISCO) is an effective technique for the purpose of groundwater remediation. Groundwater remediation with zero-valent iron nanoparticles (nZVI) has been extensively employed as a substitute to the conventional pump and treat technique or permeable reactive barrier due to prospective application and performance. Significant enhanced reactivity of nZVI is associated with a larger specific surface area that is approximately tenfold larger than the microparticle [3]. The use of nZVI has been applied widely for the degradation of COSs such as TCE, nitrobenzene, nitrate, azo dye, chloro-phenols, herbicides, hexavalent chromium, arsenic, and nitro-aromatic compounds [4, 5].

nZVI particles have a strong tendency to aggregate into micro-scale form in suspension due to their inherent magnetic forces and great surface energies. Because of the aggregation property, their transportation and injection become difficult through aqueous solution, thus inhibiting application and usage [6]. In order to address this issue, the immobilization of support materials on nZVI particles can be an efficient technique [7]. In this study, we synthesized natural zeolite-supported iron nanoparticles (Z-nZVI) according to the method reported by Wang et al. [7] to control the morphology and size of iron particles to get better performance for degradation of groundwater contaminants.

Application of Fenton's reagent in COSs remediation has been widely investigated and discussed in the literature. However, liquid H_2O_2 is found to be very unstable with a short lifetime after injection into the subsurface in groundwater and soil remediation. In addition, Fenton process is strongly dependent on the pH of the solution and has an optimum pH value of around 3. During the reaction, the subsequent precipitation of Fe^{2+} to $Fe(OH)_3$ occurred at near neutral pH that would lead to a loss of catalyst and injection plugging problems. Instead, sodium percarbonate (SPC, $2Na_2CO_3\cdot3H_2O_2$) is considered to be an attractive alternative with exceptional benefits over Fenton's reagent. Recently, SPC has gained a significant reputation as an unconventional oxidant in ISCO practice. It is a granulated powder that can be used as dry carrier of H_2O_2 having exceptional

storage, handling and transportation capabilities. It is capable of offering the same functional benefits as liquid H_2O_2 over a wide range of pH with less splashing during transportation. SPC releases free H_2O_2 in the solution that reacts with ferrous or ferric to generate oxidative/reductive radicals as shown in Eqs. 1–3 [8]. Moreover, the reaction of COSs with SPC mostly produces water, carbon dioxide, and smaller amounts of carbonate, which are naturally present in the groundwater, thus minimizing the threat of toxic end-products.

$$2Na_2CO_3 \cdot 3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow OH^. + OH^- + Fe^{3+} \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^. + H^+ \tag{3}$$

The identification of reactive oxygen species (ROSs) is an important task in COS degradation [9]. It is reported that hydroxyl radicals (OH$^.$) and hydroperoxy radicals (HO$_2^.$) are significantly responsible for the degradation of phenolic compounds in the last stages, whereas in the early stages, superoxide radical anions (O$_2^{-.}$) and triplet oxygen ($^3O_2$) are considered responsible for degradation in the ferrioxalate-induced artificial ultraviolet (UV)-A/C photo-Fenton system. Wu demonstrated that OH$^.$, O$_2^{-.}$, and SO$_4^{-.}$ were the primary reactive oxygen radicals for the degradation of tetrachloroethylene in Fe^{2+} activated persulphate system [10]. Miao et al. [11] showed that tetrachloroethylene was primarily degraded by OH$^.$, while O$_2^{-.}$ also participated in the Fe^{3+} catalyzed percarbonate system. Zhang et al. [12] also demonstrated that both OH$^.$ (dominantly) and O$_2^{-.}$ (fairly) are responsible for TCE degradation in aqueous solution by calcium peroxide activated with the ferrous ion system. Teel and Watts [13] showed that O$_2^{-.}$ is a weak reductant and nucleophile that can react with carbon tetrachloride (CT) in a dimethyl sulfoxide at a rate constant value of 3800 M^{-1} s^{-1}. Hence, the oxidation and reduction reactions may contribute to COS degradation that may occur simultaneously in zeolite-supported zero-valent nano iron (Z-nZVI) as an SPC activator. Therefore, intensive investigations were achieved with the chemical probe compound method for the identification of oxidative and reductive free radicals (OH$^.$ and O$_2^{-.}$) in this study.

Fenton and Fenton modified processes combined with electrochemical and light irradiation have been examined to accelerate the generation of free radicals (OH$^.$) and redox cycle of Fe^{3+} to Fe^{2+}. It was, however, reported that COS degradation was significantly improved with the addition of reducing agents such as ascorbic acid and hydroxylamine by (1) moderating the accumulation of Fe^{3+}, (2) accelerating the generation of OH$^.$, and (3) rapidly transforming of Fe^{3+} to Fe^{2+} [14]. Therefore, in this study, addition of a reducing agent (hydroxylamine, RA) in Z-nZVI as an SPC activator for TCE degradation was evaluated to investigate and encounter the generation of free radicals and transformation of Fe^{3+} to Fe^{2+}, which has never been reported before.

Literature survey suggested that different anions such as Cl$^-$, HCO$_3^-$, NO$_3^-$, and SO$_4^{2-}$ in groundwater plays a significant role in the degradation performance of contaminants by affecting the reaction mechanism [15]. Wu et al. [10] and Xu et al.

[16] reported adverse effects of these anions in a thermally activated persulphate system. Fu stated that HCO_3^- had a scavenging effect and Cl^- had a slightly expediting effect, while the effect of NO_3^- and SO_4^{2-} were negligible in the percarbonate system [17]. On the other hand, Zhang reported that HCO_3^- showed increased TCE degradation at higher concentration while SO_4^{2-} and NO_3^- had negligible effects [12]. HCO_3^- and NO_3^- have significant negative effects on reactivity and prolonged existence of iron nano particles [18] and low in pristine groundwater. The NO_3^- anions occupy reactive cathodic sites [19] to develop passivating oxide layers. If such oxide layers are not terminated properly, this can reduce reactivity and act like scavengers [18, 20, 21]. Because of the controversial behavior of the above mentioned anions in the system, a series of experiments were designed and performed to elucidate the possible effects of anions in the Z-nZVI system as SPC activators in the absence and presence of RA in this study.

It is well known that Fenton process depends on solution pH and the optimum solution pH is around 3. Nitrobenzene degradation was increased when pH of the solution was 7–12 [22] in the persulphate system. However, degradation results of methyl tert-butyl ether (MTBE) were reported to be efficient at acidic pH with Fenton's reagent while a significant drop in degradation was observed at neutral pH [23]. The degradation performance of pesticide derivatives was maximized at pH values of 3–5 in a report published by Muneer et al. [24]. Hence, it is expected that solution pH has a significant effect on COS degradation in Z-nZVI as a percarbonate activator in the absence and presence of RA, which needs further clarification in this study.

Therefore, the main objectives of this study by using Z-nZVI as the SPC activator in the absence and presence of RA are: (1) to identify the major ROSs being responsible for TCE degradation with specific probe compound tests, (2) to clarify the contributions of ROSs by finding the scavenging effects using free radical scavenger tests, (3) to investigate the effects of various anions such as Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-} on the degradation performance of TCE, and (4) to evaluate the influence of initial solution pH on TCE degradation.

Materials and methods

Materials/chemicals

Analytical grade of TCE (>99.0 %) was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, >99.0 %), nitrobenzene (NB, >99.0 %), tert-butyl alcohol (TBA, 99.0 %), and sodium bicarbonate (99.5 %) were obtained from Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). Methanol (>99.9 %), carbon tetrachloride (CT, 99.5 %), sodium nitrate (>99.0 %), sodium chloride (>99.5 %), n-hexane (>97 %), sodium boro-hydride (99.5 %), sodium percarbonate (SPC, >98 %), sodium sulphate (99.0 %), aluminosilicates (natural zeolite), and ferrous sulfate heptahydrate (99.5 %) were bought from Shanghai Lingfeng Reagent Co. Ltd. (Shanghai, China). pH of the solution was adjusted with 0.1 M NaOH or 0.1 M H_2SO_4. All the reagents were of

analytical grade used without further purification. All aqueous solutions were prepared from milli-Q water (Classic DI, ELGA, Marlow, UK).

Preparation of zeolite-supported nano iron (Z-nZVI)

Zeolite-supported nano iron (Z-nZVI) was prepared using the wet ion exchange method [7]. Natural zeolite (0.5 g) and ferrous sulfate heptahydrate (1.0 g) were mixed in milli-Q water (250 mL) in a three-neck flask. To inhibit the oxidation of Fe^{2+}, the initial solution pH was maintained at 4 by using nitric acid (1.0 M). This mixture was treated with ultrasound for 10 min and then stirred vigorously at room temperature for another 30 min to dissolve completely. For effective reduction of Fe^{2+}, a strong reducing agent, $NaBH_4$ (1.0 M), was added to the solution, and black particles were formed. These black, solid particles were separated from solution using a vacuum filtration flask with a 47-mm diameter membrane filter. Sulphate ions were removed from black solid particles by washing three times with milli-Q water. To remove possible traces of sulphate ions and water in the black particles, further washing was done with ethanol, and then finally, a vacuum drier was used to dry these particles.

Characterization of zeolite-supported nano iron (Z-nZVI)

The characterization of natural zeolite and synthesized Z-nZVI was accomplished by transmission electron micrographs (TEM, JEM-1400 electron microscope, operated at an accelerating voltage at 80 kV), scanning electron micrographs (SEM, JSM-630LV, Tokyo, Japan), energy-dispersive X-ray spectroscopy (EDS), and N_2-isotherm adsorption–desorption, along with pore size and pore volume distribution as shown in the supplementary material. The elemental compositions of zeolite and Z-nZVI showing total pore volume, average pore diameter, average particle size, specific surface area, and iron content are described in Table S1 in the supplementary material.

Medium preparation

The TCE (0.15 mmol L^{-1}) solution was prepared with pure non-aqueous phase liquid and ultra-pure milli-Q water with continuous, vigorous stirring for 1 h. A cylindrical glass reactor (250 mL, height 9.0 cm, inner diameter 6.0 cm) was used with two openings at the top, one for dosing and the other for sampling. The jacket reactor was maintained at a constant temperature (20 ± 0.5 °C) using a temperature bath (DC Ningbo, China) with water circulation. TCE along with predetermined amounts of SPC and Z-nZVI were added sequentially into the reactor. A magnetic stirrer was inserted into the reactor for homogenous mixing. The initial and final solution pH was recorded using a pH meter. Sequential addition of Z-nZVI and SPC was done after adding anions and other reagents. One-milliliter samples from the reactor were taken intermittently to the headspace vials containing 1.0 mL of *n*-hexane for analyses using gas chromatography (GC). The tests were performed in duplicate and average values reported. Probe compound tests were conducted to identify the ROSs using the same

method as TCE tests except TCE was replaced by NB (OH$^{\cdot}$ probe) or CT (O$_2^{-\cdot}$ probe). Control tests were also carried out in each experimental condition. Standard error was in the range of 0.015–0.041 in all experiments.

Analytical methods

Aqueous samples (1.0 mL) of TCE, NB, or CT were mixed with *n*-hexane (1.0 mL) in vials and kept in a vortex stirrer for at least 3 min and spared for 5 min to separate. Gas chromatograph (Agilent 7890A, Palo Alto, CA, USA) equipped with
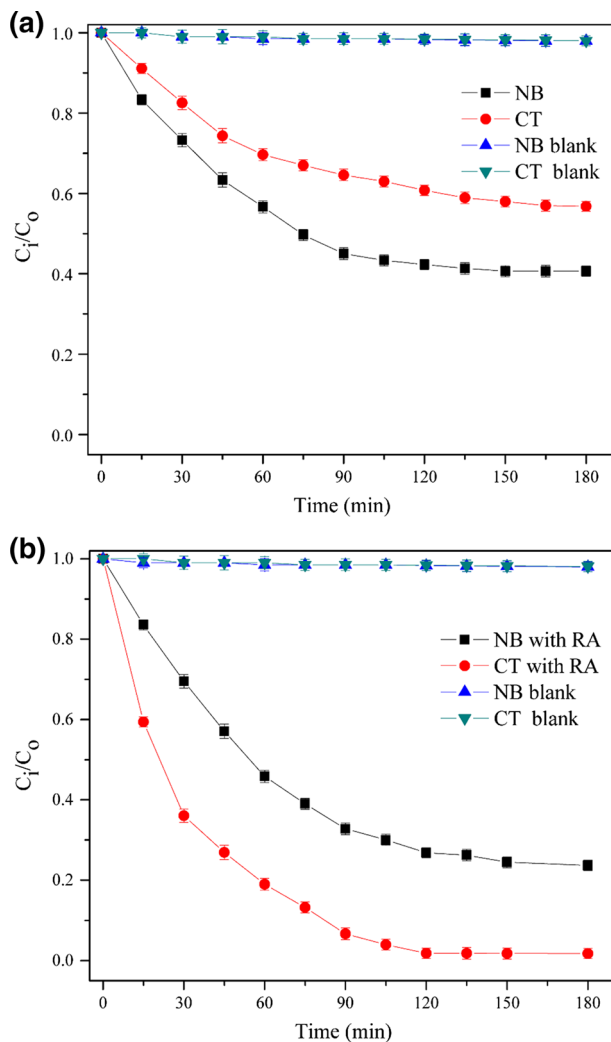

Fig. 1 Degradation of probe compounds in the Z-nZVI/SPC system: **a** in the absence of RA, **b** in the presence of RA ([NB] = 1 mmol L^{-1}, [CT] = 0.05 mmol L^{-1}, [Z-nZVI] = 100 mg L^{-1}, [SPC] = 15 mmol L^{-1}, [RA] = 7 mmol L^{-1})

an auto sampler (Agilent 7693), an electron capture detector (ECD), and a DB-VRX column (length 60 m, i.d. 250 μm and thickness 1.4 μm) was used for analysis with the split ratio of 20:1. Temperatures of 240 and 260 °C were maintained for the injector and detector, respectively. Oven temperature was maintained at 75 °C. The method adopted for CT analysis was the same as TCE with the only difference being oven temperature of 100 °C for CT. NB analyses were achieved by a flame ionization detector (FID) provided with an HP 5 column (length 30 m, i.d. 250 μm and thickness 0.25 μm). Injector, detector, and oven temperatures were 250, 300, and 175 °C, respectively. Split ratio of 5:1 was maintained with injection of 1.0 μL of NB samples. The solution pH was determined using a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

Results and discussion

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

The generation of different types of ROSs, such as $OH^.$, $O_2^{-.}$, HO_2^{-}, and $HO_2^.$, at a large ratio of Fe^{2+}/H_2O_2 in conventional and modified Fenton processes has been widely observed. Among all ROSs, $OH^.$ is more dominant and active ROS [25, 26]. Therefore, in this study, the chemical probe compound method was adopted for a comprehensive investigation to identify the generation and intensity of ROSs such as $OH^.$ and $O_2^{-.}$. The selection of probe compounds was based on reactivity with ROSs existing in the Z-nZVI activated SPC system. The NB was selected as oxidant probe for the identification of $OH^.$ due to its higher reactivity with $OH^.$ ($k_{OH} = 3.9 \times 10^9 \, M^{-1} \, s^{-1}$). CT was chosen as reductant probe due to its higher reactivity with reductants ($O_2^{-.}$) ($k_e = 1.6 \times 10^{10} \, M^{-1} \, s^{-1}$) and least reactivity with $OH^.$ oxidants ($k_{OH} = 2.0 \times 10^6 \, M^{-1} \, s^{-1}$). The initial concentrations of NB, CT, and SPC were maintained at values of 2, 0.05, and 10 mmol L^{-1}, respectively. The degradation of NB and CT in the Z-nZVI activated SPC system in the absence and presence of RA can be seen in Fig. 1. The relatively smaller degradation of NB and CT was observed in the absence of RA, as shown in Fig. 1a. However, the degradation performance of NB and CT was significantly improved in the Z-nZVI activated SPC system in the presence of RA, as shown in Fig. 1b. About 57 and 96 % of NB was degraded in the Z-nZVI activated SPC system in the absence and presence of RA, respectively. The intensity of $OH^.$ in Z-nZVI activated SPC is greater in the presence of RA than in the absence of RA. The results strongly validated the assumption that the presence of RA enhanced the generation of $OH^.$ due to increase of Fe^{2+} concentration in the aqueous solution. The degradation of CT was approximately 38 % in the Z-nZVI activated SPC system in the absence of RA and 72 % in the Z-nZVI activated SPC system in the presence of RA. This is an indication that intensity and generation of $O_2^{-.}$ was considerably increased due to the addition of RA. As previously mentioned in the literature, $O_2^{-.}$ was only responsible for CT degradation in a modified Fenton process [25]. A significant difference in degradation performance of NB and CT in the absence and presence of RA

demonstrated that the generation of OH$^.$ and O$_2^{-.}$ increased substantially by accelerating the transformation of Fe^{3+} to Fe^{2+} in the presence of RA in the Z-nZVI activated SPC system.

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

The presence of OH$^.$ and O$_2^{-.}$ in the Z-nZVI activated SPC system demonstrated a significant contribution of free radicals in oxidation and reduction reactions for the degradation of TCE. In order to elaborate the contribution of ROSs present in the Z-nZVI activated SPC system, a sequential set of experiments was designed to investigate the scavenging effects. Based on the literature survey, two types of scavengers, TBA and chloroform (CF), were selected to assess the contribution of ROSs (OH$^.$ and O$_2^{-.}$, respectively) in the Z-nZVI activated SPC system. Degradation performance of TCE in the presence of scavengers can be seen in Fig. 2. TCE removal decreased to 28, 20.7, and 10.2 % with the TBA concentrations of 1.0, 10, and 30 mmol L^{-1}, respectively, in the absence of RA, as shown in Fig. 2a. A
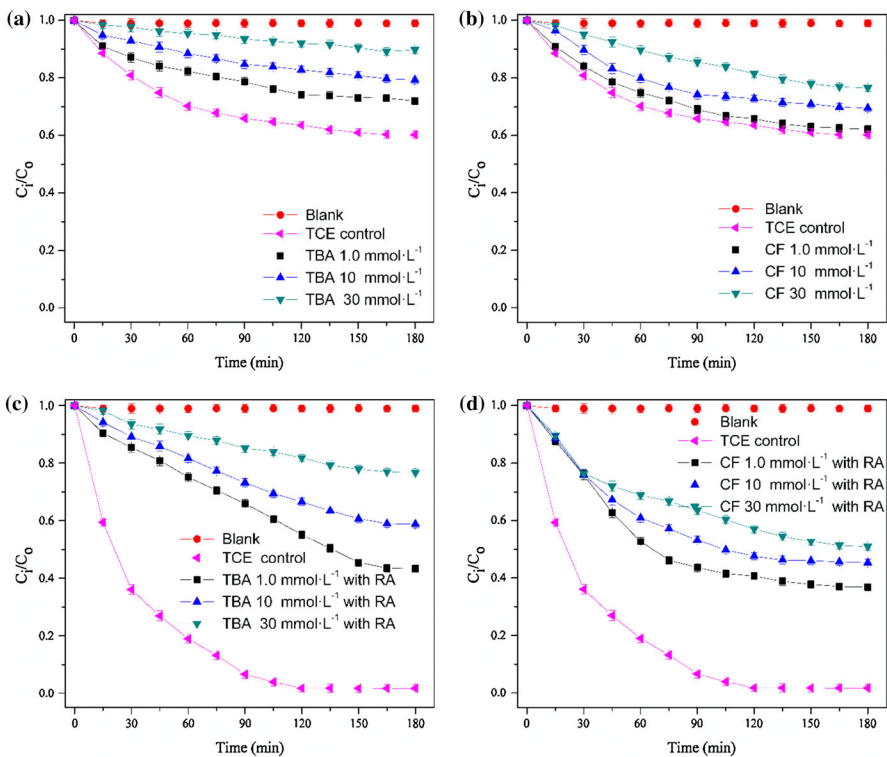

Fig. 2 Effect of scavengers on TCE degradation in the Z-nZVI/SPC system in the absence and presence of RA: **a** TBA without RA, **b** CF without RA, **c** TBA with RA, **d** CF with RA ([TCE] = 0.15 mmol L^{-1}, [Z-nZVI] = 100 mg L^{-1}, [SPC] = 15 mmol L^{-1}, [RA] = 7 mmol L^{-1})

significant inhibitive effect on the TCE degradation was also observed with addition of CF at molar concentrations of 1.0, 10, and 30 mmol L^{-1} to 37.8, 30.4, and 23.4 %, respectively, as shown in Fig. 2b. TBA contributed to scavenging $OH^{\cdot}$ radicals, whereas $O_2^{-\cdot}$ radicals were scavenged by CF. The degradation of TCE in the presence of RA and TBA in the Z-nZVI activated SPC system can be seen in Fig. 2c. A significant improvement in TCE degradation (56.7, 42, and 24 %) was observed in the presence of RA with the same concentration of TBA as previously used. The similar effect of TCE degradation was observed in the case of CF as shown in Fig. 2d, suggesting that the increased production of $O_2^{-\cdot}$ in the Z-nZVI activated SPC system strongly depends on the addition of RA. To the author's best knowledge, this is the very first report on the effects of scavengers in the Z-nZVI activated SPC system in the presence of RA.

Effect of solution matrix on TCE removal in Z-nZVI as percarbonate activator

Naturally occurring anions such as Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-} in groundwater can affect the performance of the groundwater remediation process. The TCE
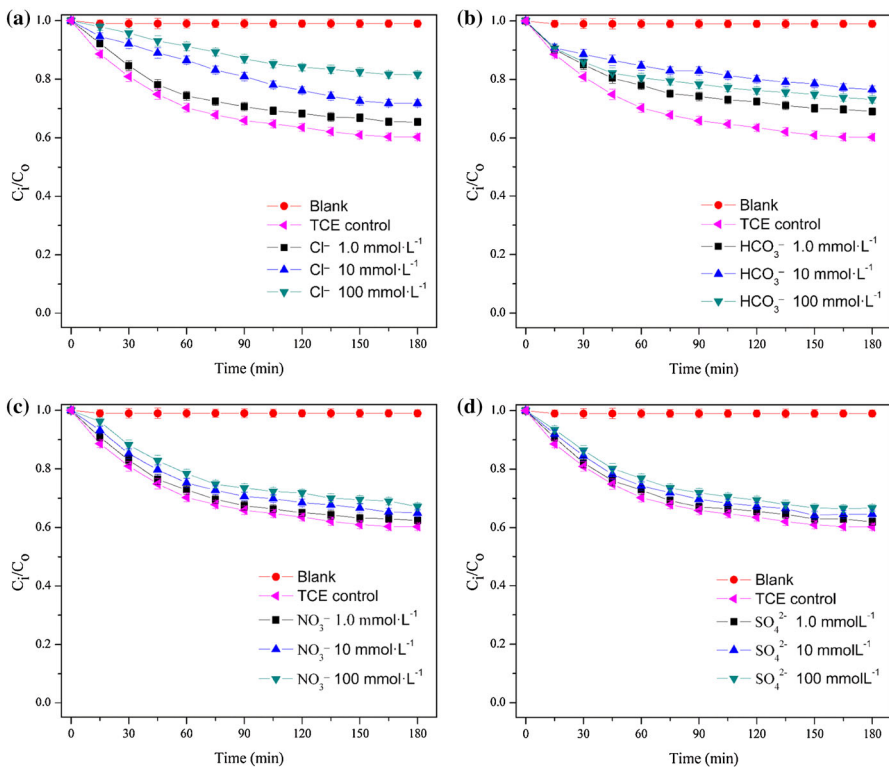
Fig. 3 Effect of solution matrix on TCE degradation in the Z-nZVI/SPC system: **a** Cl^-, **b** HCO_3^-, **c** NO_3^-, **d** SO_4^{2-} ([TCE] = 0.15 mmol L^{-1}, [Z-nZVI] = 100 mg L^{-1}, [SPC] = 15 mmol L^{-1})

degradation performance was investigated to determine the influence of anions with various concentrations in the absence and presence of RA in the Z-nZVI activated SPC system. The results from control tests without the addition of anions into the Z-nZVI activated SPC system are also shown in Figs. 3 and 4 (control line).

The effect of Cl^- anions on TCE degradation is shown in Fig. 3a. The increased Cl^- anion concentrations from 0 to 1.0, 10.0, 100.0 mmol L^{-1} resulted in a reduction of TCE degradation from 39.8 to 34.6, 28.2 %, and finally to 18.4 %. Bennedsen has reported similar results in activated persulphate system [27]. The TCE removal in the case of HCO_3^- anions from 0 to 1.0 and 10 mmol L^{-1} also dropped significantly from 39.8 to 30.9 and 27.3 %, respectively (see Fig. 3b). On the contrary, the TCE degradation was considerably increased from 27.3 to 34.7 % at 100 mmol L^{-1} concentration of HCO_3^- anion. Similarly, minor inhibitive behavior of the TCE degradation was also observed when 1.0, 10, and 100 mmol L^{-1} NO_3^- anions were added into the system (see Fig. 3c). Buxton et al. [28] found that NO_3^- anions can be added as solvated electron scavengers ($k = 9.7 \times 10^9$ M^{-1} s^{-1}). The scavenging effect provided evidence of the presence of solvated electrons in the Z-nZVI activated SPC system that scavenged and bounce-backed the degradation of TCE. The impact of SO_4^{2-} anion with 1.0, 10, and 100 mmol L^{-1}
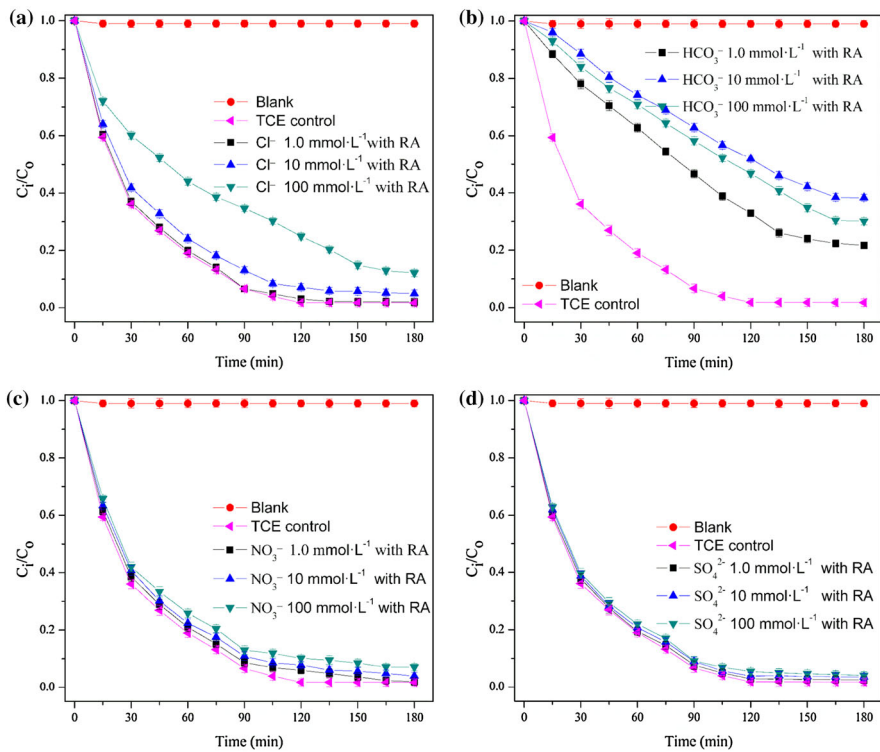

Fig. 4 Effect of solution matrix on TCE degradation in the Z-nZVI/SPC system with the presence of RA: **a** Cl^-, **b** HCO_3^-, **c** NO_3^-, **d** SO_4^{2-} ([TCE] = 0.15 mmol L^{-1}, [Z-nZVI] = 100 mg L^{-1}, [SPC] = 15 mmol L^{-1}, [RA] = 7 mmol L^{-1})

concentrations for TCE degradation had negligible inhibitive effect as shown in Fig. 3d. De Laat and Le claimed that efficiency of Fe^{3+}/H_2O_2 oxidation could be considerably declined in the presence of SO_4^{2-} anion [29]. The decomposition of H_2O_2 decreased in the Z-nZVI activated SPC system by adding SO_4^{2-} anions and Fe^{2+} promptly transformed into Fe^{3+}. Thus, the precipitation of Fe^{3+} suppressed the degradation of TCE. Furthermore, it was also suggested that Z-nZVI activated SPC dissolution was more significant in comparison with decomposition of H_2O_2, which is not analogous to Fenton process. This might be the only reason that no significant effect of the presence of SO_4^{2-} anions was found in the Z-nZVI activated SPC system.

Figure 4 shows the TCE degradation performance in Z-nZVI activated SPC system in the presence of RA and anions. The TCE degradation efficiency in the presence of Cl^- slightly decreased from 98.3 to 97.9, 94.9, and 87.8 %, respectively with the increase of Cl^- anion, as shown in Fig. 4a. The RA strongly inhibited the formation of Fe^{3+} chloro-complexes, while the reactions between Cl^- ions and Fe^{2+} increased the generation of Fe^{2+} and OH· in higher quantity. The literature also stated that OH· was the most significant ROS responsible for degradation of most COSs [30]. Reduction of Fe^{3+} to Fe^{2+} was significantly improved in the presence of RA [31]. The RA exists in the solution as NH_3OH^+ [24] to accelerate the transformation of Fe^{3+} to Fe^{2+} [25]. This substantial increase in TCE degradation even in the presence of the highest amount of Cl^- ions in the system confirmed the dominating role of RA. The effect of HCO_3^- anion in the TCE degradation with the presence of RA can be seen in Fig. 4b. Minor scavenging effect on the removal of TCE was observed with increasing HCO_3^- molar concentrations from 0 to 1.0 and 10 mmol L^{-1}, and TCE removal decreased from 98.3 to 78.3 and 61.7 %, respectively. TCE degradation at 100 mmol L^{-1} concentration of HCO_3^- increased from 61.7 to 70 %. RA enhanced the generation of peroxymonocarbonate ions (HCO_4^-), i.e. strong oxidants that significantly contributed in TCE degradation in the aqueous system [32]. The presence of RA along with HCO_3^- anion decreased the initial solution pH and buffering capacity of the aqueous solution.

The NO_3^- anions with molar concentrations of 1.0, 10, and 100 mmol L^{-1} decreased TCE removal from 98.3 to 98.0, 95.6, and 93 %, respectively as shown in Fig. 4c. A minor decrease in TCE degradation can be attributed to the scavenging of solvated electrons and reduction of Fe^{2+} to Fe^{3+}. The NO_3^- anions can also act as solvated electron scavengers [29], but the presence of RA rapidly scavenged this solvated electron scavenger to neutralize inhibitive effects. The degradation of TCE at 100 mmol L^{-1} concentration of NO_3^- anion in the absence of RA was 32.8 % while it reached 92.9 % in the presence of RA. This large increase in TCE degradation in the Z-nZVI activated SPC system is attributed to the addition of RA.

Inhibitive effect of SO_4^{2-} anion on TCE degradation in the presence of RA was quite negligible that can be seen from Fig. 4d. It seems that the presence of RA increased the generation of Fe^{2+} and reduced the formation of peroxide-complexes of Fe^{3+} and H_2O_2 decomposition. A significant increase in TCE degradation was observed in the presence of SO_4^{2-} anions in the Z-nZVI activated SPC system in the presence of RA. In summary, a significant increase in the TCE degradation, even in the presence of the most inhibitive anions (Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-}), showed

that the Z-nZVI activated SPC system is suitable and effective technique to increase the TCE degradation performance in the presence of RA.

Effect of initial solution pH in the Z-nZVI activated SPC system in the absence and presence of RA

The initial solution pH is one among the most important variables that can affect the degradation of COSs. To elucidate the effect of initial solution pH on TCE degradation in the Z-nZVI activated SPC system, various experiments were
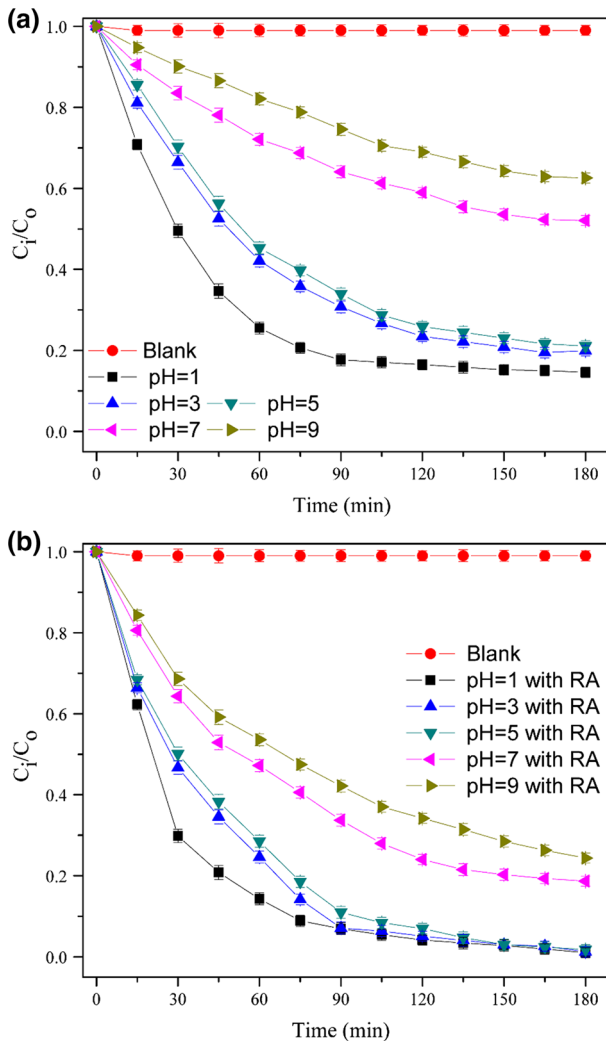

Fig. 5 Effect of initial solution pH in the Z-nZVI/SPC system on TCE degradation: **a** in the absence of RA, **b** in the presence of RA ([TCE] = 0.15 mmol L^{-1}, [Z-nZVI] = 100 mg L^{-1}, [SPC] = 15 mmol L^{-1}, [RA] = 7 mmol L^{-1})

conducted with 0.15 mmol L^{-1} molar concentration of TCE and 15 mmol L^{-1} concentration of SPC under different pH values, as shown in Fig. 5.

The degradation of TCE with various pH values in the Z-nZVI activated SPC system in the absence of RA is shown in Fig. 5a. The results demonstrated that TCE degradation was 85.4, 80.1, 78.8, 47.9, and 37.4 % for pH values of 1.0, 3.0, 5.0, 7.0, and 9.0, respectively. Small variations were observed in the experiments conducted at acidic pH (between 1.0 and 5.0). At higher pH values, the extent of TCE degradation was impeded fairly. On the other hand, the significant increase in TCE degradation was observed at all values of pH, even at a higher pH value of 9, in the Z-nZVI activated SPC system in the presence of RA, as shown in Fig. 5b. TCE degradation was 99.0, 98.7, 98.2, 81.3, and 75.6 % in the Z-nZVI activated SPC system in the presence of RA. These results are not consistent with the results of Fenton processes, in which a significant decline in COS degradation has been observed at neutral and basic pH. It is well understood that there is a strong effect of pH on the iron oxidation of Fe^{2+} to Fe^{3+}. Therefore, it is predicted that significant formation and subsequent precipitation of insoluble Fe^{3+} oxyhydroxides $Fe(OH)_3$ occurred. The oxyhydroxides elevated the solution pH and reduced the Fe^{2+} availability in the Z-nZVI activated SPC system in the absence of RA. Moreover, Buxton et al. [28] also stated that the oxidation potential of $OH^{\cdot}$ is suppressed at higher pH value. Oxidation potential of $OH^{\cdot}$ decreases to 1.90 V at pH 7.0, while this value was between 2.65 and 2.80 V at a pH value of 3 [28]. Therefore, OH· showed a weak oxidant at higher pH value; meanwhile, precipitation of Fe^{3+} has a negative effect on TCE degradation in the absence of RA in the Z-nZVI activated SPC system.

On the contrary, the presence of RA significantly reduced the subsequent formation and precipitation of insoluble Fe^{3+} oxyhydroxides $Fe(OH)_3$ by (1) lowering the pH of the solution, (2) increasing the oxidation potential up to its maximum value of 2.80 V, (3) suppressing the oxidation of Fe^{2+} to Fe^{3+}, and (4) increasing the availability of Fe^{2+} in the Z-nZVI activated SPC system. Teel also reported that TCE degradation dropped significantly at a pH value of 7, and at a pH value of 3 it reached its maximum value in the goethite Fenton system [33]. On the other hand, Guan found that the degradation of benzoic acid was significantly enhanced in the pH range of 8–11 in the UV (254 nm) peroxymonosulfate (UV/PMS) system [34]. SPC has a very strong capability to release H_2O_2 at pH less than 7; however, dissolution of SPC is weakened at higher pH value. The main reaction in SPC dissociation is the generation of H_2O_2. This H_2O_2 reacts with Fe^{2+}, which is significantly present in the system due to low pH. Significant production of Fe^{2+} strongly contributed in generating dominant ROSs ($OH^{\cdot}$ and $O_2^{-\cdot}$) to degrade TCE. Therefore, smaller release of H_2O_2 inhibited the degradation process at a pH value of 9 in the absence of RA, whereas this inhibitive effect was suppressed significantly in the presence of RA. Release rate of H_2O_2 can be adjusted by proper modification of solution pH in the system. Even though it was reported that oxidative degradation of COSs exhibited optimum results only at a pH value of 3.0 in Fenton and Fenton-like processes [26], the Z-nZVI activated SPC system shows an appropriate technique for the degradation of COSs even at higher pH value in the presence of RA.

Stability test of Z-nZVI activator

To evaluate the stability and reusability of activator, Z-nZVI was tested in three cycles for the activation of percarbonate in TCE degradation. It was observed that the activity of Z-nZVI decreased from 98 to 70 and 42 % for the second and third cycles, respectively (see Fig. S4). It might be the corrosion, which led to the decreased amount of active catalyst available for the TCE removal, and how to prevent this decrease will be the focus of our future work.

Conclusion

In the present study, the role of ROSs and effect of solution matrix were evaluated in the Z-nZVI activated SPC system for TCE degradation in the presence and absence of RA. Probe chemical compounds identified ROSs successively and the contribution of ROSs was evaluated by the scavenger tests. The scavenger tests demonstrated that $OH^.$ was the major constituent, while O_2^- was a minor contribution to TCE removal. It was also observed that the existence of Cl^- had significant scavenging effect, while higher concentrations of Cl^- demonstrated greater inhibitive effect on the TCE degradation in the absence of RA. The inhibitive effect of HCO_3^- at concentrations of 1.0 and 10.0 mmol L^{-1} was significantly greater than Cl^-, whereas 100 mmol L^{-1} of HCO_3^- slightly enhanced the TCE degradation as compared to 10 mmol L^{-1} of HCO_3^-. The minor effects of NO_3^- and SO_4^{2-} were observed in the absence of RA. However, the presence of RA significantly improved the TCE removal even in the presence of higher concentration of above-mentioned anions. The influence of initial solution pH showed that the Z-nZVI activated SPC system is highly applicable even in the higher pH value of 9. In conclusion, the Z-nZVI activated SPC system can provide new insights as a promising technique for the remediation of the TCE contaminated groundwater in the presence of RA.

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