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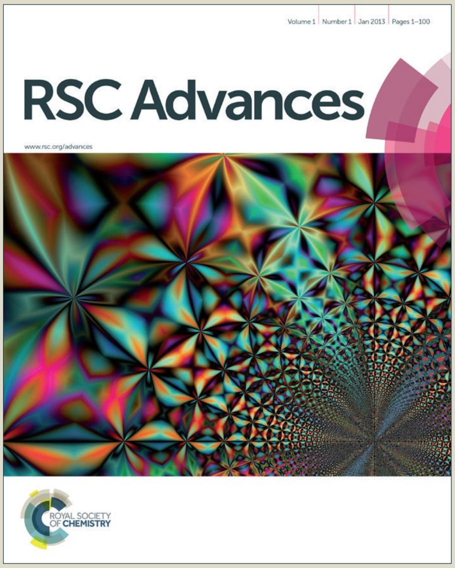

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Oxidation and reduction performance of 1,1,1-trichloroethane in aqueous solution by means of a combination of persulfate and zero-valent iron

Xiaogang Gu[a,b], Shuguang Lu[a*], Xuhong Guo[b], Jingke Sima[c], Zhaofu Qiu[a], Qian Sui[a]

[a] State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, Shanghai Key Laboratory of Functional Materials Chemistry, East China University of Science and Technology, Shanghai 200237, China

[b] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

[c] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

[*] Corresponding author: Tel: +86 021 64250709, fax: +86 021 64252737, e-mail: lvshuguang@ecust.edu.cn

Abstract

In this study, the degradation performance of 1,1,1-trichloroethane (TCA) involving both oxidation and reduction processes was investigated with an application of the persulfate-ZVI (zero-valent iron) system, in which it is generally believed that $SO_4^{-\bullet}$-induced oxidation was responsible for pollutants removal. The study was conducted with persulfate and un-pretreated ZVI through batch experiments. The results showed that TCA was stable in the presence of ZVI alone within 12 h and degraded with the addition of persulfate. TCA degradation efficiency was found to increase with increasing persulfate concentrations, but to decrease with increasing ZVI dosage. A two-stage process involving persulfate oxidation and ZVI reduction was developed during TCA degradation. The addition of isopropanol and *tert*-butyl alcohol proved the existence of sulfate and hydroxyl radicals during the 1st-stage (0~2 h), which were absent in the 2-nd stage (2~12 h) when persulfate was exhausted. The degradation performance of carbon tetrachloride, a reduction probe compound, was evidence of the persulfate-ZVI system involving an enhanced ZVI reduction, and which was mainly responsible for TCA degradation in the 2nd-stage. 1,1-Dichloroethane was the only confirmed intermediate emerging during the 2nd-stage.

Key words: 1,1,1-Trichloroethane; Persulfate-ZVI system; Persulfate oxidation; Enhanced ZVI reduction

1. Introduction

1,1,1-Trichloroethane (TCA), known as a chlorinated solvent, is a commonly identified groundwater contaminant that has been detected in at least 50% of the sites listed on the U.S. Environmental Protection Agency (USEPA) National Priorities List.[1] The appearance of TCA in soils and groundwater has elicited much attention because of its recalcitrant characteristic and potential to cause liver, nervous system and circulatory system problems from the long-term exposure. Hence, the USEPA maximum contaminant level of TCA in drinking water has been set at 0.2 mg L^{-1}.[2]

In situ chemical oxidation (ISCO) has become a widely used technology for the remediation of groundwater contaminated by chlorinated solvents. Persulfate, one of the strongest oxidants with a redox potential (E^0) of 2.01 V, has recently received considerable attention for ISCO. In most case, various methods, including heat, ultraviolet irradiation, transition metals, hydrogen peroxide, alkaline pH, etc., are used in order to activate persulfate and generate the sulfate radical ($SO_4^{-\bullet}$, $E^0 \approx 2.6$ V) and other reactive species.[3, 4] Transition metals such as Fe^{2+} have been proved to be effective to activate persulfate for the degradation of most prevalent organic contaminants (eq 1).[5-7] However, it has been found that excess Fe^{2+} can further consume the produced $SO_4^{-\bullet}$ which results in a reduction of Fe^{2+} activation (eq 2). Therefore, it is important to maintain an appropriate concentration of Fe^{2+} in the solution.

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-} \qquad (1)$$

$$Fe^{2+} + SO_4^{-\bullet} \rightarrow Fe^{3+} + SO_4^{2-} \qquad (2)$$

As an alternative source of Fe^{2+}, ZVI has been employed as a persulfate activator with promising results in the degradation of many organic contaminants.[8-10] The slow-releasing of Fe^{2+} and recycling of Fe^{3+} at the ZVI surface can prevent the accumulation of excess Fe^{2+} in solution.[11] It has been reported that persulfate activation using ZVI for degradation of organic compounds was more effective than Fe^{2+}.[12-15] Li et al.[16, 17] demonstrated that particle size of ZVI and solution pH value could influence the degradation performance of acid orange 7 (AO7) and the iron corrosion coating, respectively. Oh et al.[13] suggested that the most likely mechanism for persulfate activation by ZVI did not involve aqueous Fe^{2+}, but direct electron transfer from ZVI or surface-bound Fe^{2+}. Ahn et al.[18] believed that the near-surface Fe^{2+} on a bilayered-structured passive film was contributed to the generation of $SO_4^{-\bullet}$, rather than direct contact between persulfate and ZVI or Fe^{2+} in the solution.

According to TCA, a naturally recalcitrant hydrocarbon with one single bond, has been confirmed to be effectively removed by thermal and UV activation of persulfate.[19, 20] Xu et al.[21] reported that $SO_4^{-\bullet}$, $^{\bullet}OH$, and $O_2^{\bullet-}$ were all generated in the thermally activated persulfate system, while $^{\bullet}OH$ appeared to be the predominant radical species for TCA removal. However, there is less information regarding TCA degradation performance by persulfate activation with transition metals. In this study, a persulfate-ZVI (ZVI without pretreament) system was applied to remove TCA in aqueous solution, and it was interesting to find that TCA degraded gradually even when persulfate was exhausted. Therefore, other reaction chemistry without persulfate is supposed to be responsible for TCA removal, while most studies using persulfate-ZVI method focused on persulfate oxidation involving $SO_4^{-\bullet}$ or $^{\bullet}OH$, and direction reduction action by ZVI was less reported. Hence, the objective of this study was (1) to investigate the degradation performance of TCA in the persulfate-ZVI system, (2) to evaluate the role of persulfate in the system, and (3) to examine the potential oxidation and reduction processes responsible for TCA degradation. TCA degradation performance and the trends of dissolved Fe^{2+} and persulfate were investigated, and then the radical scavenger test and chemical probe method were conducted to examine the responsible processes for TCA removal. Furthermore, the intermediates during TCA degradation and the chloride mass balance were determined.

2. Materials and methods

2.1. Materials

1,1,1-Trichloroethane (TCA, 99.0%), ZVI powder (99%, 150 μm), isopropanol (IPA, 99.7%), *tert*-butyl alcohol (TBA, 99.0%), methyl tert-butyl ether (MTBE, 99.9%), sodium bicarbonate (99.5%), and potassium iodide (99.0%) were purchased from Shanghai Jingchun Reagent Co., Ltd. (Shanghai, China). Carbon tetrachloride (CT, 99.5%), 1,10-phenathroline (99.0%), and n-hexane (97%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Persulfate (98.0%) was purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultra-pure water from a Milli-Q water process (Classic DI, ELGA) was used for preparing aqueous solutions.

2.2. Experimental procedures

All reactions were conducted in 24 mL volatile organic analysis (VOA) vials fitted with polytetrafluoroethylene (PTFE) lined caps. Stock solution of TCA was prepared by allowing the pure nonaqueous-phase liquid TCA to equilibrate with Milli-Q water overnight with gentle stirring in the dark and later diluted to 20 mg L^{-1} (0.15 mM). When required dosage of ZVI was added to a series of reaction vials, a predetermined amount of persulfate was added to the TCA-containing solution, and later distributed by fully filling the reaction vials. All sample vials were placed in a head-to-bottom rotation drum (with a speed of 5 rpm) to enhance the movement of ZVI powder (Fig. S1).[22] The rotation drum was located in the constant temperature chamber to keep the temperature at 20 ± 1 ℃. The reaction vials were sacrificed at different intervals for immediate analyses. The initial pH in all experiments was unadjusted except in the test for investigating the influence of Fe^{2+} on ZVI reduction. All experiments were conducted in triplicate and the mean values reported.

2.3. Analytical methods

The concentration of TCA and CT was quantified after extraction with hexane by a gas chromatograph (GC, Agilent 7890A, Palo Alto, CA) equipped with an autosampler (Agilent 7693). The method detection limit (MDL) for TCA is 5 μg L^{-1}. The volatile organic intermediates formed in TCA degradation were identified by aqueous samples using an automatic purge and trap (Tekmar Atomx, Mason, OH) coupled to a GC/MS (Agilent 7890/5975). The MDL for the intermediates is 0.5 μg L^{-1}. The carboxylic acid intermediates were identified using a GC/MS (Shimadzu GC/MS-QP 2010, Kyoto, Japan) after derivatization with acidic methanol. Details of the analytical methods for TCA and the intermediates are shown in SI Text S1. The concentration of $S_2O_8^{2-}$ was determined by a spectrophotometric method using potassium iodide.[23] Ferrous ion and total iron were quantified using 1,10-phenathroline at a wavelength of 512 nm by a Hach DR 6000 spectrophotometer (Loveland, CO).[24] The pH was measured with a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland). The concentration of chloride ions was detected by anion chromatograph (Dionex ICS-I000, Sunnyvale, CA).

3. Results and discussion

3.1. Effects of persulfate concentration and ZVI dosage on TCA degradation in the persulfate-ZVI systems

Experiments were conducted to determined TCA degradation performance by a combination of persulfate and ZVI. The control experiments revealed that less than 5% loss of TCA due to volatilization and TCA was stable after addition of persulfate or Fe^{2+} alone at 20 ^{o}C (Fig. S2). Our previous study showed that TCA could be effectively removed in a soil slurry system by means of pretreated ZVI powder.[25] In this study, the control test was conducted using the same ZVI (0.05 g, 150 μm) but without pretreatment in the absence of persulfate, and the result showed no observable TCA removal over 12 h, representing that direct reduction of ZVI was not sufficient for TCA degradation as the ZVI powder had been passivated under the experimental conditions (Fig. 1a). However, TCA removal did occur when persulfate at various concentrations was applied together with ZVI, indicating that the combination of ZVI with persulfate was efficient in promoting the degradation of TCA, which is also considered as a competitive advantage for this method applied in field as ZVI could be used without pretreatment. When persulfate concentration increased from 1.5 mM to

9.0 mM, the TCA degradation efficiency increased from 29% to 97%. Further increase of persulfate concentration to 12.0 mM almost did not increase TCA removal, indicating that there was an optimum persulfate concentration at fixed dosage of ZVI in the persulfate-ZVI system. The results are also consistent with the conclusions of some other researchers.[14, 26, 27] Therefore, persulfate concentration in subsequent experiments was set at 9.0 mM.

The effect of ZVI dosage on TCA removal in the persulfate-ZVI system was evaluated by changing ZVI loading while keeping persulfate concentration at 9.0 mM (Fig. 1b). The dosages of ZVI 0.05 g, 0.10 g, 0.15 g, and 0.20 g (corresponding to 2.08~8.33 g/L) were applied. It can be seen that the degradation efficiency of TCA decreased with the increase of ZVI dosage in the persulfate-ZVI system. When increasing ZVI amount from 0.05 g to 0.20 g, TCA removal declined from 97% to 70%. However, Li et al.[16] reported that the degradation efficiency of AO7 increased with higher ZVI dosage when mili-ZVI (1 mm) and micro-ZVI (150 μm) were used in the persulfate system, and similar results were found by some other researchers as well.[13, 28, 29] In addition, other studies demonstrated an optimum dosage of ZVI in the persulfate-ZVI systems, and contaminants removal decreased when ZVI loading was increased over the optimum dosage.[12, 15, 27, 30] It was assumed that different characteristics of the contaminants and mechanisms of degradation might be responsible for the various results of the effect of ZVI dosage, and interesting results of persulfate decomposition and mechanism of TCA degradation would be discussed in the following sections. It should be noted that ZVI dosage in the following experiments was set at 0.05 g.

3.2. Trends of dissolved iron species change and persulfate decomposition in the

persulfate-ZVI systems

To further confirm the roles of persulfate and ZVI in the combination system, the trends of total dissolved iron and ferrous iron in the solution and the consumption of persulfate during the reaction process were investigated. Two possibilities for the generation of Fe^{2+} in the persulfate-ZVI system were reported: one was due to the corrosion of ZVI under both aerobic and anaerobic conditions (eqs 3-4), and the other one was due to direct oxidation by persulfate (eq 5).[11, 29, 30] Furthermore, Fe^{3+} generated upon Fe^{2+} oxidation would initiate the release of Fe^{2+} at the ZVI surface as presented in eq 6. As shown in Fig. 2, the concentration of Fe^{2+} increased with the decomposition of persulfate and reached 502.5 mg/L at 2 h when persulfate was almost exhausted, and then remained approximately constant. The same trend of total dissolved iron was observed during the first 2 h. Therefore, the corrosion of persulfate was mainly responsible for the production of dissolved iron in this study. Li et al.[16] also reported that the increase of Fe^{2+} and the total dissolved iron release rate was accompanied by a gradual persulfate decomposition.

$$2Fe^{0} + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^{-} \quad (3)$$

$$Fe^{0} + 2H_2O \rightarrow 2Fe^{2+} + H_2 + 2OH^{-} \quad (4)$$

$$Fe^{0} + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (5)$$

$$2Fe^{3+} + Fe^{0} \rightarrow 3Fe^{2+} \quad (6)$$

Since Fe^{2+} released from ZVI was believed to play a critical role in the activation of persulfate by ZVI in most existing studies, a parallel test was conducted under the same conditions, except that ZVI was replaced with Fe^{2+}, to compare the degradation efficiency of

TCA by persulfate activated with ZVI and Fe^{2+} directly. The initial concentration of Fe^{2+} was set at 500 mg L^{-1} (8.9 mM) corresponding to the final released Fe^{2+} amount in the persulfate-ZVI system. The results were showed in Fig. S3. TCA removal was 7.4% when Fe^{2+} was applied for persulfate activation, and TCA degradation only occurred within the first 10 minute and then stalled. This limited removal for TCA can be explain by the following two reasons: (a) the destruction of $SO_4^{-\bullet}$ might occurred in the presence of excess Fe^{2+}. (b) the fast reaction between Fe^{2+} and persulfate [11, 31].

As illustrated in Fig. 2, persulfate decomposed gradually and almost completely exhausted during the first 2 h, which corresponded well with the trends of the total dissolved iron and Fe^{2+} in the solution. Li et al.[16] also found a gradual and nearly complete decomposition of persulfate in 3 h and the contaminant (AO7) was completely degraded after 2 h meanwhile when a micro-ZVI/persulfate system was applied. Moreover, some studies focused on persulfalte-ZVI systems demonstrated that a rapid and complete removal of contaminants was achieved within a few minutes when persulfate was exhausted as well.[11, 16, 32, 33] However, TCA removal was only 40% at 2 h and kept increasing when persulfate was depleted in this study. Therefore, the degradation performance of TCA after 2 h was supposed to be independent of persulfate chemistry. Thus, we hypothesized that a two-stage process involving persulfate oxidation and ZVI reduction was contributed to TCA degradation in this persulfate-ZVI system: (1) in the 1st-stage (0~2 h), TCA was removed by both persulfate oxidation and ZVI reduction processes. (2) in the 2nd-stage (2~12 h), an enhanced ZVI reduction was responsible for TCA degradation. To confirm the proposed stages during TCA degradation, the radical scavenger tests, the chemical probe method, and the formation of intermediates during TCA degradation were evaluated in the persulfate-ZVI systems.

3.3. Effect of solution pH on TCA degradation performance

Because the pH of groundwater is nearly neutral, TCA degradation performance under various initial pH values (from pH 6 to 8) was investigated. The solutions were unbuffered (adjusted with 0.1 M sulfuric acid and 0.1 M sodium hydroxide) and phosphate (0.1 M) buffered, respectively. In the pH-unadjusted tests, the initial pH value of the reaction solution was 3.0, which then dropped to 2.8 at 2 h (Fig. S4) and readily increased to 5.9 at 12 h. In this study, persulfate was the limiting reagent and hence ZVI remained after persulfate had been exhausted within 2 h. The solution pH firstly decreased due to the formation of bisulfate (HSO_4^-) byproduct of persulfate and the acid intermediate products of TCA,[34] and then readily increased after 2 h due to the hypothetical ZVI reduction process. The trend of solution pH value was consistent with the results of Hussain et al.[29] and Liang and Lai.[32]

As shown in Fig. 3, the influence of the initial solution pH in the unbuffered systems (pH 6~8) was found to be negligible at the tested pH values. Similar with the unadjusted test, the solution pH in the unbuffered systems dropped to 3.1~3.2 at 2 h, and then increased to around 6.0 after 2 h. Therefore, there was no significant difference in the degradation efficiency of TCA. In the buffered solutions, the pH variation was within 0.2 unit during the course of tests, and the TCA degradation efficiency decreased with increasing pH. The maximum removal of TCA (54.4% after 12 h) occurred at pH 6, whereas no obvious TCA removal was observed at pH 8. In the pH-unadjusted and -unbuffered tests, iron corrosion and

Fe^{2+} generation were promoted in acid condition and hence enhanced TCA removal, which would be further explained in Section 3.4. However, in the buffered solutions at neutral and alkaline pHs, iron corrosion was inhibited.[26] In addition, the precipitation of iron species occurred in the alkaline condition, and consequently inhibited TCA removal.[29] It should be noted that the reactive oxygen species (e.g., $SO_4^{-\bullet}$and $^{\bullet}OH$) reacted slower with phosphate anions than with TCA, and the impact of phosphate on the TCA degradation performance in this study is deduced to be minimal.[20]

3.4. Radical scavenger tests in the persulfate-ZVI systems

As mentioned in Introduction, the persulfate oxidation process involving $SO_4^{-\bullet}$ or $^{\bullet}OH$ is believed to play an important role for the destruction of organic pollutants in the persulfate-ZVI systems. Therefore, radical scavenger tests were conducted to identify the existence of $SO_4^{-\bullet}$ and $^{\bullet}OH$ during different stages in this study. Both $SO_4^{-\bullet}$ and $^{\bullet}OH$ were scavenged in the system using isopropanol (IPA, $k_{SO_4^{-\bullet}} = 6 \times 10^7$ $M^{-1}s^{-1}$ and $k_{^{\bullet}OH} = 2.8 \times 10^9$ $M^{-1}s^{-1}$), and $^{\bullet}OH$ was scavenged by *tert*-butyl alcohol (TBA, $k_{^{\bullet}OH} = (3.8\sim7.6) \times 10^8$ $M^{-1}s^{-1}$), which is unreactive with $SO_4^{-\bullet}$ ($k_{SO_4^{-\bullet}} = (4.0\sim9.1) \times 10^5$ $M^{-1}s^{-1}$).[35] Firstly, IPA and TBA (300 mM, 2000 times more than initial TCA concentration) was introduced before reaction initiation respectively. As shown in Fig. 4a, both IPA and TBA had scavenging effects for TCA degradation, and IPA had a higher inhibition effect compared to TBA. The results revealed that the oxidation action including both $SO_4^{-\bullet}$ and $^{\bullet}OH$ was partly responsible for TCA degradation. Zhao et al.[30] demonstrated that the reaction in persulfate-ZVI system was completely quenched by adding methanol as $SO_4^{-\bullet}$ and $^{\bullet}OH$ scavengers, and moderately inhibited by adding TBA as $^{\bullet}OH$ scavenger. They suggested that $SO_4^{-\bullet}$ was the predominant radical species responsible for 4-chlorophenol degradation, and similar results of scavenger tests were obtained by Hussain et al.[27] However, in this study, 83.0% of the TCA removal was still achieved after 2h with the addition of IPA, and 90.1% in the presence of TBA. It was speculated that other processes besides persulfate oxidation were important to induce TCA degradation.

In order to further investigated the role of $SO_4^{-\bullet}$ and $^{\bullet}OH$ in TCA degradation, the scavenger tests were carried out during the hypothetical 2nd-stage. A volume of 1 mL of supernatant was removed from each reaction vial and replaced with 1 mL of IPA or TBA after 2 h of TCA degradation in the persulfate-ZVI system (corresponding to 545 mM and 436 mM for IPA and TBA, respectively), and 1 mL of water was injected into the vial for the replacement of alcohols in the control test. As shown in Fig. 4b, the influences of IPA and TBA were found to be negligible for TCA degradation when the alcohols added after 2 h, implying that there was no $SO_4^{-\bullet}$ or $^{\bullet}OH$ existing in the 2nd-stage when persulfate was exhausted. The results further confirmed that TCA degradation during the 2nd-stage was independent of persulfate oxidation process.

3.5. Enhanced reduction performance in persulfate-ZVI systems

To confirm the occurrence of reduction process in the persulfate-ZVI system, the chemical probe method was introduced in the persulfate-ZVI system. Carbon tetrachloride (CT) was often used as a probe compound for the reduction action, because CT was reported to be highly resistant to both $^{\bullet}OH$ and $SO_4^{-\bullet}$ oxidation.[36, 37] Therefore, CT was chosen as a probe compound to identify the reduction process in this study. As shown in Fig. 5a, in the control test with ZVI alone, 13.4% CT was lost likely due to volatilization and/or ZVI reduction. However, CT was completely removed after 12 h in the persulfate-ZVI system, indicating the presence of reduction process in the system.

To distinguish the reduction actions between the 1st- and 2nd-stage, TCA and CT degradation was investigated in the 2nd-stage separately. Firstly, the experiment started with persulfate and ZVI but no TCA or CT, and then after 2 h when persulfate was nearly exhausted, a volume of 1 mL of supernatant was removed from each vial and replaced with 1 mL of TCA or CT stock solution to generate the desired initial concentration (0.15 mM). It can be seen from Fig. 5b that nearly complete CT and TCA removal was achieved after 14 h when the degradation was initiated from 2 h, further revealing the presence of reduction action in the 2nd-stage and the important role played by ZVI reduction in TCA degradation.

As discussed above, a two-stage process involving persulfate oxidation and ZVI reduction was hypothesized for TCA removal. In the 1st-stage, persulfate was responsible for the generation of both $SO_4^{-\bullet}$and $^{\bullet}OH$ for the degradation of TCA. On the other hand, Fe^{2+} formed by persulfate corrosion was speculated to enhance TCA reduction by ZVI. Therefore, parallel tests were conducted with the addition of Fe^{2+} but without persulfate in ZVI system to investigate the effect of Fe^{2+} on the reduction performance of TCA (Fig. S5). The initial concentration of Fe^{2+} was set at 500 mg L^{-1} (8.9 mM) corresponding to the final released Fe^{2+} amount in the persulfate-ZVI system. In pH-unadjusted test, the solution pH increased from 5.3 to 6.9 in the Fe^{2+}-ZVI system (data not shown), and 17% TCA was removed after 12 h.

Moreover, the initial solution pH was adjusted to 3.0 (with 0.1 M H_2SO_4) to simulate TCA degradation in the persulfate-ZVI system, and resulting 38% of the TCA removal after 12 h, confirming that the presence of Fe^{2+} in the solution could improve TCA removal.

The enhanced TCA degradation in Fe^{2+}-ZVI system indicated that some surface reactions proceeded by aqueous Fe^{2+}. Li et al.[17] classified the iron compounds in persulfate-ZVI system into three groups as Fe metal (Fe^0), Fe_3O_4/FeO (Fe^{2+}), and Fe_2O_3/FeOOH (Fe^{3+}), and a two-layer structure on ZVI surface in the persulfate-ZVI system was proposed, where the inner layer was goethite (α-FeOOH) and magnetite (Fe_3O_4), and the outer layer was mainly consisted by hematite (α-Fe_2O_3). With the adsorption and incorporation of aqueous Fe^{2+} into the hematite lattice, the hematite would convert to magnetite, enhancing the conductivity of surface layer and allowing electrons to be transferred from ZVI to TCA.[38] Therefore, the presence of Fe^{2+} in solution could enhance TCA reduction by ZVI. Similar enhancement of TCE degradation was observed when Fe^{2+} was simultaneous with un-pretreated ZVI in aqueous solution.[39]

In addition, the relationship between Fe^{2+} and ZVI could also explain the effect of ZVI amount on TCA removal in Section 3.1. Since persulfate was the limiting reagent in the system, the final concentration of Fe^{2+} produced from persulfate corrosion could be considered as constant. With the increase in ZVI dosage, the amount of Fe^{2+} converted precipitates to magnetite form was increased, and hence, the amount of Fe^{2+} adsorbed into the outer layer on ZVI surface was decreased, resulting in the decrease of surface conductivity and the efficiency of electron transformation. Therefore, the degradation performance of TCA decreased with the increase of ZVI dosage in the persulfate-ZVI system.

Hence, although the persulfate chemistry involving $SO_4^{-\bullet}$ and $^{\bullet}OH$ had no effect on TCA removal in the 2nd-stage, persulfate was considered to enhance TCA reduction by ZVI in playing roles in the solution acidification, the Fe^{2+} generation, and the formation of conductive iron oxides in the persulfate-ZVI system.

3.6. Mechanism of TCA degradation in the persulfate-ZVI systems

The formation of intermediates, including the volatile chlorinated hydrocarbons and the carboxylic acid, during TCA degradation was further investigated through GC/MS analysis (Fig. 6). Since the adsorption of TCA by iron precipitates under the experimental conditions was negligible (Fig. S2), a chloride mass balance in the persulfate-ZVI system was illustrated in Fig. 7 as well. The theoretical value of Cl in parent TCA was used as the total amount of Cl in the system (100%), which was divided into 4 parts: (1) and (2) Cl in TCA and DCA (1,1-dichloroethane), i.e. the calculated percentage of Cl in TCA and DCA at the given time. (3) Cl released in the solution, i.e. the percentage of Cl^- measured in the solution. (4) unknown Cl, i.e. the percentage of Cl in the undetectable chlorinated intermediates or loss by TCA volatilization. In our previous studies, various intermediates were confirmed from $SO_4^{-\bullet}$- and $^{\bullet}OH$-induced TCA degradation in the UV/persulfate and VUV/persulfate processes.[20, 40] However, as shown in Fig. 6, DCA, a confirmed byproduct of TCA by ZVI reduction,[41] was the only chlorinated compound identified by GC/MS in the persulfate-ZVI system. During the 1st-stage, none of volatile or carboxylic acid intermediates were detected when persulfate was simultaneous with ZVI. However, the unknown Cl was 9.7% at 2 h, indicating the generation of other undetectable chlorinated intermediates during the first 2 h. In the 2nd-stage, the occurrence and accumulation of DCA was observed during TCA degradation. At the end of the reaction, the concentration of DCA was 0.058 mM, and the percentages of Cl released into the solution and Cl in DCA gradually increased to 51.5% and 25.3%, respectively. The formation of DCA after 2 h proved the existence of ZVI reduction during the 2nd-stage, but TCA dechlorination was not complete as the percentage of Cl in the undetected intermediates was 21.2% in the end. It is supposed that the undetected products are nonvolatile chlorinated compounds other than carboxylic acid intermediates.

4. Conclusions

The results in this study showed that TCA could be effectively removed by means of the persulfate-ZVI system, and both persulfate oxidation and ZVI reduction were responsible for TCA degradation. Increasing persulfate concentration from 1.5 mM to 9.0 mM ensured a significant increase in the TCA removal, and lower ZVI dosage resulted in higher TCA degradation efficiency. A two-stage process splited at 2 h was proposed during TCA degradation. The oxidation process in the 1st-stage involving both $SO_4^{-\bullet}$ and $^{\bullet}OH$ was proved by the radical scavenger tests, and an enhanced ZVI reduction action was confirmed in both stages by the results of CT degradation performance. The presence of persulfate was contributed to the generation of $SO_4^{-\bullet}$ and $^{\bullet}OH$ and the enhancement of ZVI reduction. The only confirmed intermediate was 1,1-dichloroethane and the chloride mass balance results showed that TCA dechlorination was not complete.

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Supplementary material

Text S1and Figures S1~S5 were listed in the Supporting Information.

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Figure Captions

Fig. 1 Degradation performance of TCA under various (a) persulfate concentrations (Conditions: $[TCA]_0$ = 0.15 mM, $[ZVI]_0$ = 0.05 g, 20 ℃) and (b) ZVI dosages (Conditions: $[TCA]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, 20 ℃).

Fig. 2 Trends of Fe^{2+} and the total dissolved iron and persulfate decomposition during reaction time (Conditions: $[TCA]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, $[ZVI]_0$ = 0.05 g, 20 ℃).

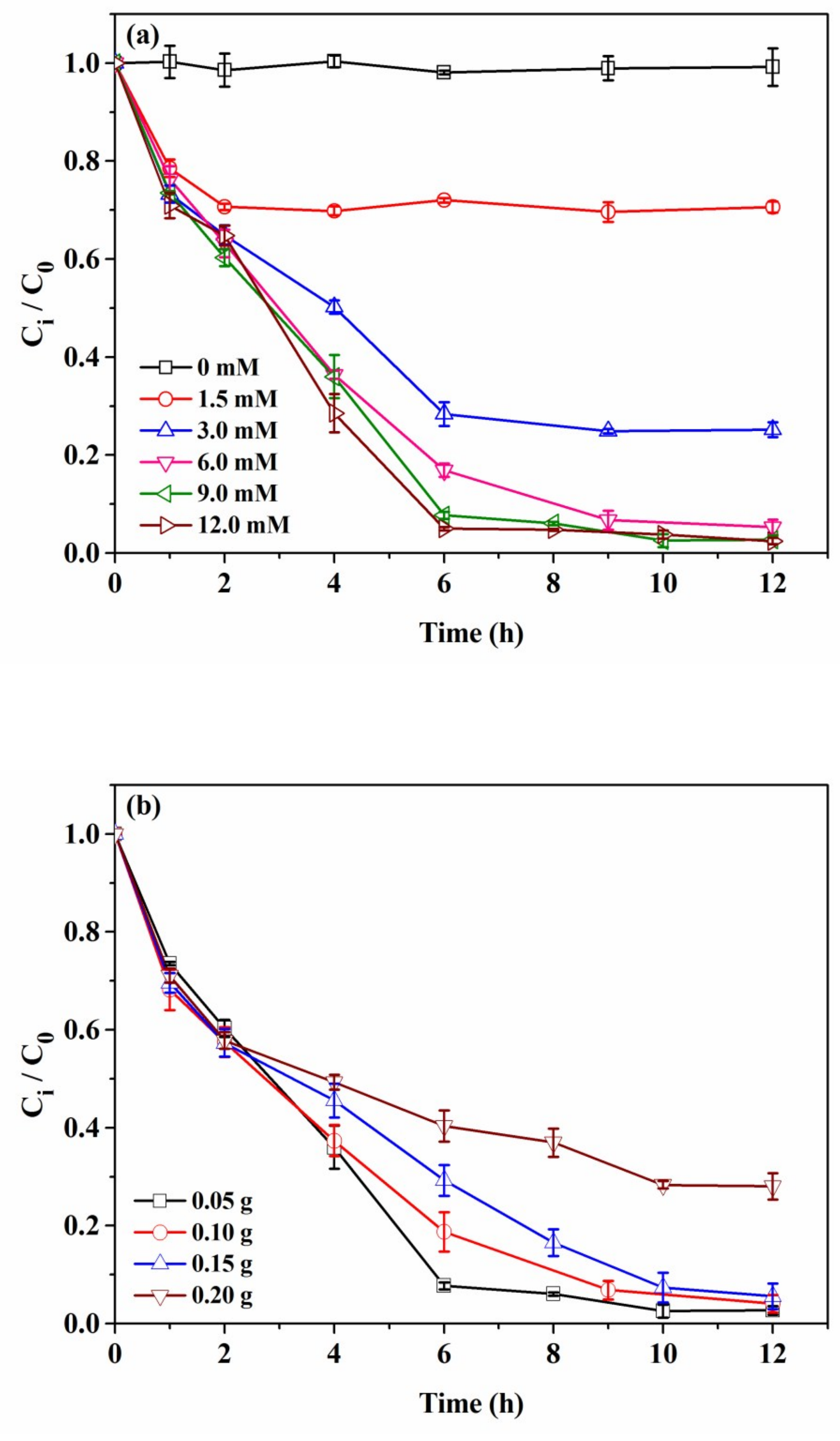
Fig. 3 Effect of initial pH on TCA removal performance (Conditions: $[TCA]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, $[ZVI]_0$ = 0.05 g, 20 ℃)

Fig. 4 Degradation performance of TCA with the addition of IPA and TBA. IPA and TBA was added (a) before reaction and (b) after 2 h of TCA degradation (Conditions: $[TCA]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, $[ZVI]_0$ = 0.05 g, $[IPA]_{a0}$ = $[TBA]_{a0}$ = 300 mM, $[IPA]_{b0}$ = 545 mM, $[TBA]_{b0}$ = 436 mM , 20 ℃).

Fig. 5 Degradation performance of TCA and CT in the persulfate-ZVI system. TCA and CT was added (a) before reaction and (b) after 2 h of the reaction between of persulfate and ZVI (Conditions: $[TCA]_0$ = $[CT]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, $[ZVI]_0$ = 0.05 g, 20 ℃).

Fig. 6 Evolution of volatile organic intermediates during TCA degradation (Conditions: $[TCA]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, $[ZVI]_0$ = 0.05 g, 20 ℃).

Fig. 7 Chloride mass balance during TCA degradation (Conditions: $[TCA]_0$ = 0.15 mM, $[persulfate]_0$ = 9.0 mM, $[ZVI]_0$ = 0.05 g, 20 ℃).



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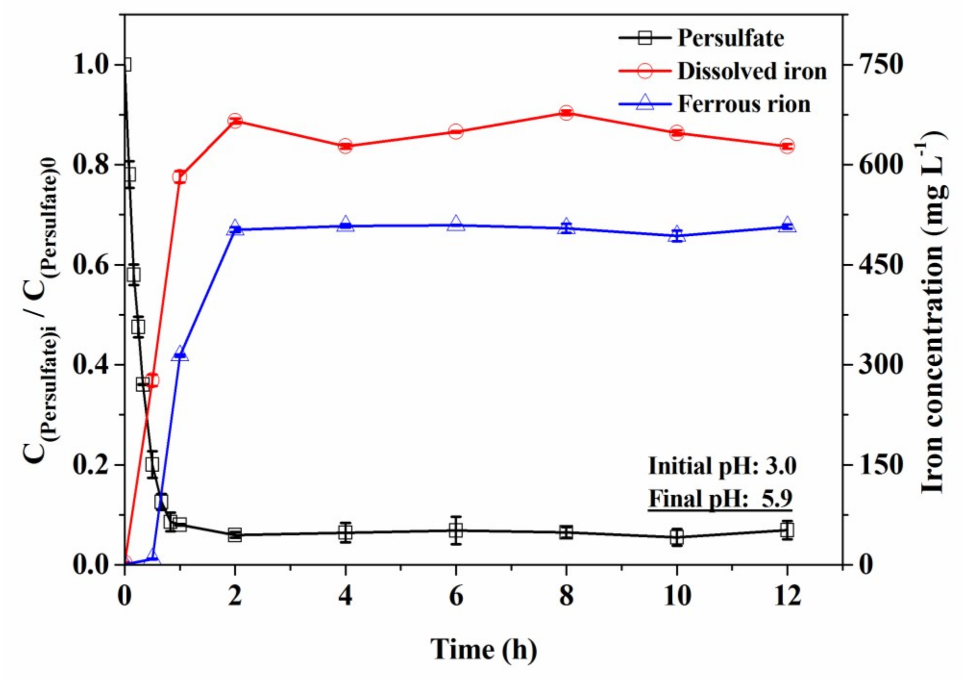

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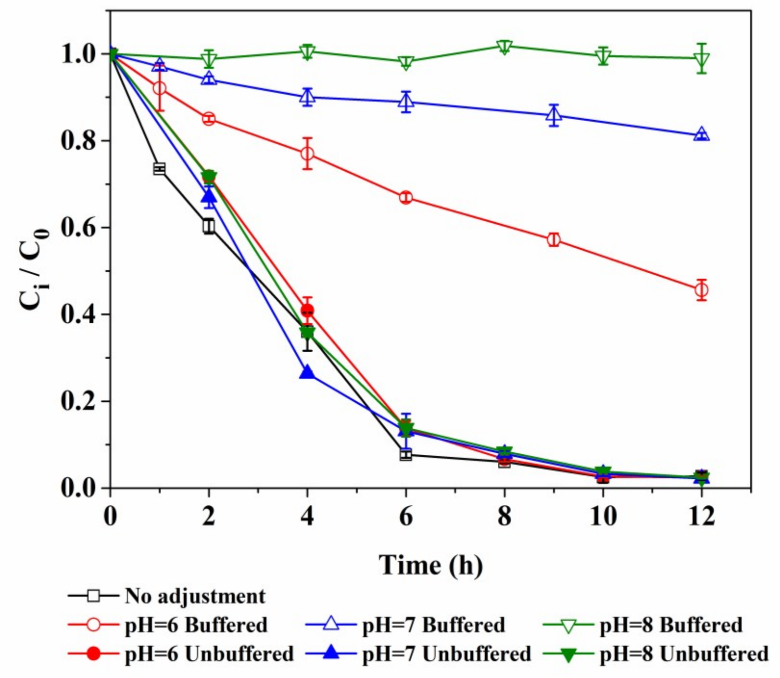

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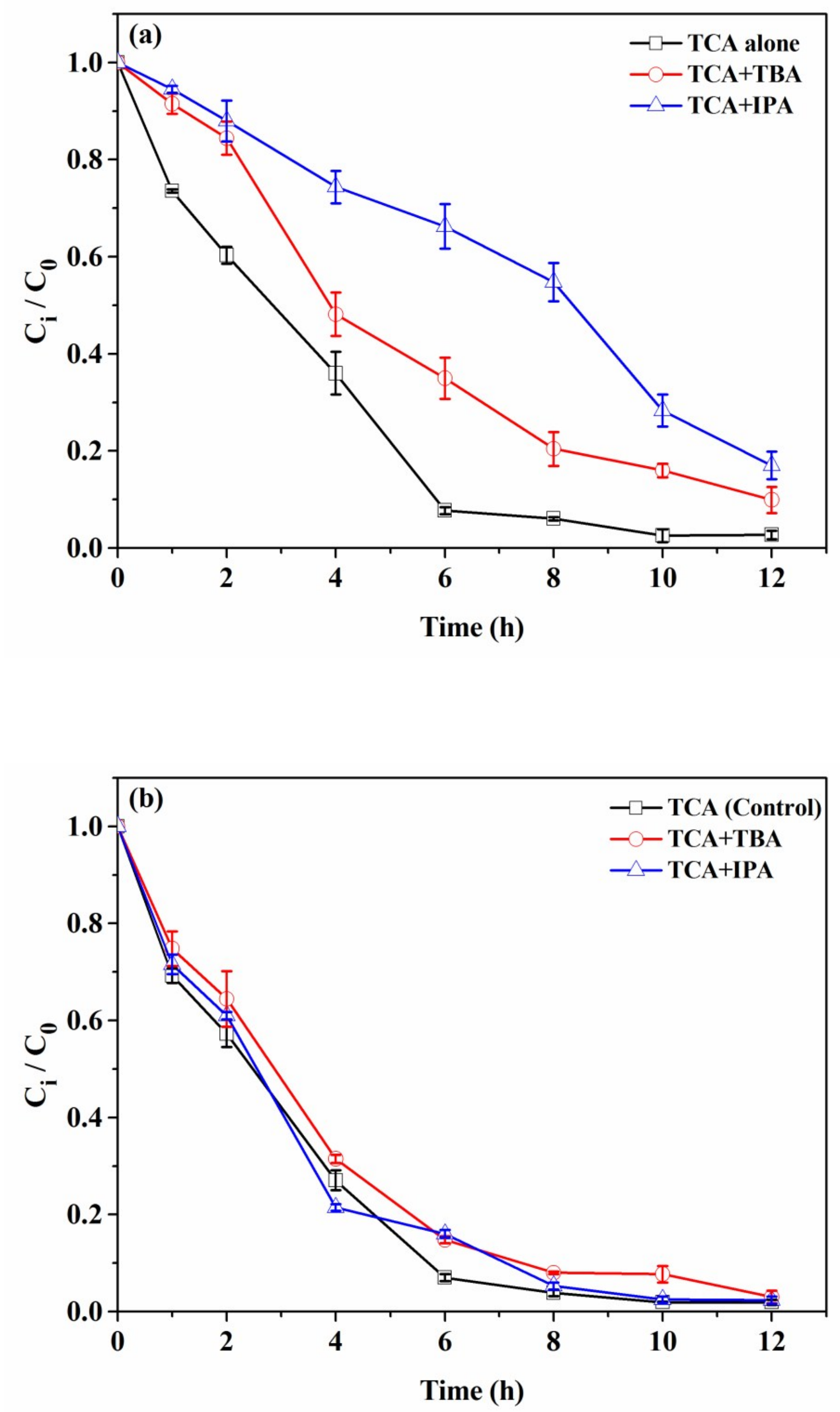

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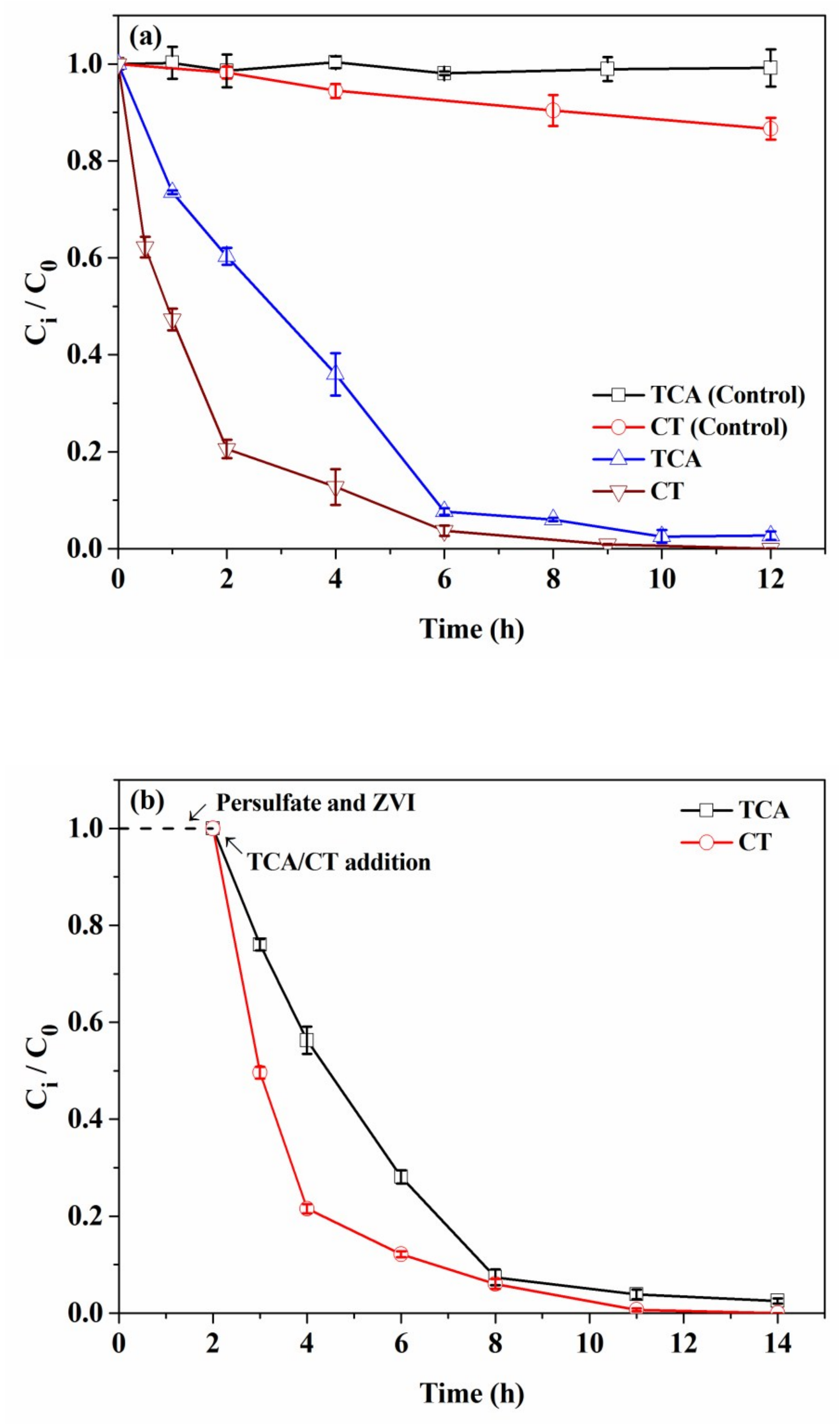

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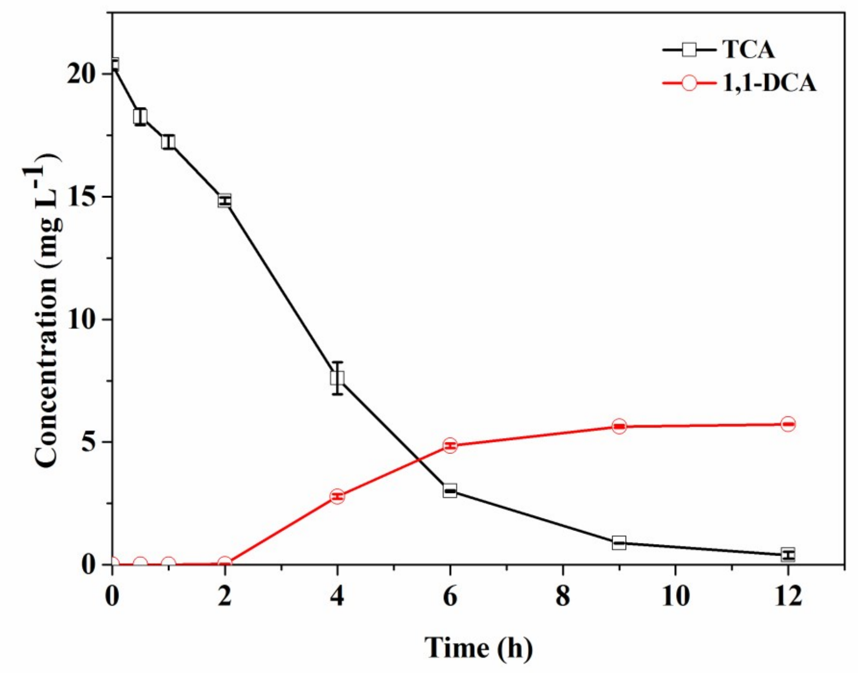

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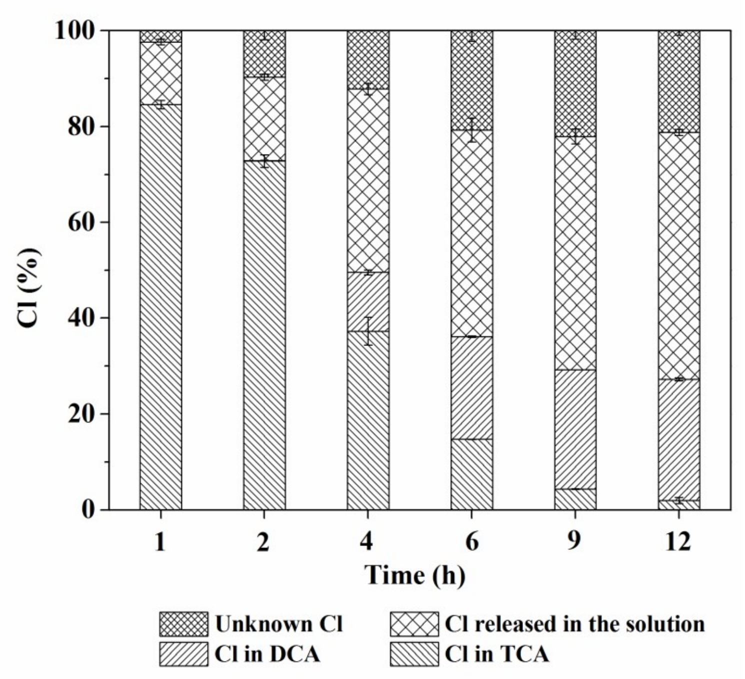

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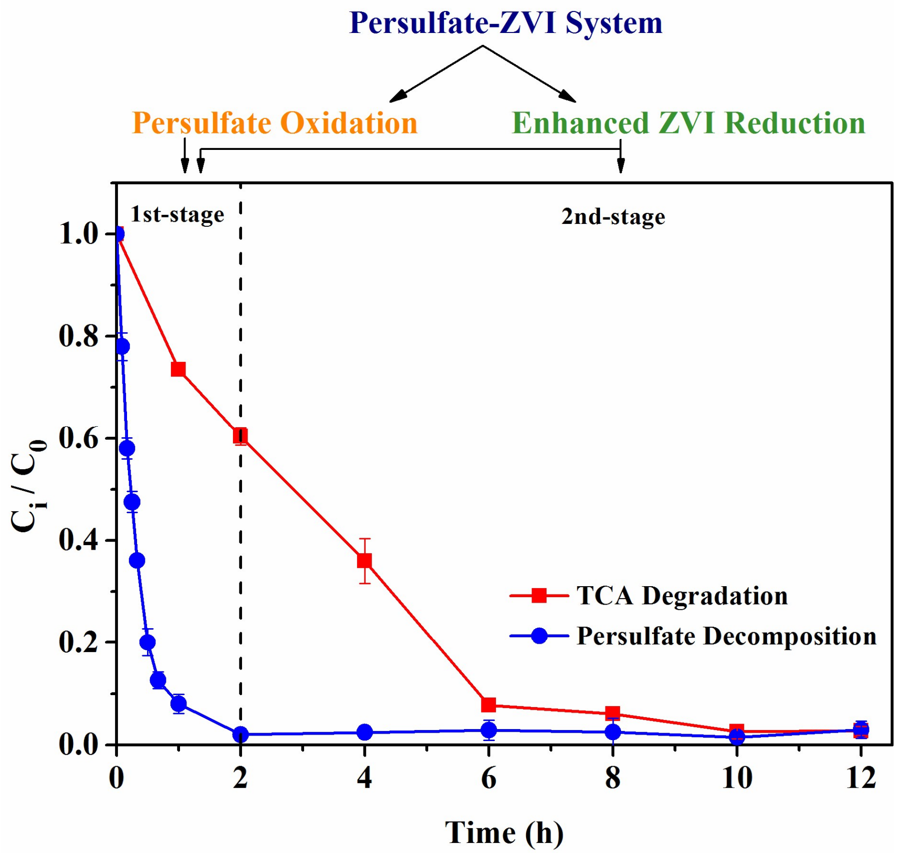
Graphical abstract



TCA degradation performance by both persulfate oxidation and enhanced ZVI reduction in the persulfate-ZVI system