Effect of Sulfate and Nitrate Anions on the Oxidative Degradation of Tetrachloroethylene by Magnetite with Glutathione

Nur Dalila Mohamad and Amnorzahira Amir

Abstract This work demonstrates the effect of sulfate (SO_4^{2-}) and nitrate (NO_3^{-}) anions during the oxidative degradation of tetrachloroethylene (PCE) by magnetite (Fe_3O_4) with glutathione. The enhanced of oxidative degradation of PCE was achieved due to the presence of SO_4^{2-} and NO_3^{-} anions to form reactive radicals in the Fe_3O_4-glutathione system. Kinetic rate constants for the oxidative degradation of PCE were accelerated 1.8 and 2.7 times higher, from 0.020 min^{-1} in the PCE-Fe_3O_4-glutathione to 0.036 and 0.054 min^{-1} in the PCE-Fe_3O_4-glutathione-NO_3^{-} and PCE-Fe_3O_4-glutathione-SO_4^{2-} systems respectively. The experimental results reveal that the oxidative degradation kinetic rate constant of PCE are strongly dependent on the presence of SO_4^{2-} and NO_3^{-} radicals. Kinetic oxidative degradation rate constant of PCE increased proportionally as the concentrations of NO_3^{-} (0.036–0.120 min^{-1}) and SO_4^{2-} (0.0540–0.160 min^{-1}) increased from 1 to 10 ppm at pH 7. The significant finding of this study is to provide the understanding of the oxidative degradation of PCE by Fe_3O_4 with glutathione in hyporheic zone and groundwater containing the SO_4^{2-} and NO_3^{-} anions for the development of novel remediation technolojgies.

Keywords Glutathione · Hydroxyl radicals · Nitrate radicals · Sulfate radicals · Tetrachloroethylene

1 Introduction

Groundwater and soil have been seriously contaminated by chlorinated organic compounds (COCs) due to the extensive usage of tetrachloroethylene (PCE) as an industrial solvent for metal parts degreasing, paint stripping, and plastics manufacturing [11, 38]. PCE is a toxic chemical due to its cytotoxicity, carcinogenicity,

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and persistence in hyporheic zone and groundwater that may pose serious human health and environmental concerns [16, 12]. Due to this reason, it has been listed as one of 14 volatile organic compounds in the United States Environmental Protection Agency (USEPA) Priority Pollutant List [12]. Hence, the development of treatment technology for PCE in the hyporheic zone and groundwater has gained significant interest by environmentalist. Additionally, hyporheic zone and groundwater contaminated with PCE has continuously attracted attention in the area of environmental technology.

Over the last few decades, a lot of studies have been made to develop novel remediation processes of diverse COCs in soil and groundwater. Chemical oxidation has been renowned as one of the effective methods for complete oxidation of COCs due to existence of COCs in aerobic environment [9, 14, 21, 22, 39]. This process is based on the decomposition of O_2, H_2O_2, $S_2O_8{}^{2-}$, and Na_2CO_3 by abiotic agents (magnetite (Fe_3O_4), mackinawite (FeS), and pyrite FeS_2), act as catalyst for the generation of sulfate $(SO_4{}^{\bullet -})$, hydroxyl $(OH^{\bullet})$ and superoxide $(O_2{}^{\bullet -})$ anion radicals to destruct COCs [5, 9, 14]. Additionally, recent studies have been done to improve the chemical oxidation of COCs by the addition of chemical reductants such as (copper bimetallic, hydroxylamine hydrochloride, sodium sulfite, ascorbic acid and sodium ascorbate) [14, 27, 40]. The addition of the reducing agents had increased the efficiency and stability of catalytic activity of abiotic iron by promoting the redox cycle of Fe^{3+}/Fe^{2+} to regenerate Fe^{2+} to enhance the generation of radicals ($SO_4{}^{\bullet -}$, $OH^{\bullet}$ and $O_2{}^{\bullet -}$).

Despite the effectiveness performance of chemical oxidation process to degrade COCs, the real applications of this process may cause limitation in the hyporheic zone and groundwater with abundance of common inorganic anions such as $SO_4{}^{2-}$ and $NO_3{}^{-}$. For instance, previous literatures reported that the performance of the degradation of synthetic organic dyes was aggravated due to the inhibitor effects of the inorganic anions. It was reported by Grebel et al. [15], Guzman-Duque et al. [17] and Devi et al. [10] that the performance of Fenton process has decreased the elimination of organic dyes due to the inorganic anions that act as $HO^{\bullet}$ scavenger. Additionally, Devi et al. [10] and Pignatello et al. [29] found the formation of low reactivity of iron-ion complexes from the possible reaction of iron species with anions. Similarly, Thiam et al. [34] and Daneshvar et al. [8] proved the presence of Na_2SO_4, and $NaNO_3$ inhibited the removal of dye solution by the photoelectron-Fenton process due to the possible formation of $NO_3{}^{-}$-iron and $SO_4{}^{2-}$-iron complexes. Consequently, the decrease in the concentration of free ferrous ions has caused limitation of the availability of $HO^{\bullet}$ radicals in the Fenton reaction. In contrast, Aquino et al. [2] and Martínez-Huitle and Brillas [26] found that electrochemical processes are significantly enhanced by the formation of new oxidative species particularly, the radicals of $SO_4{}^{\bullet -}$ and $NO_3{}^{\bullet}$ that participate in the degradation of synthetic organic dyes. Similarly, Villegas-Guzman et al. [35] showed the high efficiency of the degradation of fluoroquinolone antibiotics such as ciprofloxacin due to the availability of $SO_4{}^{\bullet -}$ and $NO_3{}^{\bullet}$ radicals in the photoelectron-Fenton system.

Furthermore, most of the previous studies have proved the performance of chemical oxidation process of COCs by abiotic iron metals (Fe_3O_4, FeS, and FeS_2) in the absence of inorganic anions that may affect the degradation rate of COCs. To date, no research has been conducted to identify the effectiveness of the oxidative degradation of COCs by Fe_3O_4 with glutathione in the presence of inorganic anions. Hence in this study, we have investigated the enhanced oxidative degradation of COCs by Fe_3O_4 with glutathione in the presence of inorganic anions. In this research, Fe_3O_4 and glutathione were selected respectively as a catalyst and reductant, and PCE was used as a representative of COCs in the hyporheic zone. The objective of this research is to evaluate the effect of common inorganic anions (SO_4^{2-} and NO_3^-) by Fe_3O_4 with glutathione on the oxidative degradation of PCE. The results from this study revealed the understanding of the oxidative degradation of COCs by biotic and abiotic interaction of Fe_3O_4 with glutathione in hyporheic zone and groundwater with abundance of SO_4^{2-} and NO_3^- anions.

2 Experimental

2.1 Chemicals

PCE (99.5%, Sigma Aldrich), magnetite (Fe_3O_4) (99.9%, Sigma Aldrich), nitrate (NO_3^-) (99.9%, Sigma, Aldrich) and sulfate (SO_4^{2-}) (99.9%, Sigma Aldrich), MOPS buffer (99.9%, Sigma Aldrich) were chemicals used in this study. Solvents of methanol (99.9%, Fisher) and n-hexane (99.9%, Friendemann Schmidt) were all HPLC grade that were used for preparation of PCE stock solution and extraction of PCE from supernatant. Sodium hydroxide (NaOH) (99.9%, Merck) and hydrochloric acid (HCl) (99.9%, Merck) were used to adjust the MOPS buffer solution. Ultra-pure deionized water (18 MΩ, Elga Purelab Ultra, United Kingdom) was used for the preparation of buffer and stock solutions in the batch experiments.

2.2 Experimental Procedures

Batch kinetic experiments were conducted to investigate the oxidative degradation kinetics of PCE in the presence of anions (NO_3^- and SO_4^{2-}). These experiments were performed using 43-mL amber glass vials and three-layered cap (PTFE tape, lead foil, PTFE-lined rubber septum) were designed to reduce the volatilization of PCE [24]. 0.1 g of Fe_3O_4 and 0.5 mM glutathione solution were filled into a vial containing 50 mM MOPS buffer solution to keep the suspension pH constant at 7. The Fe_3O_4 suspension was spiked with 0.01 mM PCE, 1 ppm NO_3^- and 1 ppm SO_4^{2-} to each vial respectively. All the vials were tightly capped with the three-layered septum cap and placed on the rotator (Multi Bio RS-24, Programmable rotator) with a rotation at 150 rpm at room temperature (25 ± 0.5 °C). Controls (PCE + UPW, PCE + UPW + Fe_3O_4, and PCE + UPW + glutathione) were prepared to check the decrease of PCE concentration by volatilization from the vial, adsorption on Fe_3O_4 surface, and oxidation with glutathione. To elucidate the effects of NO_3^- and SO_4^{2-} concentrations on the oxidative degradation of PCE, three different concentrations of 1, 5, and 10 ppm were conducted with the tested vials containing 2.33 g/L of Fe_3O_4, 0.50 mM of glutathione, 0.01 mM of PCE and 50 mM MOPS buffer solution to keep the suspensions at a constant pH of 7. The oxidative degradation kinetics of PCE at the different concentrations of NO_3^- and SO_4^{2-} concentrations were investigated by measuring the concentration of PCE in the Fe_3O_4 suspension at each sampling time. All the tested controls and samples prepared in this study were in duplicate.

2.3 Analytical Procedures

X-ray diffraction (XRD) (PAN analytical X'pert PRO) was used to identify chemical composition of pure Fe_3O_4 and Fe_3O_4 after the reaction with PCE. The phase composition of the Fe_3O_4 before and after reaction were measured by intensity of the diffracted X-ray beam hitting the sample with a source of radiation Cu-Kα generated at the voltage of 40 kV and 30 mA. An X-ray detector was used in this analysis.

The concentration of PCE in Fe_3O_4 suspension was quantitively measured by a gas chromatograph (GC) with Mass Spectroscopy (MS) (Perkin Elmer, Clarus 500) and Elite-5MS capillary column (30 m × 0.25 mm × 0.25 μm). Purified helium was used as a GC-MS carrier gas for 1.0 mL/min at a pressure 90 kPa. The temperatures of the injector and detector were 250 and 200 °C, respectively. The GC oven temperature was initially set at 50 °C, followed by a ramp of 40 °C per minute until 180 °C which was held for 2 min. The amount of sample injected was 1 μL with a split ratio of 20:1. The samples in the vials were centrifuged at 5000 rpm for 10 min to separate solid phase, and supernatants were extracted by 9 mL of n-hexane before the samples were analysed by GCMS. The samples were filtered by 0.22 μm Whatman syringe filters before injected into a GC column.

SO_4^{2-} and NO_3^- concentrations in the Fe_3O_4 suspension were analysed by DR 5000 UV-Vis Spectrophotometer. NO_3^- anion in the Fe_3O_4 suspension were measured by cadmium reduction method. NitraVer 5 Nitrate Reagent Powder Pillow was added into the sample cell containing 10 mL of sample. NO_3^- anion in the sample reacted with cadmium in the NitraVer 5 reagent and nitrite (NO_2^-) formed in the sample from the reduction of NO_3^-. An intermediate diazonium salt formed from the reaction of NO_2^- anion with sulfanilic acid in an acidic medium and subsequently reacted with gentisic acid. The salt in the sample changed from clear to amber coloured solution. The NO_3^- concentration was measured by the spectrophotometer at 400 nm. SO_4^{2-} anion in the Fe_3O_4 suspension was measured by SulfaVer 4 Method. SO_4^{2-} anion in the sample reacted with barium in the SulfaVer 4 and formed a precipitate of barium sulfate. The samples changed from clear to cloudy solution. The SO_4^{2-} concentration was measured from the turbidity of the solution and measured by the spectrophotometer at 450 nm.

3 Results and Discussion

3.1 X-ray Diffraction Analysis

Figure 1 shows the XRD patterns of (a) pure Fe_3O_4 (b) Fe_3O_4 after reaction in the Fe_3O_4-glutathione-NO_3^- system (c) Fe_3O_4 after reaction in the Fe_3O_4-glutathione-SO_4^{2-} system. XRD patterns of pure Fe_3O_4 in Fig. 1a show crystalline structure with sharp peaks at $2\theta = 30.1$, 36.8, 44.7, 59.6, and 65.6 and marked by their indices (220), (311), (400), (511) and (440) in accordance with the reference data in the library of XRD. Similar results were reported from the literatures which indicate the typical peaks of crystalline Fe_3O_4 [32, 36]. The XRD patterns of Fe_3O_4 after reaction in the presence of NO_3^- in Fig. 1b show two appearance of diffraction peaks at $2\theta = 37.3$ and 79.6, indicating the presence of maghemite (Fe_2O_3) whereas the sharp peak slightly shifts at 45.3 is most likely indicating Fe_3O_4. In the contrary, the XRD patterns of Fe_3O_4 after reaction in the presence of SO_4^{2-} in Fig. 1c show the formation of Fe_2O_3 at two diffraction peaks, $2\theta = 27.8$, and 48.3. It is notable that in the case of the Fe_3O_4 with glutathione in the presence of SO_4^{2-} and NO_3^-, the XRD peaks became slightly broad and decreased in heights as compared to the XRD peaks of the pure Fe_3O_4. The results indicate that the crystallinity of Fe_3O_4

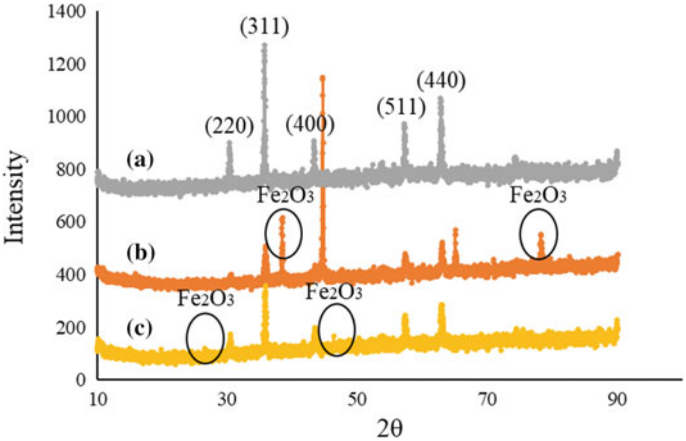

Fig. 1 XRD patterns of **a** pure Fe_3O_4 **b** Fe_3O_4 after reaction in the Fe_3O_4-glutathione-NO_3^- system **c** Fe_3O_4 after reaction Fe_3O_4-glutathione-SO_4^{2-} system

decreased due to formation of amorphous Fe_3O_4 with organic products, glutathione and NO_3^- and SO_4^{2-} anions. Similar XRD patterns were obtained by Ruan et al. [30] showed that the Fe_3O_4 after reaction displayed peaks of Fe_3O_4 with broad peaks and decrease in the peak heights and appearance of Fe_2O_3 peaks.

From the results of XRD, it can be suggested that the oxidation of Fe^{2+} may convert to Fe^{3+} through the surface oxidation of Fe_3O_4 and subsequently, induced the formation of Fe_2O_3 in the Fe_3O_4-glutathione-NO_3^- and Fe_3O_4-glutathione-SO_4^{2-} systems respectively. It can be suggested that the oxidation of Fe_3O_4 to Fe_2O_3 may induce the formation of radicals that responsible for the oxidative degradation of PCE. Furthermore. there were no other compounds were detected from the XRD patterns indicating that there was no formation of complexation between Fe-NO_3^- and Fe-SO_4^{2-} when NO_3^- and SO_4^{2-} were added in the Fe_3O_4 suspension. This indicates that the presence of NO_3^- and SO_4^{2-} anions in the Fe_3O_4 suspension did not inhibit the availability of free ferrous iron to induce the formation of radicals. Contrarily, the results from this study was contradict from the previous studies that the performance of Fenton process was decelerated due to the formation of NO_3^--iron and SO_4^{2-}-iron complexes in the system [8, 10, 29].

3.2 Oxidative Degradation of PCE by Fe_3O_4 in the Presence of Glutathione and Anions of SO_4^{2-} and NO_3^-

Figure 2 shows the oxidative degradation of PCE by Fe_3O_4 in the presence of glutathione and anions of NO_3^- and SO_4^{2-}. The experimental results show the additional of NO_3^- and SO_4^{2-} significantly affect the oxidative degradation of PCE by Fe_3O_4 in the presence of glutathione. The control test (C1) containing only PCE shows 100% of PCE was recovered throughout the reaction time, indicating no loss and degradation of PCE in all the tested vials. Approximately 63 and 69% of PCE were degraded in the PCE-NO_3^- (C2) and PCE-SO_4^{2-} (C3) systems and reached equilibrium after 360 min respectively. A complete oxidation of PCE was achieved within 320 min in the Fe_3O_4-glutathione system (S1). Interestingly, the oxidative degradation of PCE was improved with reaction time that 100% of PCE were completely oxidized within 270 min in the Fe_3O_4-glutathione-NO_3^- (S2) and Fe_3O_4-glutathione-SO_4^{2-} (S3) systems respectively. The oxidative degradation kinetics of PCE in the Fe_3O_4 suspension were calculated, as described by Eq. (1):

$$-\frac{dC}{dt} = kC \tag{1}$$

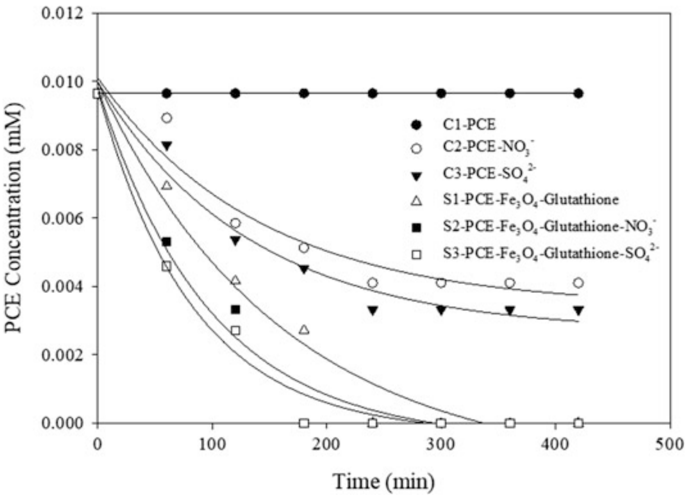

Fig. 2 Oxidative degradation of PCE by Fe_3O_4 in the presence of glutathione and anions of NO_3^- and SO_4^{2-}. [PCE] = 0.01 mM, [Fe_3O_4] = 2.33 g/L, [glutathione] = 0.5 mM, [NO_3^-] = 1 ppm [SO_4^{2-}] = 1 ppm, initial pH = 7.0

And Eq. (1) can be rewritten as:

$$\ln \frac{C}{Co} = -kt$$

where C and C_0 are the concentrations of PCE (mM) at time t and time zero, respectively and k is the pseudo-first-order rate constant (min^{-1}). The oxidative degradation kinetics of PCE in the three systems (Fe_3O_4-glutathione (S1), Fe_3O_4-glutathione-NO_3^- (S2) and Fe_3O_4-glutathione-SO_4^{2-} (S3)) were well-fitted by a pseudo-first-order rate law (R^2 = 0.991, 0.993 and 0.994) respectively.

Table 1 summarizes the kinetic rate constants of oxidative degradation of PCE under different operational systems. The oxidative degradation kinetic of PCE-NO_3^- (0.0072) and PCE-SO_4^{2-} (0.0090) were 2.7 and 2.2 times slower than the oxidative degradation kinetic of PCE-Fe_3O_4-glutathione system (0.020) respectively. The results imply the oxidative degradation of PCE may still occur even without Fe_3O_4 and glutathione. The addition of NO_3^- and SO_4^{2-} anions into the PCE-Fe_3O_4-glutathione systems show faster kinetics of the oxidative degradation of PCE than the PCE-Fe_3O_4-glutathione system. The oxidative degradation kinetic of PCE was accelerated 1.8 times higher, from 0.020 min^{-1} in the PCE-Fe_3O_4-glutathione to 0.036 min^{-1} in the PCE-Fe_3O_4-glutathione-NO_3^- system. Contrarily, the oxidative degradation kinetic of PCE was increased by 2.7 times higher, from 0.020 min^{-1} in the PCE-Fe_3O_4-glutathione system to 0.054 min^{-1} in the

Table 1 Kinetic rate constants of oxidative degradation of PCE under different operational systems

Operational system	Kinetic rate constants, k (min^{-1})
PCE-NO_3^-	0.0072
PCE-SO_4^{2-}	0.0090
PCE-Fe_3O_4-glutathione	0.020
PCE-Fe_3O_4-glutathione-NO_3^-	0.036
PCE-Fe_3O_4-glutathione-SO_4^{2-}	0.054

PCE-Fe_3O_4-glutathione-SO_4^{2-}. The enhanced oxidative degradation in both Fe_3O_4-glutathione-NO_3^- and Fe_3O_4-glutathione-SO_4^{2-} systems as compared to Fe_3O_4-glutathione system could possibly due to the generation and accumulation of new radical species (e.g., $SO_4^{\bullet-}$ and $NO_3^{\bullet}$) in the systems. Furthermore, the oxidative degradation kinetic rate constant in the PCE-Fe_3O_4-glutathione-SO_4^{2-} system was significantly faster compared to the PCE-Fe_3O_4-glutathione-NO_3^- system. This result suggests that SO_4^{2-} anion in the Fe_3O_4 suspension are much more reactive to promote generation of radical species as compared to NO_3^- anion. Similar results found by Serna-Galvis et al. [31] and Villegas-Guzman et al. [35] that the degradation of organic dyes by Fenton process was significantly enhanced by the contribution of SO_4^{2-} anion to produce more reactive $SO_4^{\bullet-}$ radicals as compared to $NO_3^{\bullet}$ radicals.

Based on the experimental results, the potential reaction mechanism of the oxidative degradation of PCE is initiated by the oxidation of Fe^{2+} on the surface of Fe_3O_4 to decompose O_2 and subsequently to $OH^{\bullet}$ radicals through Eqs. (2), (3), and (4) [23, 28, 37]: Eq. (2) the oxidation of Fe^{2+} on Fe_3O_4 surface to produce perhydroxyl ($HO_2^{\bullet}$), superoxide $O_2^{-\bullet}$ radicals and Fe^{3+}: $Fe^{2+} + O_2 \rightarrow Fe^{3+} + HO_2^{\bullet}/O_2^{-\bullet}$ Eqs. (2) and (3) the reduction of $HO_2^{\bullet}$ and $O_2^{-\bullet}$ by Fe^{2+} to produce hydrogen peroxide (H_2O_2), and Fe^{3+}: $Fe^{2+} + HO_2^{\bullet}/O_2^{-\bullet} \rightarrow Fe^{3+} + H_2O_2$ Eqs. (3) and (4) the decomposition of H_2O_2 by Fe^{2+} to yield hydroxyl $OH^{\bullet}$ radicals and Fe^{3+}: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$ (Eq. (4)). NO_3^- and SO_4^{2-} anions are reduced to $NO_3^{\bullet}$ and $SO_4^{\bullet-}$ radicals by $OH^{\bullet}$ radicals through Eqs. (5) and (6) [10, 17, 35]: Eq. (5) the reduction of NO_3^- by $OH^{\bullet}$ radicals to yield $NO_3^{\bullet}$ radicals and OH^-: $NO_3^- + HO^{\bullet} \rightarrow NO_3^{\bullet} + OH^-$ Eqs. (5) and (6) SO_4^{2-} anion is reduced by $OH^{\bullet}$ radicals to yield $SO_4^{\bullet-}$ radicals and OH^-: $SO_4^{2-} + HO^{\bullet} \rightarrow SO_4^{\bullet-} + OH^-$ Eq. (6). As the oxidative degradation of PCE proceeded, the accumulation of Fe^{3+} may occur and consequently decrease the stability and availability of Fe^{2+} in the Fe_3O_4 suspension. Glutathione may responsible to reduce the accumulation of Fe^{3+} and accelerate the redox cycle $Fe^{3+/}Fe^{2+}$ to regenerate Fe^{2+} through Eq. (7) [3, 13, 18, 19]: $Fe^{3+} + GSH \rightarrow Fe^{2+} + GSSG$.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + HO_2^{\bullet}/O_2^{-\bullet} \tag{2}$$

$$Fe^{2+} + HO_2^{\bullet}/O_2^{-\bullet} \rightarrow Fe^{3+} + H_2O_2 \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \tag{4}$$

$$NO_3^{-} + HO^{\bullet} \rightarrow NO_3^{\bullet} + OH^{-} \tag{5}$$

$$SO_4^{2-} + HO^{\bullet} \rightarrow SO_4^{\bullet -} + OH^{-} \tag{6}$$

$$Fe^{3+} + GSH \rightarrow Fe^{2+} + GSSG \tag{7}$$

3.3 Effect of NO_3^- Concentrations on the Oxidative Degradation Kinetics of PCE

Figure 3 shows the effect of NO_3^- concentrations on the oxidative degradation of PCE by Fe_3O_4 with glutathione at pH 7. A complete oxidative degradation of PCE was improved from 320 min in the Fe_3O_4-glutathione system to 240 min in the Fe_3O_4-glutathione-NO_3^- system at the concentrations of NO_3^- (1–10 ppm). The oxidative degradation kinetics of PCE at the different NO_3^- concentrations (0–10 ppm) was properly-fitted by a pseudo-first-order rate law (R^2 = 0.991, 0.993, 0.994 and 0.999) respectively. Inset Fig. 3 shows the oxidative degradation kinetic

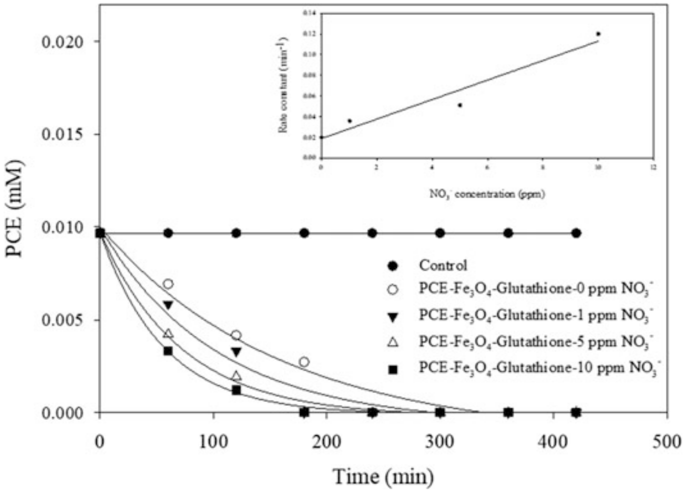

Fig. 3 Effect of NO_3^- concentrations on the oxidative degradation of PCE by Fe_3O_4 with glutathione. Inset Fig. 3: kinetic rate constants of the degradation of PCE in the Fe_3O_4-glutathione-NO_3^- system. [PCE] = 0.01 mM, [Fe_3O_4] = 2.33 g/L, [glutathione] = 0.5 mM, initial pH = 7.0

rate constant of the degradation of PCE at 0 ppm NO_3^- was 0.020 min^{-1} and increased by 6 times at 0.12 min^{-1} as the NO_3^- concentrations increased 1–10 ppm. This explains that the accumulation of $NO_3^\bullet$ radicals is directly proportional to the degradation rate of PCE and $OH^\bullet$ radicals play an important role to generate $NO_3^\bullet$ radicals in the Fe_3O_4 suspension (Eq. 5) [10, 17]. Additionally, it is proved that the enhancement of the degradation rate of PCE in the presence of NO_3^- due to the redox potential (2.3 V) of $NO_3^\bullet$ radicals is much higher than $OH^\bullet$ radicals (1.8 V) [4, 25, 33, 39], that act as predominant oxidant for complete mineralization of PCE.

Figure 4 shows the reduction of NO_3^- concentrations in the Fe_3O_4-glutathione-NO_3^- system. 100% complete removal of NO_3^- anion in the in the Fe_3O_4-glutathione-NO_3^- system was achieved within 240 min. The trend of the reduction of the NO_3^- concentrations is consistent with the oxidative degradation of PCE in the Fe_3O_4-glutathione-NO_3^- system that the NO_3^- concentration decreased during the oxidative degradation of PCE. The results highlight that NO_3^- anion in the Fe_3O_4-glutathione-NO_3^- system has contributed to the generation of $NO_3^\bullet$ radicals, replacing $OH^\bullet$ radicals that responsible to oxidize PCE in the Fe_3O_4-glutathione system.

The possible reduction pathway of NO_3^- in the Fe_3O_4-glutathione-NO_3^- system can be possibly suggested through $NO_3^\bullet$ radicals donating oxygen to PCE and simultaneously, PCE transferring electrons to $NO_3^\bullet$ radicals. NO_3^- is reduced to nitric oxide (NO) or nitrous oxide (N_2O) as intermediate products and eventually to nitrogen gas (N_2) through Eq. (8) [6].

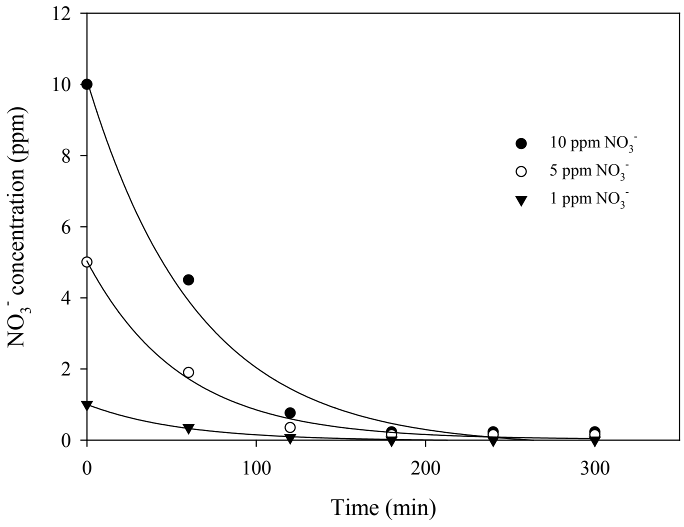

Fig. 4 The reduction of NO_3^- concentrations in the Fe_3O_4-glutathione-NO_3^- system. [PCE] = 0.01 mM, [Fe_3O_4] = 2.33 g/L, [glutathione] = 0.5 mM, initial pH = 7.0

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow NO \quad (8)$$

Interestingly, the simultaneous oxidative degradation of PCE and denitrification of NO_3^- has a positive effect that may reduce both the toxicity PCE and NO_3^- in the hyporheic zone and groundwater. The overall possible reaction mechanism of a simultaneous oxidative degradation of PCE and the reduction of NO_3^- anion in the Fe_3O_4-glutathione-NO_3^- system can be described through Eq. (9):

$$Cl_2C = CCl_2 + 2NO_3^- + 4H^+ \rightarrow 2CO_2 + 4Cl^- + 2H_2O + N_2 \quad (9)$$

3.4 Effect of SO_4^{2-} Concentrations on the Oxidative Degradation Kinetics of PCE

Figure 5 shows the effect of SO_4^{2-} concentrations on the oxidative degradation of PCE by Fe_3O_4 with glutathione. A complete oxidative degradation of PCE was improved from 320 min in the Fe_3O_4-glutathione system to 240 min in the Fe_3O_4-glutathione-SO_4^{2-} system at the concentrations of SO_4^{2-} (1–10 ppm). The oxidative degradation kinetics of PCE at the different SO_4^{2-} concentrations (1–10 ppm) were well-fitted by a pseudo-first-order rate law (R^2 = 0.994, 0.996 and 0.999) respectively. Inset Fig. 5 shows the oxidative degradation kinetic rate constants of PCE at 0 ppm SO_4^{2-} was 0.020 min^{-1} and increased by 8 times at

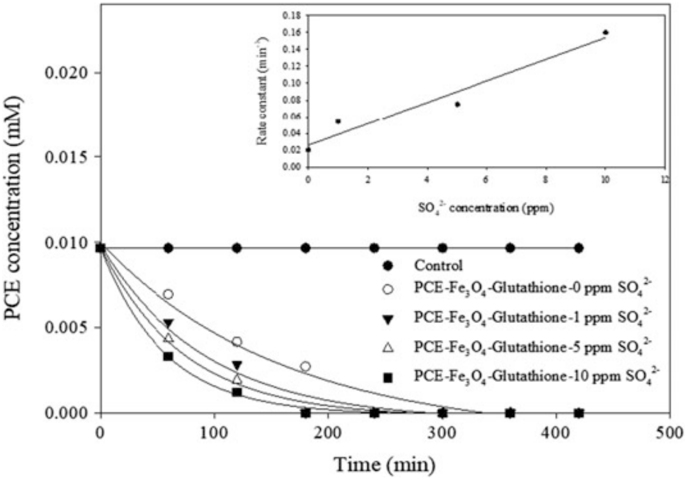

Fig. 5 Effect of SO_4^{2-} concentrations on the oxidative degradation of PCE by Fe_3O_4 with glutathione. Inset Fig. 5: kinetic rate constants of the degradation of PCE in the Fe_3O_4-glutathione-SO_4^{2-} system. [PCE] = 0.01 mM, [Fe_3O_4] = 2.33 g/L [glutathione] = 0.5 mM, initial pH = 7.0

0.160 min^{-1} as the SO_4^{2-} anion concentration increased 0–10 ppm. It is clearly shown that the addition of SO_4^{2-} anion has similar effect as NO_3^- anion that induced generation more radical species to oxidize PCE. This implies that $SO_4^{\bullet-}$ radicals are more predominant that may act as strong oxidant than $OH^\bullet$ radicals to oxidize PCE due to the redox potential of $SO_4^{\bullet-}$ radicals is much higher (2.5–3.1 V) than $OH^\bullet$ radicals (1.8 V) [4, 25, 33, 39]. According to Zhang et al. [41] and Anipsitakis and Dionysiou [1], $SO_4^{\bullet-}$ radicals exhibit high oxidation efficiencies and hence more efficient for the degradation of PCE.

Figure 6 shows the reduction of SO_4^{2-} concentrations in the Fe_3O_4-glutathione-SO_4^{2-} system. A complete removal of SO_4^{2-} anion in the Fe_3O_4-glutathione system was achieved within 240 min. The trend of the reduction of SO_4^{2-} is consistent to the oxidative degradation of PCE as SO_4^{2-} anion decreased during the oxidative degradation of PCE in the Fe_3O_4-glutathione-SO_4^{2-} system. These results suggest that the presence of SO_4^{2-} anion in the Fe_3O_4-glutathione-SO_4^{2-} system has replaced the role of $OH^\bullet$ radicals in the Fe_3O_4-glutathione system for the oxidation of PCE by the generation of $SO_4^{\bullet-}$ radicals through the reduction of SO_4^{2-} anion by the $OH^\bullet$ radicals.

The possible reduction pathway of the SO_4^{2-} anion in the Fe_3O_4-glutathione-SO_4^{2-} system can be possibly suggested through the $SO_4^{\bullet-}$ radicals donating oxygen to PCE and simultaneously, PCE transferring electron to $SO_4^{\bullet-}$ radicals. SO_4^{2-} is reduced to sulfite (SO_3^{2-}) and eventually to sulphide (H_2S) through Eq. (10) [7, 20, 27].

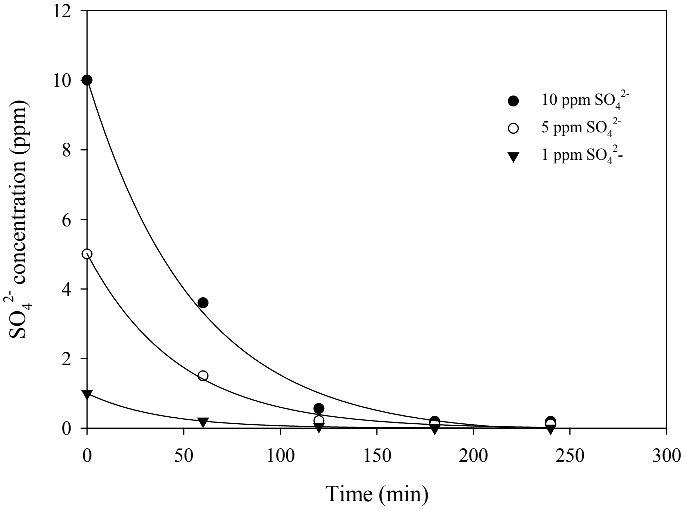

Fig. 6 The reduction of SO_4^{2-} concentrations in the Fe_3O_4-glutathione-SO_4^{2-} system. [PCE] = 0.01 mM, [Fe_3O_4] = 2.33 g/L, [glutathione] = 0.5 mM, initial pH = 7.0

$$SO_4^{2-} \rightarrow SO_3^{2-} \rightarrow H_2S \tag{10}$$

The simultaneous reaction mechanism between the reduction of SO_4^{2-} and the oxidative degradation of PCE has also given a beneficial effect as similar as NO_3^- that may decrease the existence of both organic and inorganic pollutants in the hyporheic zone and groundwater. The overall possible reaction mechanism of a simultaneous oxidative degradation of PCE and the reduction of SO_4^{2-} anion in the Fe_3O_4-glutathione-SO_4^{2-} system can be described through Eq. (11):

$$Cl_2C = CCl_2 + 2SO_4^{2-} \rightarrow 2CO_2 + 4Cl^- + 2H_2S + 4H_2O \tag{11}$$

4 Conclusions

The findings from the investigation showed the enhancement of the oxidative degradation of PCE by Fe_3O_4 with glutathione in the presence of NO_3^- and SO_4^{2-} anions. The results proved that the effectiveness of the oxidative degradation of PCE can be suggested due to the synergistic effect of NO_3^- and SO_4^{2-} anions in the Fe_3O_4-glutathione system to produce new radical species ($NO_3^\bullet$ and $SO_4^{\bullet-}$), as major radicals for the enhancement of oxidative degradation of PCE. In comparison of the three systems (Fe_3O_4-glutathione, Fe_3O_4-glutathione-NO_3^- and Fe_3O_4-glutathione-SO_4^{2-}), it is proved that the Fe_3O_4-glutathione-SO_4^{2-} system showed the highest efficiency on the oxidative degradation of PCE. Furthermore, the findings from this study show the simultaneous reaction of oxidative degradation of PCE and reduction of NO_3^- and SO_4^{2-} that is beneficial for the remediation of both inorganic and organic pollutants in the hyperhoic zone and groundwater. The results from this study can contribute to the novel remediation technologies for the degradation of COCs to be applied at the area of hyporheic zone and groundwater with abundance of electrolytes.

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