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Enhanced effect of EDDS and hydroxylamine on Fe(II)-catalyzed SPC system for trichloroethylene degradation

Xiaori Fu^{a,b}, Dionysios D. Dionysiou^c, Mark L. Brusseau^b, Waqas Qamar Zaman^a, Xueke Zang^{d,*}, Shuguang Lu^{a,*}, Zhaofu Qiu^a, and Qian Sui^a

^aState Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China

^bSoil, Water and Environmental Science Department, School of Earth and Environmental Sciences, The University of Arizona, 429 Shantz Bldg., Tucson, AZ 85721, United States

^cEnvironmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering (DBCEE), College of Engineering and Applied Science, University of Cincinnati, OH 45221-0012, USA

^dShanghai Institute of Geological Engineering Exploration, Shanghai, 200072, China

Abstract

This study presents a performance comparison of Fe(II)-catalyzed sodium percarbonate (SPC), Fe(II)-EDDS-catalyzed SPC, and of the innovative hydroxylamine hydrochloride (HA)-Fe(II)-EDDS-catalyzed SPC for the degradation of TCE in water. TCE degradation was greater in the Fe(II)-EDDS-catalyzed SPC system compared to the Fe(II)-catalyzed SPC system, indicating the effectiveness of adding EDDS as an enhancement factor for the removal of TCE. Moreover, TCE degradation was faster in the HA-Fe(II)-EDDS-catalyzed SPC system compared to the Fe(II)-EDDS-catalyzed SPC system, illustrating that HA can play a synergistic role in TCE degradation. Analysis of iron distribution in the three systems demonstrated that EDDS addition maintained iron in soluble form, and that the generation of soluble ferrous from ferric iron was expedited with addition of HA. Studies using nitrobenzene and carbon tetrachloride probes provided insights on the generation of hydroxyl radical ($\text{HO}^\bullet$) and superoxide anion radical ($\text{O}_2^{\bullet-}$) in the three systems. A gradual increasing contribution of $\text{O}_2^{\bullet-}$ to TCE removal in Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and HA-Fe(II)-EDDS-catalyzed SPC systems was verified through free-radical scavenger tests. Finally, monitoring of Cl^- concentrations manifested the complete dechlorination of TCE. A possible mechanism of TCE degradation involving two pathways of $\text{HO}^\bullet$ oxidation and $\text{O}_2^{\bullet-}$ reaction was proposed.

Keywords

sodium percarbonate (SPC); tetrachloroethene (TCE); Fe(II)-EDDS; hydroxylamine; groundwater remediation

Corresponding author: Shuguang Lu^{a,}: Tel: +86 21 64250709, Fax: +86 21 64252737, lvshuguang@ecust.edu.cn (S. Lu). Xueke Zang^{d,*}: Tel: +86 15921586514, 841346088@qq.com (X. Zang).

1. Introduction

In past decades, extensive usage, uncontrolled disposal, and unavoidable leakage of chlorinated organic compounds have led to serious environmental contamination because of their harmful characteristics, such as toxicity and carcinogenicity. Trichloroethylene (TCE), a typical chlorinated organic compound used widely in electronics processing, organic synthesis, and metal degreasing, is one of the most ubiquitous groundwater contaminants. Its maximum contaminant level in drinking water is regulated at $5 \mu\text{gL}^{-1}$ by USEPA [1]. Therefore, a large number of technologies, including bioremediation, permeable reactive barriers (PRB), and in situ chemical oxidation (ISCO), have been conducted for TCE-contaminated groundwater remediation [2–4].

Among numerous remediation processes, ISCO technology is a promising alternative, and has attracted much attention for being highly efficient and cost effective. Many oxidants, including permanganate [5], Fenton's reagent [6], ozone [7], persulfate [8,9], and percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, SPC) [10–12] have been employed in ISCO remediation application. Recently, the application of SPC, a solid substitute of hydrogen peroxide (H_2O_2) that releases H_2O_2 when mixed with H_2O , has created significant interest due to its numerous advantages such as wider pH range applicability and alkaline properties, therefore avoiding unacceptable acidification of groundwater in contrast with liquid H_2O_2 . For example, Miao et al. [13] illustrated effective degradation of TCE using the percarbonate process activated by ferrous iron. Their system employed relatively large chemical dosages for complete TCE degradation in Fe(II)-catalyzed SPC system. In order to improve the utilization of ferrous iron, several primary organic chelating agents such as citric acid, oxalic acid, and glutamate were employed to enhance soluble state maintenance [14–17]. Moreover, the higher reactivity of chelated-Fe(II) with SPC also improved the utilization of SPC, resulting in further enhancement of contaminant removal for the ferrous-iron activated percarbonate process [18]. However, some drawbacks still exist. First, an unavoidable acidification of groundwater takes place due to the addition of acidic chelating agents to the Fe(II)-catalyzed SPC system. Second, the soluble iron in chelated-Fe(II) catalyzed SPC system is in the ferric form, which is less reactive with H_2O_2 and leads to lower contaminant degradation efficiency [18]. Therefore, it is advantageous to seek a neutral chelating agent and a suitable reducing agent for the ferrous-iron activated percarbonate process.

In recently reported research studies, the application of a natural iron chelating agent, ethylenediamine- $\text{N,N}'$ -disuccinic acid (EDDS) as a replacement of EDTA, was evaluated for various oxidation processes in ISCO. EDDS is a biodegradable structural isomer of EDTA, and has been studied as an environmentally safe neutral chelating agent. Huang et al. [19] have already shown EDDS to be an efficient chelating agent for the degradation activity of ferric iron against bisphenol A in a wider pH range. In addition, reducing agents have been used to alleviate the drawback of rapid Fe(II) consumption. For example, ascorbic acid was employed in the traditional Fe(II) catalyzed persulfate process to enhance the regeneration of Fe(II) from Fe(III), and consequently the removal efficiency of Acid Orange 7 [20]. Chen [21] and Zou [22] also reported selection of hydroxylamine hydrochloride (HA) as a reducing agent to accelerate Fe(II)/Fe(III) cycling.

Based on the above discussion, it is expected that the addition of reducing agents to chelated-iron catalyzed systems can enhance the removal efficiency of contaminants via improving utilization of Fe(II) and SPC. However, to the best of our knowledge, no research study has so far focused on determining the effectiveness of the Fe(II)-EDDS catalyzed SPC system for contaminant degradation, nor on the effect of HA on the Fe(II)-EDDS catalyzed SPC system. Therefore, the objectives of this study were to (1) compare the removal performance of TCE in Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and HA-Fe(II)-EDDS-catalyzed SPC systems; (2) study the effects of EDDS and HA addition on the generation of hydroxyl radical ($\text{HO}^\bullet$) and superoxide anion radical ($\text{O}_2^{\bullet-}$); (3) investigate the contributions of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ to TCE degradation using free-radical scavengers; and (4) elucidate TCE degradation pathways through analysis of intermediate products for the Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems.

2 Materials and methods

2.1 Materials

Trichloroethylene (TCE, > 99.0%), hydroxylamine hydrochloride (HA, > 98.5%) and 1,4-benzoquinone (> 97%) were obtained from Aladdin (Shanghai, China). Nitrobenzene (> 97%), ferrous sulfate heptahydrate (> 99%), tert-butyl alcohol (> 99%) and carbon tetrachloride (> 97%) were purchased from Shanghai Jingchun Reagent Ltd. Co. (Shanghai, China). Sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$, SPC, 98%) and (S,S)-ethylenediamine-N,N-disuccinic acid (EDDS, 35% in water) was obtained from Acros Organics (Shanghai, China) and Sigma-Aldrich (Shanghai, China), respectively. All reagents were employed without further purification. Milli-Q water process (Classic DI, ELGA) was selected to produce ultrapure water for aqueous solutions preparation.

2.2 Experimental procedures

Twenty five mL TCE stock solution (concentration is 1.5 mM) was diluted to the desired concentration in a 250 mL cylindrical glass reactor where a magnetic stirrer was used to provide mixing (initial TCE concentration = 0.15 mM). Pre-determined amounts of EDDS, ferrous sulfate heptahydrate, and HA were added to the reactor successively, and then SPC was added to the reactor to initiate the reaction. A temperature bath (DC, Ningbo, China) was used to provide temperature control at 20 °C. Aqueous samples (1.0 mL) were collected at the desired time intervals and extracted with hexane (1.0 mL) for 3 min using a vortex stirrer following separation for 5 min. The organic phase was analyzed immediately by a gas chromatograph (Agilent 7890A, Palo Alto, CA).

2.3 Analytical methods

The specific conditions of TCE analysis can be found in our previous research [23]. The recovery of TCE was in the range of 87–95%. Chloride anion was analyzed by ion chromatography (Dionex ICS-I000, Sunnyvale, CA), and the measured Cl^- concentration before SPC addition in HA-Fe(II)-EDDS-catalyzed SPC system served as a background level. Total soluble iron including total free iron (Fe^{2+} and Fe^{3+}) and EDDS chelated iron (Fe(II)-EDDS and Fe(III)-EDDS) in Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems was determined with inductively coupled plasma-optical emission

spectrometry (ICP-OES, Agilent 725ES, Santa Clara, USA). Free ferrous ions (Fe^{2+}) as well as total free iron (Fe^{2+} and Fe^{3+}) were measured with the 1,10-phenanthroline method [24]. The solution pH was recorded by a pH meter (Mettler-Toledo DELTA 320).

3. Results and discussion

3.1 The enhanced effect of EDDS and HA on the generation of free-radicals

According to our previous research studies, both hydroxyl radical ($\text{HO}^\bullet$) and superoxide anion radical ($\text{O}_2^{\bullet-}$) have been observed in catalyzed SPC systems [18,23]. In this study, nitrobenzene (NB) was selected as an oxidant probe compound to examine the generation of $\text{HO}^\bullet$ given it is extremely reactive with $\text{HO}^\bullet$ ($k_{\text{HO}^\bullet} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Carbon tetrachloride (CT), a reductant probe, was applied to explore the generation of $\text{O}_2^{\bullet-}$ due to CT high reactivity with $\text{O}_2^{\bullet-}$ ($k = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) but low reactivity with $\text{HO}^\bullet$ ($k_{\text{HO}^\bullet} < 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) [25]. The concentrations of SPC, Fe(II), EDDS, HA, NB and CT were 0.75, 0.45, 0.4, 2.25, 2.0 and 0.05 mM, respectively. Fig. 1 shows that NB and CT could be degraded in the Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and HA-Fe(II)-EDDS-catalyzed SPC systems. These results indicate the generation of $\text{HO}^\bullet$ and superoxide anion radical ($\text{O}_2^{\bullet-}$) in all three systems.

As depicted in Fig. 1a, only 48% NB was removed from the Fe(II)-catalyzed SPC system which is limited by the poor recovery of Fe(II) from Fe(III). While higher removal of NB (59%) was observed in the Fe(II)-EDDS-catalyzed SPC system, suggesting that the addition of EDDS could enhance the generation of $\text{HO}^\bullet$. This may be induced by the Fe(II)/Fe(III)-EDDS complex, which can maintain iron in soluble form and accelerate the regeneration of Fe(II) from Fe(III) (Eqs.1–2) [19]. The results also showed that NB removal (%) in the first 10 min was almost the same in both Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems, suggesting that addition of HA at the beginning of the reaction had no effect on the generation of $\text{HO}^\bullet$. However, to be noted, a slight decrease of final NB removal (55%) was observed in the HA-Fe(II)-EDDS-catalyzed SPC system, confirming that the addition of HA adversely affected $\text{HO}^\bullet$ generation while the reaction proceeded. This phenomenon might be due to 1) the increasing pH with the reaction process in Fe^{2+} -EDDS-catalyzed SPC system turned HA into a termination agent of $\text{HO}^\bullet$ more than a $\text{HO}^\bullet$ accelerating agent because NH_2OH was easier to react with $\text{HO}^\bullet$ when the solution pH was higher than 4, and could act as a $\text{HO}^\bullet$ scavenger when the solution pH reached above 6.0 [21, 22], 2) a certain amount of $\text{HO}^\bullet$ were consumed by adventitious Cl^- upon addition of HA because Cl^- could also react with $\text{HO}^\bullet$ according to previous research [26,27]. In addition, we know that the degradation of most NB occurred in the first 20 min, and minor degradation of NB was observed in the last 70 min, which can also manifest the rapid generation and consumption of $\text{HO}^\bullet$ in all three systems. This is due to the low Fe(II) concentration in the Fe(II)-catalyzed SPC system and the rapid consumption of H_2O_2 (data were not shown) in Fe(II)-EDDS catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems.

Fig. 1b shows that 11%, 20% and 28% of CT was degraded in the Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and HA-Fe(II)-EDDS-catalyzed SPC systems, respectively, indicating that the superoxide anion radical ($\text{O}_2^{\bullet-}$) existed in all three systems. Higher

removal efficiency of CT in the Fe(II)-EDDS-catalyzed SPC system compared to the Fe(II)-catalyzed SPC system demonstrated that the addition of EDDS could enhance the generation of $O_2^{\bullet-}$, which may be due to two reasons: 1) the Fe(III)-EDDS complex from the oxidation of Fe(II)-EDDS could favor the reaction between Fe(III) and H_2O_2 because of the presence of higher concentration of soluble iron in the Fe(II)-EDDS-catalyzed SPC system (as depicted in Eq. 2), and 2) high solution pH in the Fe(II)-EDDS-catalyzed SPC system (above 6.0) favors the generation of $O_2^{\bullet-}$ from hydroperoxyl radical ($HO_2^{\bullet}$) and maintains $O_2^{\bullet-}$ as the other predominant species in the system (as depicted in Eq. 3, $pK_a = 4.88$) [19].

In addition, the highest CT removal (%) for the HA-Fe(II)-EDDS-catalyzed SPC system confirmed that the addition of HA can further enhance the generation of $O_2^{\bullet-}$. According to the results of prior research, the enhanced formation of $O_2^{\bullet-}$ in the presence of NH_2OH may be supported by the following two reasons: 1) the formation of $H_2NO^{\bullet}$ radical from NH_2OH by one-electron oxidation or H-atom abstraction, and 2) $H_2NO^{\bullet}$ radical deprotonation to $HNO^{\bullet-}$ radical ($pK_a = 12.6 \pm 0.3$) that could react with O_2 through one electron-transfer mechanism to form $O_2^{\bullet-}$ with a rate constant of $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (as depicted in Eqs. 4–6) [28]. Thus the addition of EDDS to the Fe(II)-catalyzed SPC system enhanced the generation of both $HO^{\bullet}$ and $O_2^{\bullet-}$, and meanwhile the addition of HA to the Fe(II)-EDDS-catalyzed SPC system also elevated the generation of $O_2^{\bullet-}$, but receded the generation of $HO^{\bullet}$ to a certain extent.

3.2 TCE degradation performance in these three systems

TCE degradation performance in Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and HA-Fe(II)-EDDS-catalyzed SPC systems is shown in Fig. 2. The results show 33%, 83% and 81% of TCE removal from these three systems after 180 min, respectively, while minimal mass loss was observed in the control. It is noted that the degradation of TCE for the Fe(II)-catalyzed SPC system with a SPC/Fe(II)/TCE molar ratio of 5/3/1 proceeded rapidly in the first min followed by no further degradation. This was mainly due to the rapid consumption of soluble iron and the unproductive scavenging of HO• as discussed in our previous study [11].

Conversely, continuous degradation of TCE was observed for the Fe(II)-EDDS-catalyzed SPC system where 32% degradation of TCE occurred in the first min and a further 50% degradation was observed in remaining time. This indicated that the addition of EDDS (0.4 mM) could enhance the continuous degradation of TCE, resulting in the improvement of TCE removal (%). This is because of the enhanced generation of HO• and O₂•⁻, which can degrade TCE through oxidation and reduction processes, respectively, in the Fe(II)-EDDS-catalyzed SPC system (see discussion in section 3.1). The effect of EDDS dosage with a SPC/Fe(II)/TCE molar ratio of 5/3/1 on TCE degradation performance is shown in Fig. 3.

TCE removal kinetics in the Fe(II)-EDDS-catalyzed SPC system followed the pseudo-first-order reaction kinetics model. The rate constant (k) and linear correlation coefficient (R^2) of the fitting line (Fig. S1) according to Eqs. 7 and 8, where C_i and C_0 are the TCE concentrations (mM) at various time t (min) and time equal to zero, respectively, are listed in Table 1.

$$-dC_i/dt = kC_i \quad (7)$$

$$\ln (C_i/C_0) = k \bullet t \quad (8)$$

The corresponding rate constant increased from 0.0004 min⁻¹ to 0.0098 min⁻¹ with the increase of EDDS concentration from 0.0 to 0.4 mM. Further increase in EDDS concentration to 1.0 mM led to a decrease in removal (%) of TCE (declined to 34.0%) and a decrease in rate constant (0.0014 min⁻¹) due to high reactivity of free EDDS with HO•, and the higher pH being unfavorable to the generation of HO•.

As depicted in Fig. 4, almost all iron resided in solution during the reaction process in the Fe(II)-EDDS-catalyzed SPC system compared to the rapid consumption and extremely low concentration of soluble iron in the Fe(II)-catalyzed SPC system. This indicates that the addition of EDDS can maintain iron in soluble form. This improves the effective utilization of iron, further enhancing TCE treatment efficiency. In addition, the decreasing concentration of EDDS (data not shown) due to oxidation by HO• led to an increasing

concentration of total free iron as the reaction proceeded. Unfortunately, the concentration of chelated-iron, Fe(II)-EDDS and Fe(III)-EDDS, could not be determined in our study.

Fig. 5 shows the effect of HA on TCE degradation in the HA-Fe(II)-EDDS-catalyzed SPC system with a SPC/Fe(II)/TCE molar ratio of 5/3/1 when EDDS concentration was 0.4 mM. The kinetics of TCE removal in the HA-Fe(II)-EDDS-catalyzed SPC system also followed the pseudo-first-order reaction kinetics model, and the fitting line is shown in Fig. S2, and its k and R^2 are listed in Table S2. The results showed that the removal of TCE reached 60%, 67%, 79% at 30 min when the HA concentration was 0.75, 1.5, and 2.25 mM, compared to 58% of TCE degradation at 30 min in the Fe(II)-EDDS-catalyzed SPC system without HA addition. Meanwhile, the rate constants (k) increased from 0.0098 min^{-1} to 0.0423 min^{-1} with an increase in HA concentration from 0.0 mM to 2.25 mM. The obtained results demonstrated that the addition of HA to the Fe(II)-EDDS-catalyzed SPC system could improve the TCE degradation efficiency and shorten the degradation period. However, excess HA addition decreased TCE removal (%) due to the quenching effect of $\text{HO}^\bullet$ by NH_2OH and Cl^- . Hence, appropriate concentrations of EDDS and HA should be selected so as to achieve a higher TCE removal (%) with less cost. Moreover, higher concentration of free ferrous ions (Fe^{2+}) in the HA-Fe(II)-EDDS-catalyzed SPC system compared to the Fe(II)-EDDS-catalyzed SPC system (shown in Fig. 4) indicated that the addition of HA enhanced the generation of free ferrous ions (Fe^{2+}) from free ferric ions (Fe^{3+}), which prompted speculation that the enhanced generation of Fe(II)-EDDS from Fe(III)-EDDS, even though we could not determine the valent of the chelated-iron in the HA-Fe(II)-EDDS-catalyzed SPC system.

3.3 The role of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ in TCE degradation

Due to the generation of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ in the Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and HA-Fe(II)-EDDS-catalyzed SPC systems, as discussed in section 3.1, it is important to compare the role of these two reactive oxygen species radicals in TCE degradation in these three systems. This was done at a SPC/Fe(II)/TCE molar ratio of 5/3/1 with EDDS (0.4 mM) and HA (2.25 mM). In this study, two free radical scavengers, tert-butyl alcohol (TBA) and 1,4-benzoquinone (BQ), were selected to investigate the role of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ because of their high reactivity with $\text{HO}^\bullet$ ($k = 5.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) and $\text{O}_2^{\bullet-}$ ($k = 9.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), respectively [25,29]. In addition, we introduced the term of contribution degree (CD) to examine the relevant contribution role of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$, as depicted in Eq. 9 where R_s and R_0 represent the final removal (%) of TCE with or without addition of scavengers. It should be noted that the CD describes the relevant role of the two free radicals on TCE degradation, but cannot quantify their actual contribution on TCE degradation due to the interrelations of formation and consumption of such radicals.

$$C = (R_0 - R_s)/R_0 \times 100 \% \quad (9)$$

Fig. 6a shows minimal degradation of TCE when TBA was added to the system while slight inhibition of TCE degradation with BQ addition was observed in the Fe(II)-catalyzed SPC system, indicating that $\text{HO}^\bullet$ played a dominant role in TCE degradation even though $\text{O}_2^{\bullet-}$

existed in the Fe(II)-catalyzed SPC system. The results depicted in Figs. 6b and 6c suggest that $\text{HO}^\bullet$ is the main free radical responsible for TCE degradation because 48% and 40% inhibition of TCE degradation were observed when 30 mM TBA was added to Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems. Meanwhile, 31% and 39% of TCE was degraded, suggesting that a non- $\text{HO}^\bullet$ oxidation mechanism occurred in both systems. In addition, removal (%) of TCE decreased from 79% and 80% to 48% and 45%, respectively, in systems with addition of BQ scavenger, demonstrating that $\text{O}_2^{\bullet-}$ also played an important role in TCE degradation in the Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems. In addition, the CD of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ on TCE degradation were 92%, 61%, 51% and 6%, 38%, 44% in Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems, respectively. This also confirmed the decreased effect of $\text{HO}^\bullet$ and increased effect of $\text{O}_2^{\bullet-}$ on TCE removal in Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems compared to the Fe(II)-catalyzed SPC system.

3.4 Mechanism of TCE degradation

Many reported research studies measured Cl^- concentration to investigate the dechlorination extent of chlorinated hydrocarbons as being crucial to its mineralization [30,31]. In this study, Cl^- concentration accompanied with TCE degradation was measured to investigate the dechlorination degree of TCE in the Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems. Theoretically, 3 mol Cl^- will be generated after total dechlorination of 1.0 mol of TCE. As depicted in Fig. 7, concentrations of Cl^- measured in both Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems increased along with the degradation of TCE. The presence of some intermediate products was hypothesized due to the difference between the measured and theoretical concentrations of chloride ions before the total release of Cl^- . However, the final measured Cl^- concentrations in both systems match the theoretical concentrations of Cl^- within 60 min and 120 min in Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems, respectively. In addition, only formic acid without any chlorinated intermediate products was detected in both systems, and a lower concentration of formic acid was observed in the HA-Fe(II)-EDDS-catalyzed SPC system compared to the Fe(II)-EDDS-catalyzed SPC system. All these results indicate that 1) the possibly existing intermediate products could be further degraded, leading to a complete dechlorination of TCE in both systems, and 2) the addition of HA to the Fe(II)-EDDS-catalyzed SPC system could enhance the mineralization of TCE.

Li et al. proposed three probable degradation pathways of TCE in the UV/ H_2O_2 process: addition of $\text{HO}^\bullet$ to the C=C bond, direct photolysis and addition of chlorine atom to the C=C bond [32]. Based on the previous research and the only detected product (formic acid), one degradation pathway of TCE corresponding to $\text{HO}^\bullet$ oxidation was proposed (Fig. 8): $\text{HO}^\bullet$ attacked the double bond of TCE to form a geminal chlorohydrin radical at a rate constant of $2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Eq. 10), which eliminated HCl rapidly and generated carbon-centered radicals ($\text{OHC-C}^\bullet\text{Cl}_2$) (Eq. 11, $k = 5.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$). These unstable carbon-centered radicals undergo a series of reactions (Eq. 12–16) to form formic acid, which could be thoroughly oxidized to CO_2 and H_2O [32].

A nucleophilic addition of $\text{O}_2^{\bullet -}$ to chloroalkenes was proposed as the reasonable initial step for the degradation of these compounds in previous research studies [33,34]. Also, due to the important role of $\text{O}_2^{\bullet -}$ in TCE degradation, a degradation pathway of TCE by $\text{O}_2^{\bullet -}$ in the two systems is hypothesized (Fig. 8): Nucleophilic reaction of $\text{O}_2^{\bullet -}$ to TCE as well as the subsequent release of Cl^- lead to the formation of vinyl-peroxy-radical, which can further undergo subsequent degradation with $\text{HO}^\bullet$ and/or $\text{O}_2^{\bullet -}$ to release Cl^- , CO_2 and H_2O .

4. Conclusions

A comparison of TCE degradation by Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC, and an innovative HA-Fe(II)-EDDS-catalyzed SPC system was successfully investigated. The addition of EDDS to the Fe(II)-catalyzed SPC system enhanced TCE removal (%), and HA addition to the Fe(II)-EDDS-catalyzed SPC system accelerated TCE degradation. Appropriate dosages of EDDS and HA should be employed in order to achieve optimal TCE degradation because excess HA and EDDS can suppress TCE degradation. $\text{HO}^\bullet$ and $\text{O}_2^{\bullet -}$ were verified in the three systems through the effective degradation of radical probe compounds, nitrobenzene and carbon tetrachloride. The addition of EDDS promoted the

generation of both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$, whereas the addition of HA enhanced the generation of $\text{O}_2^{\bullet-}$ but slightly decreased the generation of $\text{HO}^\bullet$. The analysis of iron distribution in the three systems indicated the addition of EDDS could maintain iron in soluble form, and the generation of soluble ferrous ions from ferric ions could be enhanced due to the addition of HA. In addition, the result of free-radical scavengers tests demonstrated both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ were predominant species responsible for TCE removal, and that the relative contribution of $\text{O}_2^{\bullet-}$ increased gradually in Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems. Finally, the complete release of Cl^- indicated the complete dechlorination of TCE, and two possible degradation pathways were proposed in this study. The results acquired from this study explicitly elaborate that the innovative HA-Fe(II)-EDDS-catalyzed SPC system is superior to the Fe(II)-catalyzed SPC and Fe(II)-EDDS-catalyzed systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.

Free radical probe tests for the Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems ($[SPC]_0 = 0.75$ mM, $[Fe(II)]_0 = 0.45$ mM, $[EDDS]_0 = 0.4$ mM, $[HA]_0 = 2.25$ mM): (a) NB ($[NB]_0 = 2.0$ mM), (b) CT ($[CT]_0 = 0.05$ mM).

Fig. 2. TCE degradation in the Fe(II)-catalyzed SPC, Fe(II)-EDDS-catalyzed SPC and HA-Fe(II)-EDDS-catalyzed SPC systems ($[\text{SPC}]_0 = 0.75 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.45 \text{ mM}$, $[\text{EDDS}]_0 = 0.4 \text{ mM}$, $[\text{HA}]_0 = 2.25 \text{ mM}$, $[\text{TCE}]_0 = 0.15 \text{ mM}$).

Fig. 3. Effect of EDDS dosage on TCE degradation in the Fe(II)-EDDS-catalyzed SPC system at a fixed SPC/Fe(II)/TCE molar ratio of 5/3/1 ($[TCE]_0 = 0.15$ mM).

Fig. 4.

Total soluble iron, total free iron and free ferrous ions concentrations in Fe(II)-catalyzed SPC (system 1), Fe(II)-EDDS-catalyzed SPC (system 2) and HA-Fe(II)-EDDS-catalyzed SPC system (system 3) ($[\text{SPC}]_0 = 0.75 \text{ mM}$, $[\text{Fe(II)}]_0 = 0.45 \text{ mM} = 25.6 \text{ mg/L}$, $[\text{EDDS}]_0 = 0.4 \text{ mM}$, $[\text{HA}]_0 = 2.25 \text{ mM}$, $[\text{TCE}]_0 = 0.15 \text{ mM}$).

Fig. 5.

Effect of HA dosage on TCE degradation in the HA-Fe(II)-EDDS-catalyzed SPC system at a fixed SPC/Fe(II)/TCE molar ratio of 5/3/1 ($[TCE]_0 = 0.15$ mM, $[EDDS]_0 = 0.4$ mM).

Fig. 6. Effect of scavengers on TCE degradation at a fixed SPC/Fe(II)/TCE molar ratio of 5/3/1 in (a) the Fe(II)-catalyzed SPC system, (b) the Fe(II)-EDDS-catalyzed SPC system, (c) the HA-Fe(II)-EDDS-catalyzed SPC system ($[TCE]_0 = 0.15$ mM, $[EDDS]_0 = 0.4$ mM, $[HA]_0 = 2.25$ mM).

Fig. 7.

Concentrations of Cl⁻ and formic acid along with TCE degradation at a fixed SPC/Fe(II)/TCE molar ratio of 5/3/1 in (a) the Fe(II)-EDDS-catalyzed SPC system, (b) the HA-Fe(II)-EDDS-catalyzed SPC system ([TCE]₀ = 0.15 mM, [EDDS]₀ = 0.4 mM, [HA]₀ = 2.25 mM).

Fig. 8.
Proposed TCE degradation pathway