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## Mechanism of carbon tetrachloride reduction in ferrous ion activated calcium peroxide system in the presence of methanol

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### Abstract

This study investigated the reductive initiation for the depletion of highly oxidized/perhalogenated pollutants, specifically the degradation of carbon tetrachloride (CT) was induced by adding methanol (MeOH) into a ferrous ion (Fe(II)) activated calcium peroxide (CaO<sub>2</sub>) system. The results indicated that CT could be completely degraded within 20 min at CaO<sub>2</sub>/Fe(II)/MeOH/CT molar ratio of 30/40/10/1 in this system. Scavenging tests suggested that both superoxide radical anion (O<sub>2</sub><sup>•-</sup>) and carbon dioxide radical anion (CO<sub>2</sub><sup>•-</sup>) were predominant reactive species responsible for CT destruction. Hydroxymethyl radicals (•CH<sub>2</sub>OH), an intermediate in the transformation of MeOH, could also initiate CT degradation by reducing C-Cl bond. GC/MS analysis identified CHCl<sub>3</sub>, C<sub>2</sub>Cl<sub>4</sub>, and C<sub>2</sub>Cl<sub>6</sub> as the intermediates accompanied by CT destruction, and a reduction mechanism for CT degradation was proposed accordingly. In addition, the impact of solution matrix and initial solution pH were evaluated, and the results showed that Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and HCO<sub>3</sub><sup>-</sup> had adverse effects on CT degradation. Moreover, the alkaline condition was unfavorable to CT depletion. In conclusion, the results obtained in the actual groundwater tests encouragingly demonstrated that the CaO<sub>2</sub>/Fe(II)/MeOH process is a highly promising technique for the remediation of CT-contaminated groundwater.

### Keywords

carbon tetrachloride; calcium peroxide; methanol; reductive radicals; groundwater remediation

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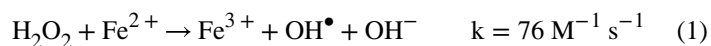
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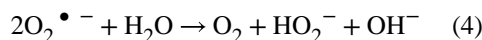
## 1. Introduction

Halogenated aliphatic hydrocarbon organic compounds, which are frequently detected in the environment, are toxic, mutagenic, and generally resistant to complete microbiological degradation, hence, possess long environmental impacts. Carbon tetrachloride (CT), a typical perchlorinated aliphatic hydrocarbon, was widely utilized in the past as a cleaning solvent, flame retardant, refrigerant, and intermediate for industrial products [1]. The occurrence of CT in groundwater has received much attention because of its high toxicity, environmental persistence, and relatively high solubility (800 mg L<sup>-1</sup> at 20°C). CT is highly harmful to liver, lungs and kidneys, and has been classified as a 2B carcinogenic compound by the International Agency for Research on Cancer (IARC) [2] and, hence, the maximum allowable concentration in groundwater is regulated at 0.005 mg L<sup>-1</sup> [3].

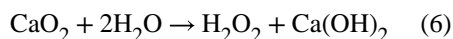
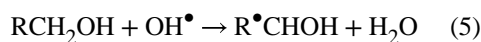
Advanced oxidation processes (AOPs) with persulfate, ozone, permanganate, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) have been widely applied to sites remediation contaminated by organic compounds. Reactive oxygen species (ROSs) generated in these AOPs, including S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (E<sub>0</sub> = 2.01 V), O<sub>3</sub> (E<sub>0</sub> = 2.1 V), MnO<sub>4</sub><sup>-</sup> (E<sub>0</sub> = 1.7 V), OH (E<sub>0</sub> = 2.7 V), are strong oxidants and can degrade multiple unsaturated organics including halogenated aliphatic compounds, halogenated aromatic compounds, and benzene, toluene, ethylbenzene and xylene (BTEX) [3]. However, highly oxidized/perhalogenated organic pollutants, such as hexachlorobenzene, bromotrifluoromethane, and CT, are hardly degraded by these oxidants due to the inefficient reaction between oxidants and C-Cl bonds. Therefore, the use of reduction-based technique will be an alternative approach that is more effective for the degradation of these contaminants.

It is well documented that superoxide radical anion (O<sub>2</sub><sup>•-</sup>, E<sub>0</sub> = -2.4 V) [4], carbon dioxide radical anion (CO<sub>2</sub><sup>•-</sup>, E<sub>0</sub> = -2.0 V) [5], and excited electron [6] have the potential to transfer an electron to C-Cl bonds, therefore contributing to effective CT destruction. Thus, it is essential to generate these reductants and keep them full activity in the system aiming to destruct these oxidized/perhalogenated organic pollutants. O<sub>2</sub><sup>•-</sup>, as a reductive species, can be easily generated in catalytic hydrogen peroxide (CHP) process (reactions 1–3) [4]. Unfortunately, it is found that O<sub>2</sub><sup>•-</sup> is unstable and has very short life-time because of rapid disproportionation through reaction 4 [7], and hence it is considered incapable of reducing CT in solution at low concentration. In contrast, Smith et al found that increasing H<sub>2</sub>O<sub>2</sub> concentration (>0.1 mol L<sup>-1</sup>) or adding organic solvents like ethanol, acetone or other aprotic solvents could significantly strengthen the reactivity of O<sub>2</sub><sup>•-</sup> due to solvent effects [4, 8]. However, high H<sub>2</sub>O<sub>2</sub> concentrations are typically difficult to maintain for subsurface environments, and it also poses issues for handling and implementation. Conversely, the use of small quantities of biodegradable solvents is an effective and practical option for promotion of reductive treatment of recalcitrant pollutants. In addition, adding solvents to the CHP process may also produce other reductants that are favorable for reduction of oxidized/perhalogenated organics.





$\alpha$ -hydroxyalkyl radical ( $\text{R}^\bullet\text{CHOH}$ ), generated from the reaction of aliphatic alcohols with  $\text{OH}^\bullet$  (reaction 5), is an organic reducing radical that can also transfer an electron to C-Cl bonds [9, 10]. Our previous work has confirmed that hydroxyethyl radical ( $^\bullet\text{CHCH}_3\text{OH}$ ) could be generated in the Fe(II)-activated calcium peroxide ( $\text{CaO}_2$ ) system in the presence of ethanol, and concomitantly CT was observed to be completely degraded [11]. According to the chain reactions 1–5, though they cannot directly reflect action with CT, massive  $\text{H}_2\text{O}_2$  and  $\text{OH}^\bullet$  are important factors for CT reduction because  $\text{H}_2\text{O}_2$  and  $\text{OH}^\bullet$  was produced initially and acted as precursor to generate the reducing species,  $\text{O}_2^{\bullet -}$  and  $\text{R}^\bullet\text{UHOH}$ .  $\text{CaO}_2$  as a green chemical agent is generally recognized as an effective solid  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  release resource and, hence widely used in in-site chemical oxidation remediation and biological wastewater treatment practices [12]. Compared with liquid  $\text{H}_2\text{O}_2$ ,  $\text{CaO}_2$  is demonstrated more effective because of regular  $\text{H}_2\text{O}_2$  release (reaction 6) [13]. Therefore, in this work,  $\text{CaO}_2$  was adopted to release  $\text{H}_2\text{O}_2$  and later initiated to generate  $\text{OH}^\bullet$  under the aid of Fe(II) activation, and meanwhile, the selected aliphatic alcohol methanol ( $\text{MeOH}$ ) was used for the enhancement of reducing radical's generation.



Though the use of alcohol amendment for promoting reduction of chlorinated aliphatic compounds has been confirmed, the reaction mechanism of CT degradation under Fe(II)-activated  $\text{CaO}_2$  with  $\text{MeOH}$  remains unclear. Hence, the purposes of this work are (1) to compare the CT degradation in the  $\text{CaO}_2/\text{Fe(II)}$  system without or with the presence of  $\text{MeOH}$ , (2) to explore the main radicals responsible for CT destruction, (3) to propose possible CT degradation pathway, and (4) to evaluate the application of the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process for CT degradation in an actual groundwater remediation.

## 2. Materials and methods

### 2.1. Materials and analytical methods

All the materials and analytical methods adopted were provided in Supplementary Material (Text S1 and S2).

### 2.2. Experimental procedures

The CT stock solutions ( $1.3 \text{ mmol L}^{-1}$ ) were prepared by equilibrating the pure non-aqueous phase liquid CT with Milli-Q water or actual groundwater under gentle stirring for 2 h. Then the CT Stock solution was added into a 250 mL cylindrical glass reactor (an inner diameter of 6.0 cm and a height of 9 cm) with two openings at the top: one for dosing and the other for sampling. Subsequently, the predetermined amounts of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and MeOH were added into the reactor. The initial solution pH was unadjusted with the exception of experiments for assessing the pH influence, in which the initial solution pH was adjusted with NaOH ( $0.1 \text{ mol L}^{-1}$ ) or  $\text{H}_2\text{SO}_4$  ( $0.1 \text{ mol L}^{-1}$ ). The addition of anions and other reagents were then fulfilled. A thermostat circulating water bath (DC, Ningbo, China) was utilized to control the temperature at  $20 \pm 0.5^\circ\text{C}$ , and a magnetic stirrer was used to keep the uniformity of mixtures in the aqueous solution. The reaction was then initiated by adding the desired  $\text{CaO}_2$  dosage. Control tests were conducted in the absence of  $\text{CaO}_2$  condition. At the determined time, 1 mL solution was transferred to a brown bottle containing 1 mL *n*-hexane to stop the reaction before analysis. In order to identify the reactive species for CT degradation, isopropanol (IPA), 1,4-benzoquinone (BQ), and methyl viologen dichloride ( $\text{MV}^{2+}$ ) as radical scavengers were applied in the scavenging tests to observe CT degradation changes. Each test was conducted at least in triplicate with the standard deviations below 5%. The average values were used for all presentation and discussion.

## 3. Results and discussion

### 3.1. Enhancement of CT degradation in the Fe(II)-activated $\text{CaO}_2$ system by MeOH

The comparison of CT degradation in the Fe(II)-activated  $\text{CaO}_2$  system without and with the presence of MeOH were performed, and the results were presented in Fig. 1. Control tests without  $\text{CaO}_2$  showed less than 6.5% CT loss due to volatilization and other mass loss reason during the test period. As shown in Fig. 1a, CT degradation was minimal under low chemical dosages when the amounts of  $\text{CaO}_2$  and Fe(II) were set equal. However, when the oxidants was increased to much higher than the Fe(II) dosage, greater removal of CT was observed with 25% of CT reduction at the  $\text{CaO}_2/\text{Fe(II)}/\text{CT}$  molar ratio of 300/30/1. It was noted that CT removal efficiencies were continuously increased to 31% and 59% when the dosages were further raised to 600/60/1 and 900/90/1, respectively.

In general, the  $\text{CaO}_2/\text{Fe(II)}$  system favored unsaturated organic pollutant degradation owing to its high oxidation of  $\text{OH}^\bullet$  [3, 14, 15]. But in this work, the reason for CT degradation should differ from those because CT depletion was only reached at remarkably higher  $\text{CaO}_2$  dosage condition. Theoretically, when the amount of  $\text{CaO}_2$  equals to Fe(II), ROS production, mainly  $\text{OH}^\bullet$  and minor  $\text{O}_2^{\bullet-}$ , would be maximized based on the stoichiometric quantities of reactions 1–3. To the best of our knowledge, the reactions of  $\text{OH}^\bullet$  with C-Cl bonds are

recognized as relatively inefficient, in contrast, the reactions of  $O_2^{\bullet-}$  with C-Cl bonds are more feasible through electron transfer. However,  $O_2^{\bullet-}$  is characterized as minimal reactivity in aqueous solution due to its high solvation by water molecules, which accelerates its rapid disproportionation forming  $O_2$  and  $HO_2^{\bullet-}$ . Teel and Watts [8] reported that high concentrations of  $H_2O_2$  can improve the solvation sphere surrounding  $O_2^{\bullet-}$  and thus reduce its disproportionation. In the experiments where the addition of  $CaO_2$  was much higher than  $Fe(II)$ ,  $H_2O_2$  released from  $CaO_2$  gradually accumulated to a high concentration over the test period. Therefore the effect of high  $H_2O_2$  on  $O_2^{\bullet-}$  caused hyperactive  $O_2^{\bullet-}$  and thus favored CT degradation. However, the drawbacks with such high  $CaO_2$  caused elevation of solution pH, in turn, hampered more  $H_2O_2$  release from  $CaO_2$ , and at the same time produced a large amount of  $O_2$  [16] which was uncondusive to CT degradation. In addition, the operation costs of the use of high  $CaO_2$  concentration would be costly and impractical for field-scale CT remediation.

Compared with the  $CaO_2/Fe(II)$  system, the  $CaO_2/Fe(II)/MeOH$  process presented significant enhancement in CT depletion (Fig. 1b). CT removal efficiencies of 18%, 35% and 83% were obtained at the  $CaO_2/Fe(II)/MeOH/CT$  molar ratios of 10/10/2/1, 20/20/4/1, and 30/30/6/1 within 20 min, respectively, while no CT degradation occurred at the same  $CaO_2$  and  $Fe(II)$  dosages without MeOH addition. Based on the literatures [8, 17], the addition of MeOH promoted CT removal in two ways. On one hand, MeOH addition improved the circumstance surrounding  $O_2^{\bullet-}$  through a mixture of MeOH and water molecules, which reduced  $O_2^{\bullet-}$  disproportionation and improved its reactivity in aqueous solution. On the other hand, MeOH generated other reducing species responsible for CT degradation through the reaction between  $OH^{\bullet}$  and MeOH. As aforementioned, a large amount of  $H_2O_2$  released by  $CaO_2$  may play a similar action in increasing  $O_2^{\bullet-}$  reactivity through the solvent effect, but the strength was weaker than MeOH. Overall, the greater  $O_2^{\bullet-}$  reactivity and other generated reactive reducing species were the reasons for remarkable CT degradation in the  $CaO_2/Fe(II)/MeOH$  process. Similar tests were repeated by adding equimolar concentration of acetone (CP) and dimethyl sulfoxide (DMSO) separately. The results showed that CT degradation was also increased to 25% and 36% by CP and DMSO, respectively (Fig. S1). In a word, these results strongly indicated the positive contribution and potential of small- molecule organic compounds in enhancement of CT degradation.

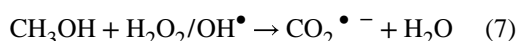
Additional experiments were further conducted to explore the effect of various  $CaO_2$ ,  $Fe(II)$  or MeOH dosages on CT degradation, and the results described briefly in Text S3 and Fig. S2 showed that the  $CaO_2/Fe(II)/MeOH/CT$  molar ratio of 30/40/10/1 was most suitable for CT removal with over 99% CT depletion. Overall, these significantly encouraging results were obtained by the  $CaO_2/Fe(II)/MeOH$  process in this study, which is of great interest to researchers for further indentifying MeOH function in CT degradation mechanism.

### 3.2. Identification of main reactive species for CT degradation in the $CaO_2/Fe(II)/MeOH$ system

$OH^{\bullet}$  and  $O_2^{\bullet-}$  are easily generated in the  $Fe(II)$ -activated  $CaO_2$  process [14], and their roles in CT degradation need to be confirmed. Taking into account that  $CO_2^{\bullet-}$ , an intermediate during the mineralization of MeOH, can also reduce C-Cl bonds readily [17], the function of

$\text{CO}_2^{\bullet-}$  also requires clarification of its contribution to CT removal. Therefore, CT degradation performance was tested both in the absence and presence of appropriate quenchers of these species, individually. The scavengers applied were as below: IPA for  $\text{OH}^{\bullet}$  ( $k_{\text{OH}^{\bullet}} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [4, 18], BQ for  $\text{O}_2^{\bullet-}$  ( $k_{\text{O}_2^{\bullet-}} = 9.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) [19] and  $\text{MV}^{2+}$  for  $\text{CO}_2^{\bullet-}$  ( $k_{\text{CO}_2^{\bullet-}} = (6.3 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [20], and the results of scavenging tests were shown in Fig. 2.

Over 99% of CT was degraded with the addition of excess IPA in the initial 3 min, while 84% of CT was removed in the absence of the scavenger (Fig. 2a). A small enhancement caused by IPA not only confirmed that  $\text{OH}^{\bullet}$  was not the reactant contributing to direct destruction of CT, but also figured out that IPA played a similar role as MeOH in CT degradation, which consisted with reports in other literatures [8, 19, 21]. Since the concentration of IPA was more than 10 fold higher than that of MeOH, IPA might play a major part in reductants formation and reactivity, thereby causing faster CT removal. The results of  $\text{O}_2^{\bullet-}$  scavenging tests with BQ were presented in Fig. 2b. The removal of CT decreased from 93% to 37% and 29%, respectively, in the presence of 15 and 30 mmol  $\text{L}^{-1}$  of BQ. Teel and Watts adapted excess chloroform (CF) as  $\text{O}_2^{\bullet-}$  scavenger in a modified Fenton's reaction and observed that CT degradation was decreased to a minimum level, thus indicating that  $\text{O}_2^{\bullet-}$  was a main reactive species for CT destruction [4]. Similarly, Xu et al also identified that  $\text{O}_2^{\bullet-}$  contributed to CT degradation in the thermally activated persulfate system through a BQ scavenging test [19]. The inhibition by  $\text{O}_2^{\bullet-}$  scavenger in this work strongly suggested that  $\text{O}_2^{\bullet-}$  played a significant role in CT destruction in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  system. Since  $\text{CO}_2^{\bullet-}$  was probably involved in the oxidation of MeOH by  $\text{OH}^{\bullet}$  in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  system according to the literatures [17, 22],  $\text{CO}_2^{\bullet-}$  scavenging test was also carried out to confirm its function. As presented in Fig. 2c, an obvious inhibition on CT removal appeared in the scavenging tests with  $\text{MV}^{2+}$ . 62% and 75% drop in CT removal were observed in the tests with 0.15 and 1.5 mmol  $\text{L}^{-1}$   $\text{MV}^{2+}$ , respectively. The performance that the removal of CT was quenched along with the addition of  $\text{CO}_2^{\bullet-}$  scavenger further indirectly demonstrated that  $\text{CO}_2^{\bullet-}$ , possibly generated through reaction 7, was one of the active species for the degradation of CT in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process.



Besides  $\text{O}_2^{\bullet-}$  and  $\text{CO}_2^{\bullet-}$ , hydroxymethyl radical ( $^{\bullet}\text{CH}_2\text{OH}$ ) generated between the reaction of MeOH and  $\text{OH}^{\bullet}$  (reaction 8) can also transfer an electron to C-Cl bonds, which was the intrinsic cause for CT destruction [23]. We have observed hydroxyethyl radical by electron paramagnetic resonance (EPR) technique in the  $\text{Fe(II)}$ -activated  $\text{CaO}_2$  system in the presence of ethanol [11]. Therefore, the EPR technique was similarly applied in this work. However, the signal of  $^{\bullet}\text{CH}_2\text{OH}$  was not detected due to the difficulty in distinguishing its weak response values in this work. Nevertheless,  $^{\bullet}\text{CH}_2\text{OH}$  should still be deduced as a reactive species for CT degradation in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  system. Overall, the reactive reducing radicals including  $\text{O}_2^{\bullet-}$ ,  $\text{CO}_2^{\bullet-}$ , and  $^{\bullet}\text{CH}_2\text{OH}$  were directly involved in the reductive destruction of CT, while  $\text{OH}^{\bullet}$  might played an indirect role by controlling the yield of these reductants.





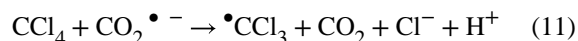
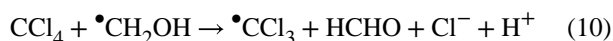
### 3.3. Mechanism of CT reduction in the $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$ system

Based on the outstanding CT depletion performance, the intermediates, including the volatile chlorinated organics and chloride ions in solution were further investigated to reveal the pathway of CT destruction through GC/MS and ion chromatography analyses. Chloroform (CF), hexachloroethane (HCA), and tetrachloroethene (PCE) were identified by GC/MS analyses and regarded as the chlorinated organic intermediates as presented in Fig. S3. Further experiments showed that all three of the chlorinated intermediates were produced within the initial 5 min reaction and subsequently degraded within later 15 min (Fig. 3). The generation and later elimination of CF, HCA, and PCE demonstrated that CT destruction might follow a multi-step process in system. Since CF, HCA and PCE were the main intermediates of CT, it was worthy to confirm the role of MeOH in the removal of these chlorinated products, individually. The results of CF, HCA, and PCE depletion in the Fe(II)- activated  $\text{CaO}_2$  system without or with the presence of MeOH were compared in Fig. S4. It suggested that the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process is also suitable for HCA degradation, but not favorable for PCE which should be more amenable to an oxidation process instead of a reductive one [24, 25]. Meanwhile, CF is minimally degraded by the two systems.

The amounts of the chlorinated organic intermediates produced along with CT degradation were detected by GC/MS, and it was found that their contents were far less than the amount of CT depleted. Besides chlorinated organics, the  $\text{Cl}^-$  concentration in solution was also monitored in the experiment along with the CT depletion by ion chromatography in order to check the extent of CT mineralization.  $\text{Cl}^-$  released in solution at maximum represented 85% of total theoretical  $\text{Cl}^-$  formation, suggesting that CT dechlorination performed well in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process. The Cl balance was quantified by combining the amount of the chlorinated organic intermediates produced and the  $\text{Cl}^-$  released from CT compound (Fig. 4). The theoretical quantity of Cl in parent CT was regarded as the total amount of Cl in system (100%), which was shared by four parts: (1) Cl in CT compound, (2) Cl in chlorinated organic intermediates, (3) Cl released in solution and, (4) unknown Cl. As it can be seen, Cl content in chlorinated organic intermediates was much less, while Cl released in solution appeared larger and increased gradually versus CT degradation. The unknown Cl was caused by CT volatilization and other possible chlorinated-acid formation [17]. Since the addition of MeOH would increase the TOC level, which is a discouraging point in practical treatment, TOC analysis was conducted to evaluate the mineralization of MeOH. The final TOC was below  $7.2 \text{ mg L}^{-1}$  while the initial TOC value was  $17.2 \text{ mg L}^{-1}$ . HCHO, identified by GC/MS (showed in Fig. S3), was regarded as an oxidation product of MeOH, and it could be continually mineralized when considering that the theoretical organic carbon of CT only contributed to  $1.6 \text{ mg L}^{-1}$  of TOC in this process. Based on the literature [26], after a series of complex reactions with  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{OH}^\bullet$ , HCHO would be transformed into HCOOH, which has been confirmed to produce  $\text{CO}_2^{\bullet-}$  under the aid of  $\text{OH}^\bullet$  [23, 27]. Unfortunately, the presence of HCOOH was not detected in the experiment, probably due to its low concentration and short life-time. Although adding MeOH is indeed a risk for actual

groundwater, the fact that MeOH and its by-products showed less toxicity and favorable biodegradability compared with CT make it reasonable and acceptable. Nevertheless, more efforts are needed to improve the process and investigate the risk in actual remediation, and more environmentally friendly chemicals instead of MeOH will be focused on in our future work.

According to the above discussion, a CT degradation pathway was proposed for understanding the mechanisms involved (Fig. 5). In the first step, a series of OH<sup>•</sup>-based chain reactions generated the reductants including O<sub>2</sub><sup>•-</sup>, CO<sub>2</sub><sup>•-</sup>, and <sup>•</sup>CH<sub>2</sub>OH. Once the reductants were produced and the associated reactivity was maximized, all of the reductants attacked CT by transferring electron to C-Cl bonds yield <sup>•</sup>CCl<sub>3</sub> (reactions 9–11), after that <sup>•</sup>CCl<sub>3</sub> was continually dechlorinated to :CCl<sub>2</sub> by these reductants. Finally, :CCl<sub>2</sub> rapidly hydrolyzed to generate chlorinated-acid, Cl<sup>-</sup>, and CO<sub>2</sub> under the influence of water molecule. It has to be mentioned that, accompanied with the formation of <sup>•</sup>CCl<sub>3</sub> and :CCl<sub>2</sub>, recombination between them would yield HCA and PCE, and H-abstraction from MeOH by <sup>•</sup>CCl<sub>3</sub> would form CF. But once the chlorinated organic intermediates yielded, all of them would be degraded subsequently to completion. The CT dechlorination pathway in this system was similar to that in other system [28–33] where Fe<sup>0</sup>, ascorbic acid, CO<sub>2</sub><sup>•-</sup>, Zn<sup>0</sup> and other reactive species acted as the electron donor transferring an electron to C-Cl bonds, but the quantity and evolution of the intermediates were different.



As aforementioned, CT could be destructed by high CaO<sub>2</sub> concentration, and therefore we also carried out the experiments to evaluate the intermediate of CT in Fe(II)-activated CaO<sub>2</sub> system in the absence of MeOH. The results presented in Fig. 6 showed that CT depletion was accompanied with significant CF formation even at complete CT destruction in 260 mmol L<sup>-1</sup> CaO<sub>2</sub> dosage. Since CF appears more persistent and toxic than CT in the environment [34], and considering the difference of CT degradation effectiveness as well as the intermediates evolution in the CaO<sub>2</sub>/Fe(II) and CaO<sub>2</sub>/Fe(II)/MeOH processes, our study strongly suggested that the CaO<sub>2</sub>/Fe(II)/MeOH process possesses much more advantageous than the CaO<sub>2</sub>/Fe(II) process. In addition, MeOH addition would also increase the CT solubility at actual CT DNAPLs contaminated sites, which will be benefit for CT reaction. Since ethanol has the similar ability to enhance CT destruction [11], the comparison of CT degradation in the CaO<sub>2</sub>/Fe(II) system with the presence ethanol and MeOH were performed and the results were presented in Fig. S5. Although the enhancement of ethanol on CT

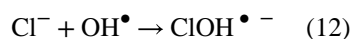


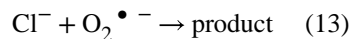
degradation seemed to be better than MeOH, ethanol used in the  $\text{CaO}_2/\text{Fe(II)}/\text{CT}$  process would cause more complex intermediates like 1,1,1-trichloroethane and 1,1-dichloroethylene. In addition, TOC caused by ethanol would be double when compared to MeOH. Based upon the above two aspects, MeOH has obviously comparative advantage compared to ethanol in practical remediation.

### 3.4. CT degradation performance in actual groundwater application

Although CT degradation was effective in ultrapure water condition, it was critical to carry out further test to assess CT degradation in actual groundwater because the solution matrix including inorganic anions (such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ ), solution pH, and natural organic matter (NOM) can affect the category and intensity of reactive species, and ultimately influence overall remediation effectiveness [35, 36]. Hence, the experiments were further conducted to evaluate the effect of solution matrix individually, and finally using the actual groundwater (Table S1) to assess the applicability of the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process for actual CT contaminated groundwater remediation.

**3.4.1 Effect of inorganic anions, initial solution pH and NOM**—As shown in Fig. 7a and b,  $\text{NO}_3^-$  and  $\text{Cl}^-$  had a slight suppression on CT removal, whereas the effect of  $\text{SO}_4^{2-}$  was found to be negligible (Fig. 7c), meanwhile  $\text{HCO}_3^-$  had an obvious inhibitive effect (Fig. 7d). Hasan et al. confirmed that solvated electrons could be produced by decomposition of  $\text{H}_2\text{O}_2$  [37], and similarly here, it was speculated that solvated electrons were also generated and were responsible for CT destruction. Since high concentration of  $\text{NO}_3^-$  was a stronger scavenger of solvated electrons [18], the presence of  $\text{NO}_3^-$  would reduce CT depletion in terms of hampering solvated electrons-based reduction. Moreover,  $\text{NO}_3^-$  might also compete with CT for other reductants. The presence of  $\text{Cl}^-$  also suppressed CT degradation, and the inhibitory effect was slightly higher than  $\text{NO}_3^-$ . An approximate 7% drop in CT removal was observed when  $\text{Cl}^-$  concentration was  $100 \text{ mmol L}^{-1}$ . The reasons for this inhibitive effect were that  $\text{Cl}^-$  could scavenge the precursor  $\text{OH}^\bullet$  for the reductants through reaction 12 [38], and consume  $\text{O}_2^{\bullet-}$  through competing reaction (reaction 13) [39]. Although  $\text{NO}_3^-$  and  $\text{Cl}^-$  only appeared slight inhibition in this work, a higher concentration of their presence would obviously suppress CT degradation. Compared with  $\text{NO}_3^-$  and  $\text{Cl}^-$ , a much more significantly inhibitive influence occurred in the presence of  $\text{HCO}_3^-$ . CT degradation efficiency was reduced to 20% and 15% with the addition of 10 and  $100 \text{ mmol L}^{-1}$   $\text{HCO}_3^-$ , respectively. The main reasons were as follow: (1) the presence of  $\text{HCO}_3^-$  would increase the solution pH and buffering capacity which were unfavorable to CT destruction (discussion in later section). (2)  $\text{HCO}_3^-$  could sweep  $\text{OH}^\bullet$  through reactions 14 and 15 [40], which was emphasized to be vital for reductants formation in the system. (3)  $\text{HCO}_3^-$  could directly consume  $\text{O}_2^{\bullet-}$  and  $\text{CO}_2^{\bullet-}$  via reactions 16 and 17 [41, 42].





As depicted in Fig. 7e, it was apparent that CT depletion was greater at acidic pH range from 3.0–6.0, whereas CT depletion was markedly suppressed at pH over 7.0. This phenomenon was caused by the following three reasons. First, a high solution pH encouraged Fe(II) precipitation, and thus blocked the chain reaction of reducing species generation. Second, the elevated solution pH constrained  $\text{H}_2\text{O}_2$  release from  $\text{CaO}_2$  dissolution [16]. Third, the reactivity of ROSs involved in this process was also influenced by high pH condition. It is noted that a slightly inhibitory effect could also appear at  $\text{pH} < 3$ , and this result was due to the relatively low reaction rate between Fe(II) and  $\text{H}_2\text{O}_2$  [43]. Although CT degradation performed well in acidic pH range from 3.0–6.0 in this work, pH should still need to pay attention in practical application because the actual groundwater, in general, has a high pH buffering capacity.

Fig. 7f showed a significant inhibitive effect on CT degradation by humic acid (HA), a main fraction of NOM. CT degradation decreased by 28%, 22% and 16% in the initial 3 min when the addition of HA was 10, 50 and 100  $\text{mg L}^{-1}$ , respectively. On one hand, it has been documented that the presence of HA could consume  $\text{OH}^\bullet$  [44], which was vital for reductants formation in this work, therefore the diminution of  $\text{OH}^\bullet$  would hinder CT degradation ultimately. On the other hand, a slight alleviation of CT degradation inhibition with increasing the concentration of HA from 1.0 to 100  $\text{mg L}^{-1}$  was speculated to be related to chelation of Fe(II) with HA [45].

**3.4.2 The performance of CT degradation in actual groundwater**—To validly evaluate the applicability of the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process for actual groundwater remediation, tests were conducted using the actual groundwater. Fig. 8 shows the removal of CT in the actual groundwater when the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}/\text{CT}$  molar ratios were set at

30/40/10/1, 60/80/20/1, 120/160/40/1, 180/240/60/1 and 240/320/80/1, respectively. It was observed that CT degradation was greatly reduced in the actual groundwater compared to the complete CT depletion in ultrapure water system at the same chemical addition (30/40/10/1). This may be caused by the presence of various constituents in actual groundwater, such as the high anion contents of  $\text{NO}_3^-$  (27.37 mg L<sup>-1</sup>),  $\text{Cl}^-$  (35.73 mg L<sup>-1</sup>) and  $\text{HCO}_3^-$  (251.31 mg L<sup>-1</sup>), the pH buffer capacity (pH = 6.86), as well as high total organic carbon (20.59 mg L<sup>-1</sup>). Nevertheless, complete CT removal could still be achieved after a relatively longer reaction time by increasing dosages of reagents to 180/240/60/1, encouragingly suggesting that the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process can be applied for remediation of CT contaminated groundwater.

#### 4. Conclusions

In this work, the degradation of CT in the  $\text{CaO}_2/\text{Fe(II)}$  system was greatly promoted by addition of MeOH. The optimal CT removal was achieved at the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}/\text{CT}$  molar ratio of 30/40/10/1. The enhancement of CT degradation by three other solvents, namely CP, DMSO, and IPA, indicated that small-molecule solvent amendment is a viable approach for CT remediation. Radical scavenger tests demonstrated that  $\text{O}_2^{\bullet-}$  and  $\text{CO}_2^{\bullet-}$  were the dominant species, and meanwhile  $\cdot\text{CH}_2\text{OH}$ , based on literature survey, was also regarded as a reductant responsible for CT degradation. The detected intermediates, CF, HCA and PCE, were quantitatively analyzed and a chlorine balance was calculated along with CT degradation, indicating that CT could be well mineralized. Moreover, a multi-step process for CT mineralization was proposed. The solution matrix tests showed that  $\text{NO}_3^-$  and  $\text{Cl}^-$  had a slight scavenging effect on CT depletion, whereas  $\text{HCO}_3^-$  and HA had a significant inhibitive function. The CT removal performed well in weak acidic to nearly neutral pH condition. Finally, CT degradation in actual groundwater demonstrated that the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process has a great potential for application in CT contaminated groundwater remediation.

#### Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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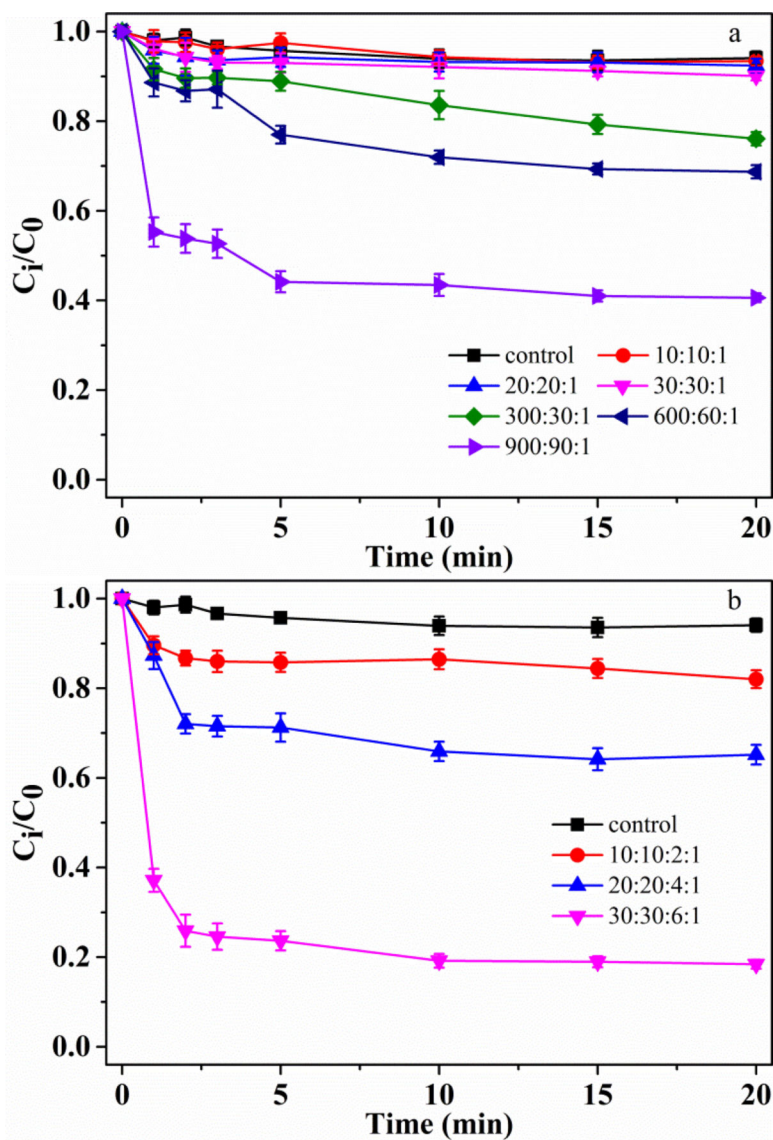
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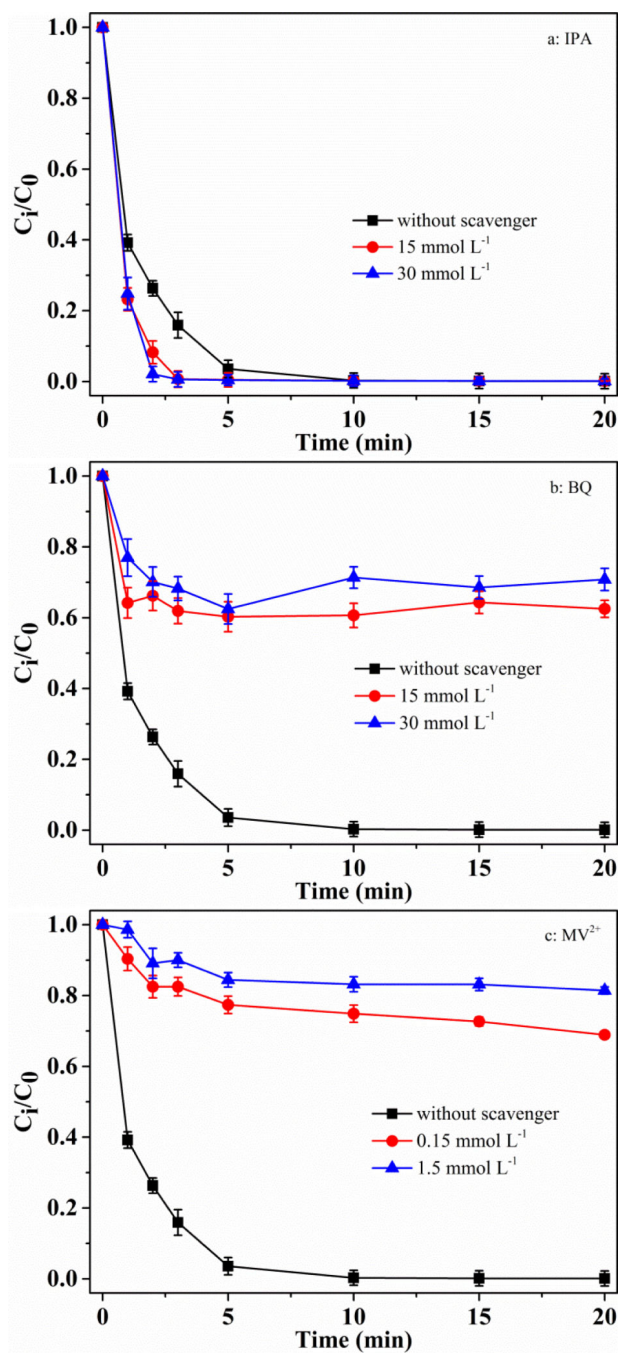


**Highlights:**

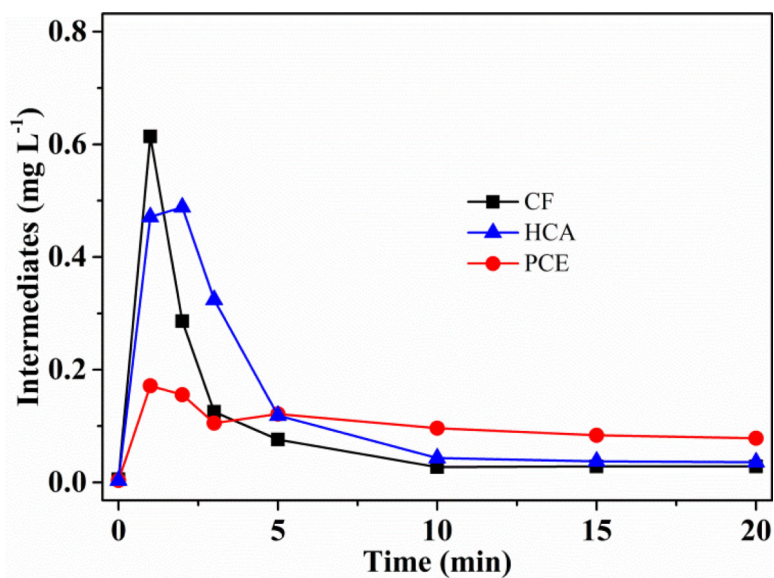
- CT degradation in  $\text{CaO}_2/\text{Fe(II)}$  system is promoted by MeOH addition.
- The leading species for CT degradation are  $\text{O}_2^{\bullet-}$ ,  $\text{CO}_2^{\bullet-}$ .
- $\text{CHCl}_3$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{C}_2\text{Cl}_6$  were the intermediates of CT.
- A reduction mechanism for CT degradation was proposed.
- Efficient removal of CT in groundwater was attained.



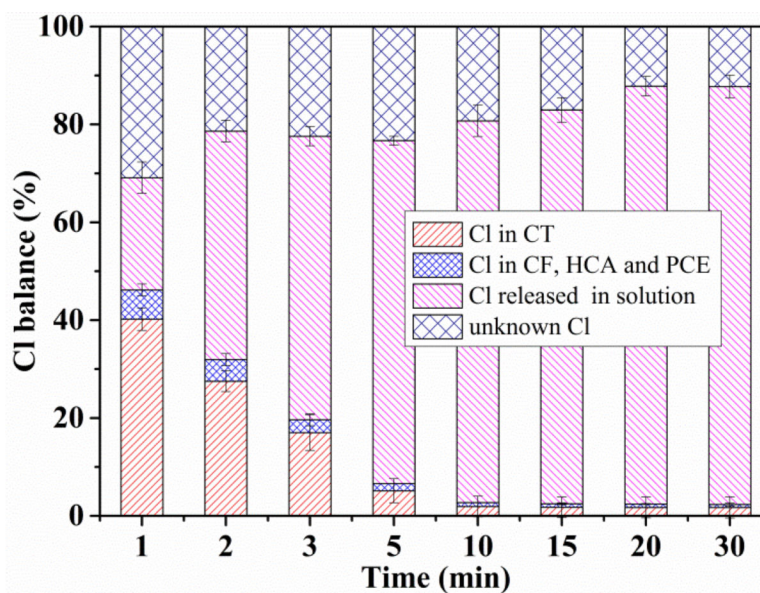
**Fig. 1.** Comparison of CT degradation in the Fe(II)-activated CaO<sub>2</sub> system: (a) without MeOH and (b) with MeOH ([CT]<sub>0</sub> = 0.13 mmol L<sup>-1</sup>).

**Fig. 2.**

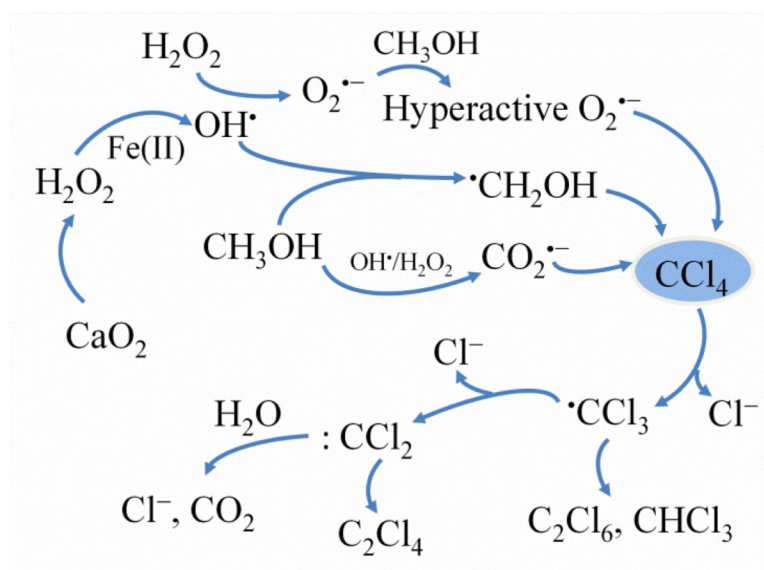
The degradation of CT in the CaO<sub>2</sub>/Fe(II)/MeOH system with the addition of different scavengers: (a) IPA; (b) BQ and (c) MV<sup>2+</sup> ([CaO<sub>2</sub>]<sub>0</sub> = 3.90 mmol L<sup>-1</sup>, [Fe(II)]<sub>0</sub> = 5.20 mmol L<sup>-1</sup>, [MeOH]<sub>0</sub> = 1.30 mmol L<sup>-1</sup>, [CT]<sub>0</sub> = 0.13 mmol L<sup>-1</sup>).

**Fig. 3.**

Evolution of the chlorinated organic intermediates in the CaO<sub>2</sub>/Fe(II)/MeOH system ([CaO<sub>2</sub>]<sub>0</sub> = 3.90 mmol L<sup>-1</sup>, [Fe(II)]<sub>0</sub> = 5.20 mmol L<sup>-1</sup>, [MeOH]<sub>0</sub> = 1.30 mmol L<sup>-1</sup>, [CT]<sub>0</sub> = 0.13 mmol L<sup>-1</sup>).

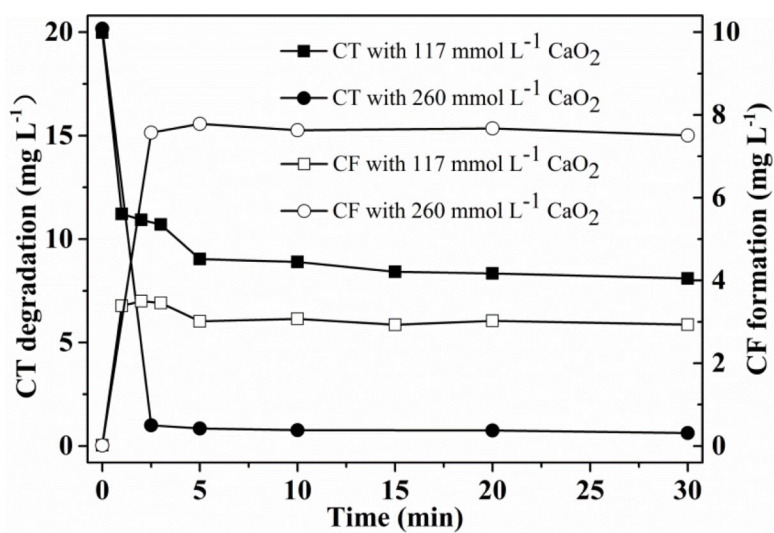


**Fig. 4.** Cl balance during CT degradation in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process ( $[\text{CaO}_2]_0 = 3.90 \text{ mmol L}^{-1}$ ,  $[\text{Fe(II)}]_0 = 5.20 \text{ mmol L}^{-1}$ ,  $[\text{MeOH}]_0 = 1.30 \text{ mmol L}^{-1}$ ,  $[\text{CT}]_0 = 0.13 \text{ mmol L}^{-1}$ )

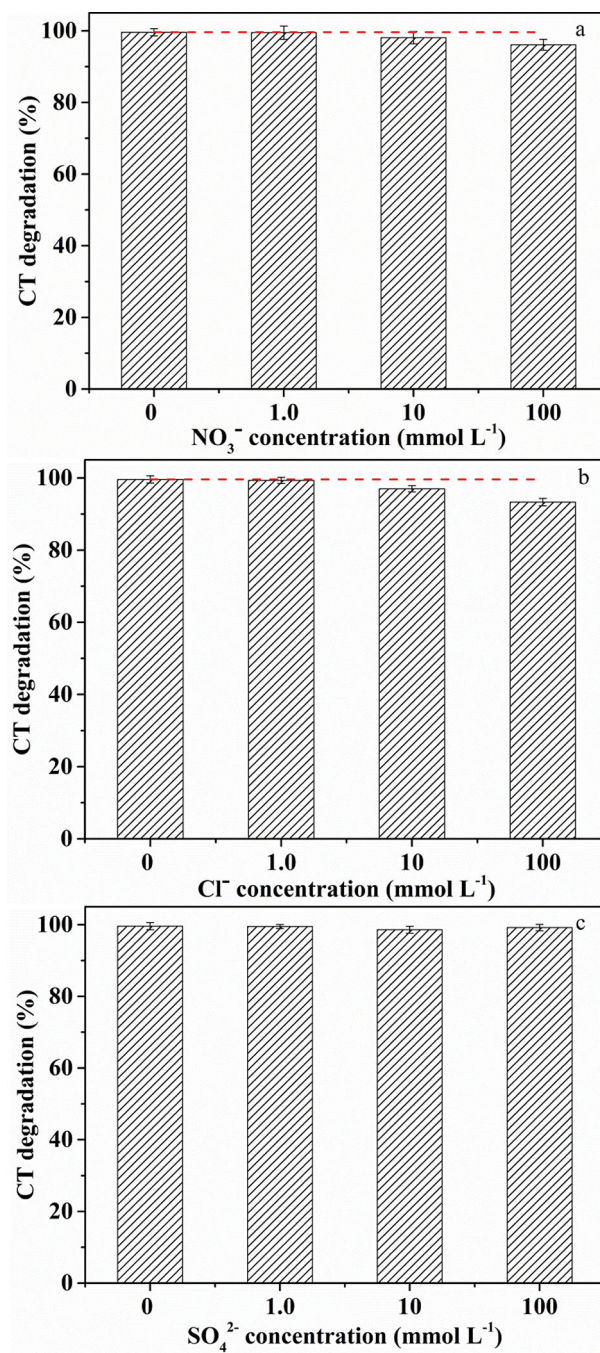


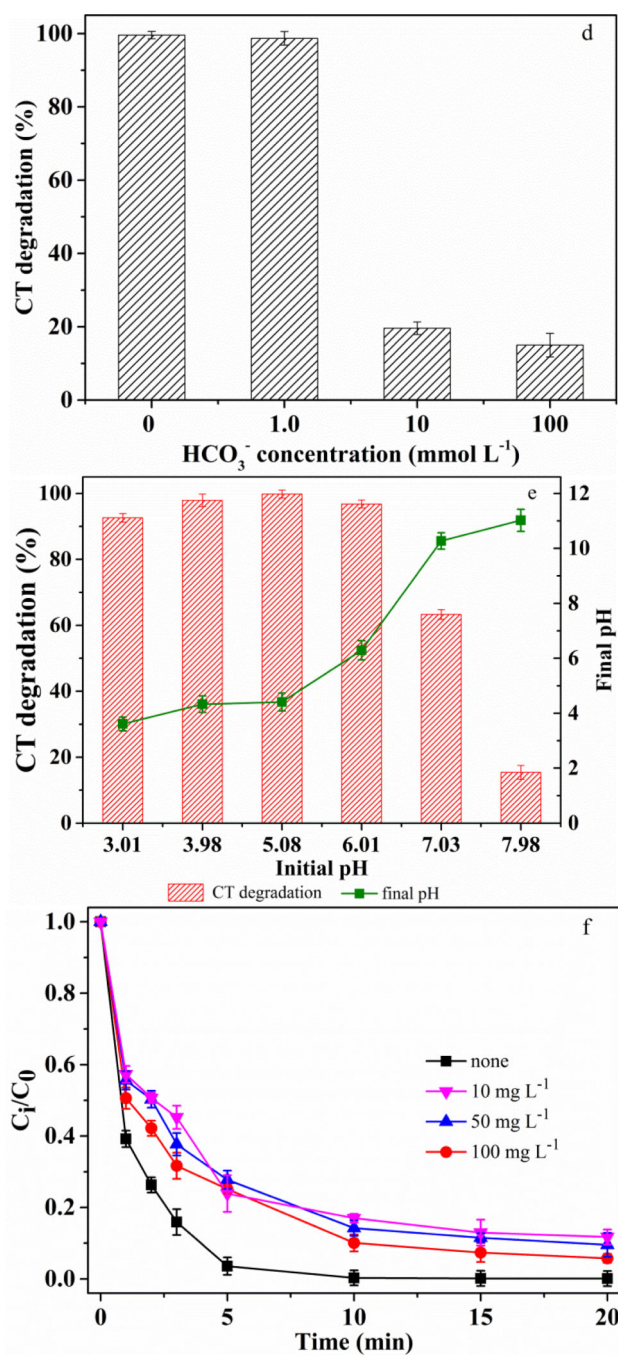
**Fig. 5.**  
Proposed CT degradation pathway in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  process.



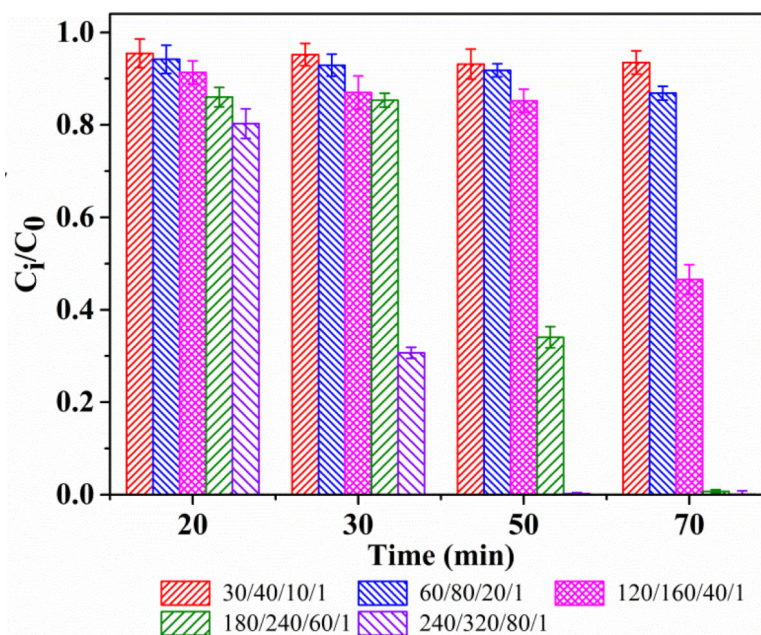


**Fig. 6.** Evolution of CF during CT degradation in the CaO<sub>2</sub>/Fe(II) process (CaO<sub>2</sub>/Fe(II) molar ratio = 10/1, [CT]<sub>0</sub> = 0.13 mmol L<sup>-1</sup>)





**Fig. 7.** Effect of solution matrix on CT degradation in the  $\text{CaO}_2/\text{Fe(II)}/\text{MeOH}$  system (a)  $\text{NO}_3^-$ ; (b)  $\text{Cl}^-$ ; (c)  $\text{SO}_4^{2-}$ ; (d)  $\text{HCO}_3^-$ ; (e) pH and (f) NOM ( $[\text{CaO}_2]_0 = 3.90 \text{ mmol L}^{-1}$ ,  $[\text{Fe(II)}]_0 = 5.20 \text{ mmol L}^{-1}$ ,  $[\text{MeOH}]_0 = 1.30 \text{ mmol L}^{-1}$ ,  $[\text{CT}]_0 = 0.13 \text{ mmol L}^{-1}$ ).



**Fig. 8.**  
CT degradation performance in the actual groundwater ( $[CT]_0 = 0.13 \text{ mmol L}^{-1}$ ).