

Effective degradation of 1,2-dichloroethane in calcium peroxide activated by Fe(III): performance and mechanisms

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ABSTRACT

As a kind of refractory chlorinated hydrocarbon, 1,2-dichloroethane (1,2-DCA) has been frequently detected in contaminated groundwater, and it is hard for common technology to degrade it due to its stability. Moreover, the existence of 1,2-DCA can do harm to human organs. Hence, it is urgent to develop an effective technology for the remediation of 1,2-DCA-contaminated groundwater. In this study, a calcium peroxide (CaO₂) system activated by Fe(III) was applied to the degradation of 1,2-DCA and 83.3% of 1,2-DCA could be effectively removed within 3 h when the molar ratio of CaO₂/Fe(III)/1,2-DCA was 30/120/1. The results of probe experiments, electron paramagnetic resonance (EPR) detection, and scavenging tests demonstrated that both HO[•] and O₂^{-•} were the key factors for 1,2-DCA degradation. The released amount of Cl⁻ (84.1%) revealed that most of the chlorine in 1,2-DCA could be dechlorinated. GC-MS was applied for the detection of intermediates during 1,2-DCA degradation and the possible degradation pathway was proposed that 1,2-DCA was first reduced to vinyl chloride (VC) and then oxidized to CO₂ and H₂O. Finally, 73.4% removal of 1,2-DCA could be achieved in actual groundwater when the molar ratio of CaO₂/Fe(III)/1,2-DCA was 100/400/1, demonstrating that the CaO₂/Fe(III) system has a remarkable prospect in 1,2-DCA-contaminated groundwater remediation.

Key words: 1,2-dichloroethane, calcium peroxide, degradation mechanism, groundwater remediation, reactive oxygen species

HIGHLIGHTS

- Efficient degradation of 1,2-DCA in the CaO₂/Fe(III) system was achieved.
- HO[•] and O₂^{-•} were the key factors for 1,2-DCA removal in the CaO₂/Fe(III) system.
- The possible degradation pathway of 1,2-DCA was proposed.
- The effect of water matrices on 1,2-DCA degradation in the CaO₂/Fe(III) system was investigated.

1. INTRODUCTION

1,2-Dichloroethane (1,2-DCA) is widely used as the chlorinated organic solvent and raw material for insecticide production, resulting in ubiquitous contamination in soil and groundwater due to improper usage and disposal (Vilhunen *et al.* 2010; Lin *et al.* 2021; Rahim *et al.* 2022). The existence of 1,2-DCA in groundwater can do harm to human organs, thus, it has been listed as one of the priority pollutants by the United Kingdom (UK) and the United States Environmental Protection Agency (USEPA) due to the negative impact on the environment and human health (Morris 2000; Bejankiwar *et al.* 2005; Gwinn *et al.* 2011). Therefore, it is urgent to establish an efficient technology for the remediation of 1,2-DCA in contaminated groundwater. Various methods have been applied to the removal of 1,2-DCA up to now, such as adsorption, catalytic degradation, pyrolysis, and biodegradation (Dai *et al.* 2015). However, the limitation of catalyst deactivation resulted in the inefficient degradation of 1,2-DCA in actual groundwater (Huang *et al.* 2022). A high cost is required to achieve the desired removal by adsorption, while biodegradation is generally time-consuming and is seriously dependent on the underground environment (Bejankiwar *et al.* 2005). Furthermore, a study concerning advanced oxidation processes (AOPs) on 1,2-DCA removal has not been reported.

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Advanced oxidation processes (AOPs) have attracted much attention and have been extensively employed to degrade refractory organic pollutants in contaminated sites due to their high efficiency and low cost (Martins *et al.* 2013; Santos-Juanes *et al.* 2017). Among various AOPs, the traditional Fenton process has the advantages of simple operation and effective performance and has been widely used in the remediation of contaminated soil and groundwater. The hydroxyl radical (HO^\bullet) and superoxide radical (O_2^-) will be generated in the Fenton process and they play leading roles in the degradation of pollutants (Seol *et al.* 2003). However, the traditional Fenton process has been gradually modified by researchers because of its shortcomings, such as fast reaction, short-term reaction time and difficulty in storage of H_2O_2 . As a kind of solid H_2O_2 source, calcium peroxide (CaO_2) can slowly release H_2O_2 in aqueous solution (Equations (1) and (2)) and degrade pollutants effectively and persistently (Zhang *et al.* 2015a), and hence has attracted much more interest from researchers recently.



The activation of CaO_2 is commonly implemented by transition metals. Among numerous transition metals, Fe(III) has been widely applied for the activation of CaO_2 due to its environmental friendliness and availability. Zhang *et al.* (2016) reported that 96% of trichloroethene was degraded within 180 min in actual groundwater in a $\text{CaO}_2/\text{Fe}(\text{III})/\text{citric acid}$ (CA) system. As far as we know, the removal of 1,2-DCA in a CaO_2 oxidation process activated by Fe(III) has not been reported yet. The mechanisms of reactive oxygen species (ROS) generated in a $\text{CaO}_2/\text{Fe}(\text{III})$ system need to be clarified. In addition, the possible degradation pathways of 1,2-DCA need to be revealed.

Hence, in this work, 1,2-DCA removal in a $\text{CaO}_2/\text{Fe}(\text{III})$ system was investigated. The objectives of this work are to: (1) evaluate the performance of 1,2-DCA removal in the various systems and explore the effect of experimental parameters on 1,2-DCA degradation; (2) identify the dominant ROS for 1,2-DCA removal in the $\text{CaO}_2/\text{Fe}(\text{III})$ system; (3) determine the effect of the water matrix on 1,2-DCA degradation; (4) illuminate the dechlorination performance of 1,2-DCA and propose the possible degradation pathways of 1,2-DCA in the $\text{CaO}_2/\text{Fe}(\text{III})$ system; and finally (5) assess the effectiveness of the $\text{CaO}_2/\text{Fe}(\text{III})$ system for 1,2-DCA removal in actual groundwater. It is expected that the outcomes of this research will provide fundamental support for the practical implementation of the $\text{CaO}_2/\text{Fe}(\text{III})$ system in the remediation of 1,2-DCA-contaminated groundwater.

2. MATERIALS AND METHODS

2.1. Materials and chemicals

All the materials and equipment used in this work are provided in Tables 1 and 2.

2.2. Experimental procedures

In the 1,2-DCA degradation experiments, the reactor (250 mL) was placed on a magnetic stirrer at a constant speed of 600 rpm and the reaction temperature was controlled at 20 ± 0.5 °C. The predetermined dosage of Fe(II) or Fe(III) was added into the reactor containing 1,2-DCA (0.2 mM) solution and then the reaction began immediately after CaO_2 addition. At a given time, a 1.0 mL sample was taken out to a brown vial pre-filled with 1.0 mL *n*-hexane to terminate the reaction and extract the remaining 1,2-DCA. The concentration of 1,2-DCA in the extracted samples was analyzed by gas chromatograph (GC, 7890A, Agilent, USA). In order to investigate the influence of anions, various anions were added before reaction began.

In the test of HO^\bullet quantification, 1,2-DCA was replaced by BA and then a 1.0 mL sample was mixed with 1.0 mL NaOH (0.1 mM) and 0.1 mL methanol (Xue *et al.* 2018b). The mixture was filtered into a vial containing 0.5 mL H_2SO_4 (1.0 mM) to adjust pH. The concentration of *p*-hydroxybenzoic acid (*p*-HBA) in the sample was analyzed by high performance liquid chromatography (HPLC, LC-20AT, Shimadzu, Japan).

In the scavenging experiments, tertiary butyl alcohol (TBA) and trichloromethane (CF) were selected as the scavengers of HO^\bullet and O_2^- , respectively (Wang *et al.* 2016). In the probe tests, nitrobenzene (NB) and tetrachloride (CT), as the probe compounds of HO^\bullet and O_2^- , respectively, were used to replace 1,2-DCA (Buxton *et al.* 1988; Teel & Watts 2002).

In the test of dechlorination investigation, a 5.0 mL sample was taken out in the given time and mixed with 1.0 mL methanol to stop the reaction in an exposed bottle. Then the sample was stood still for 12 h and the concentration of Cl^- in the sample was analyzed by ion chromatography (IC, Dionex ICS-1000, Sunnyvale, USA). To ensure the accuracy of the experiments, all tests were conducted at least three times.

Table 1 | Materials and chemicals

Reagent	Purity	Manufacturer (Shanghai, China)
1,2-Dichloroethane (C ₂ H ₄ Cl ₂)	99.00%	Aladdin Reagent Co. Ltd
Iron sulphate heptahydrate (FeSO ₄ ·7H ₂ O)	99.50%	Aladdin Reagent Co. Ltd
Iron sulfate hydrate (Fe ₂ (SO ₄) ₃ ·xH ₂ O)	AR	Aladdin Reagent Co. Ltd
<i>n</i> -Hexane (C ₆ H ₁₄)	97.00%	Aladdin Reagent Co. Ltd
Tertiary butyl alcohol ((CH ₃) ₃ OH)	≥99.0%	Aladdin Reagent Co. Ltd
5,5-Dimethyl-1-pyrroline N-oxide (C ₆ H ₁₁ NO)	97.00%	Aladdin Reagent Co. Ltd
Phosphoric acid (H ₃ PO ₄)	HPLC, 85% ~ 90%	Aladdin Reagent Co. Ltd
Benzoic acid (C ₇ H ₆ O ₂)	99.50%	Aladdin Reagent Co. Ltd
Potassium peroxymonosulfate sulfate (KHSO ₅)	≥99.0%	Shanghai Lingfeng Chemical Reagent Co. Ltd
Titanium (IV) oxysulfate–sulfuric acid hydrate (TiOSO ₄ ·xH ₂ SO ₄ ·xH ₂ O)	93.00%	Shanghai Lingfeng Chemical Reagent Co. Ltd
Sulfuric acid (H ₂ SO ₄)	98.00%	Shanghai Lingfeng Chemical Reagent Co. Ltd
Carbon tetrachloride (CCl ₄)	99.50%	Shanghai Lingfeng Chemical Reagent Co. Ltd
Calcium peroxide (CaO ₂)	≥75%	Shanghai Titan Scientific Co. Ltd
Sodium chloride (NaCl)	96.00%	Shanghai Titan Scientific Co. Ltd
Sodium bicarbonate (NaHCO ₃)	≥99.5%	Shanghai Titan Scientific Co. Ltd
Sodium hydroxide (NaOH)	≥96.0%	Shanghai Titan Scientific Co. Ltd
Anhydrous sodium sulfate (Na ₂ SO ₄)	≥99.0%	Sinopharm Chemical Reagent Co. Ltd
Sodium nitrate (NaNO ₃)	99.50%	Sinopharm Chemical Reagent Co. Ltd
Chloroform (CHCl ₃)	99.00%	Sinopharm Chemical Reagent Co. Ltd
Nitrobenzene (NB)	99.00%	Shanghai Chemical Reagent Co. Ltd
Groundwater	–	15 m deep below the surface (Minhang, Shanghai, China)

Table 2 | Main experimental equipment

Equipment	Model	Manufacturer
Gas chromatograph (GC)	Agilent 7890A	Agilent Technologies Co. Ltd (USA)
High performance liquid chromatography (HPLC)	LC-20AT	Shimadzu Co. Ltd (Japan)
Thermostatic magnetic stirrer	Feb-85	Shanghai Minhang Hongpu Instrument Factory (China)
Electron sequential resonator (EPR)	EMX-8/2.7C	Burker Co. Ltd (Germany)
UV–visible spectrophotometer	DR-6000	Hach Co. Ltd (China)
Ion chromatography (IC)	ICS-1000	Dionex Co. Ltd (USA)
pH meter	P8–10	Sartorius Co. Ltd (Germany)
Electronic analytical balance	AL204	Mettler Toledo Co. Ltd (Switzerland)
Eddy current shaker	XW-80A	Shanghai Qingpu Huxi Instrument Factory (China)
Ultrapure water machine	CLASSIC UV MK2	ELGA Co. Ltd (England)

2.3. Analytical methods

The concentration of 1,2-DCA was analyzed by GC at the oven, injector and detector temperatures of 90, 220, and 240 °C, respectively. The ROS generated in aqueous solution were determined by electron paramagnetic resonance (EPR). The

concentrations of BA and *p*-HBA were determined by HPLC coupled with a UV-vis detector (SPD-20A) and an auto-sampler (SIL-20A) at the detection wavelengths of 255 and 225 nm, respectively. The mobile phase was a mixture of 0.1% phosphoric acid and methanol (58/42 (v/v)), the oven temperature was 35 °C and the injection value was 10 µL. The Fe(II) concentrations in aqueous solution were analyzed by *o*-phenanthroline spectrophotometry at the detection wavelength of 512 nm (Tamura *et al.* 1974). The H₂O₂ concentrations were analyzed by the TiSO₄ method at the detection wavelength of 400 nm (Vega *et al.* 2022). The concentrations of Cl⁻ were determined by IC. The pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland) was used to measure the solution pH. CT was analyzed by GC at a split ratio of 20:1, and the temperatures of the oven, injector, and detector were 75, 240, and 260 °C, respectively. NB was analyzed by the HPLC at the temperature of 35 °C. The mobile phase was a mixture of 40% water (solvent A) and 60% methanol (solvent B) at a total flow rate of 1.0 mL min⁻¹. The injection volume was 10 µL and the wavelength of the UV detector was fixed at 254 nm.

3. RESULTS AND DISCUSSION

3.1. The performance of 1,2-DCA degradation in various systems

The 1,2-DCA degradation performance in different systems is shown in Figure 1, in which the initial concentrations of 1,2-DCA, CaO₂, Fe(II), and Fe(III) were set as 0.2, 6.0, 24, and 24 mM, respectively. Without addition of any chemicals, the volatilization loss of 1,2-DCA was less than 1% at 20 ± 0.5 °C. When only CaO₂, Fe(II), and Fe(III) was added, the removal of 1,2-DCA in aqueous solution was 1.62%, 0.39%, and 1.95% within 180 min, respectively. Moreover, only 2.4% of 1,2-DCA was removed in the CaO₂/Fe(II) system. It is reported that excessive Fe(II) could not only scavenge the generated HO[•], but also consume the O₂^{-•}, resulting in the low removal of 1,2-DCA (Equation (3)) (Yamazaki & Piette 1990; Zhang *et al.* 2015b; Wang *et al.* 2019). However, 83.3% of 1,2-DCA removal was obtained within 180 min in the CaO₂/Fe(III) system, indicating that CaO₂ could be effectively activated by Fe(III) and produce ROS to remove 1,2-DCA. On the one hand, Fe(III) could be slowly converted to Fe(II) and the regenerated Fe(II) could persistently catalyze H₂O₂ released by CaO₂ to generate ROS in the CaO₂/Fe(III) system (Equations (4)–(6)) (Walling 1975; Xue *et al.* 2019). On the other hand, CaO₂ can be directly activated by Fe(III) and generate numerous ROS.



The concentration of Fe(II) is generally a key factor affecting the production of ROS in AOPs and the variation of Fe(II) in different systems in this work is shown in Figure 2(a). The initial concentrations of CaO₂, Fe(III), 1,2-DCA, and CF were 6.0,

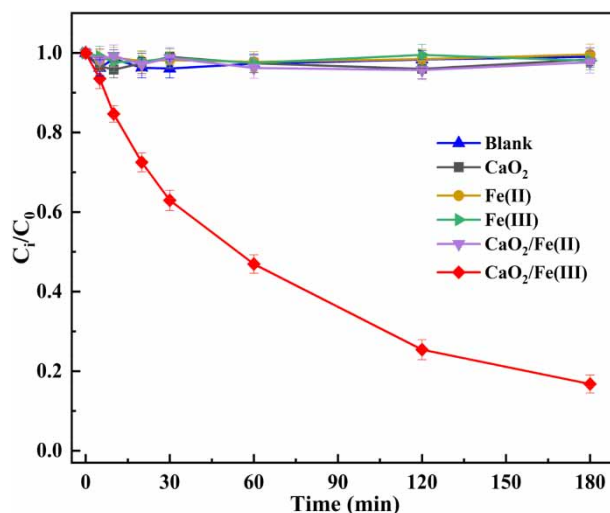


Figure 1 | The performance of 1,2-DCA removal in various systems ([CaO₂]₀ = 6.0 mM, [Fe(II)]₀ = [Fe(III)]₀ = 24 mM, 1,2-DCA = 0.2 mM).

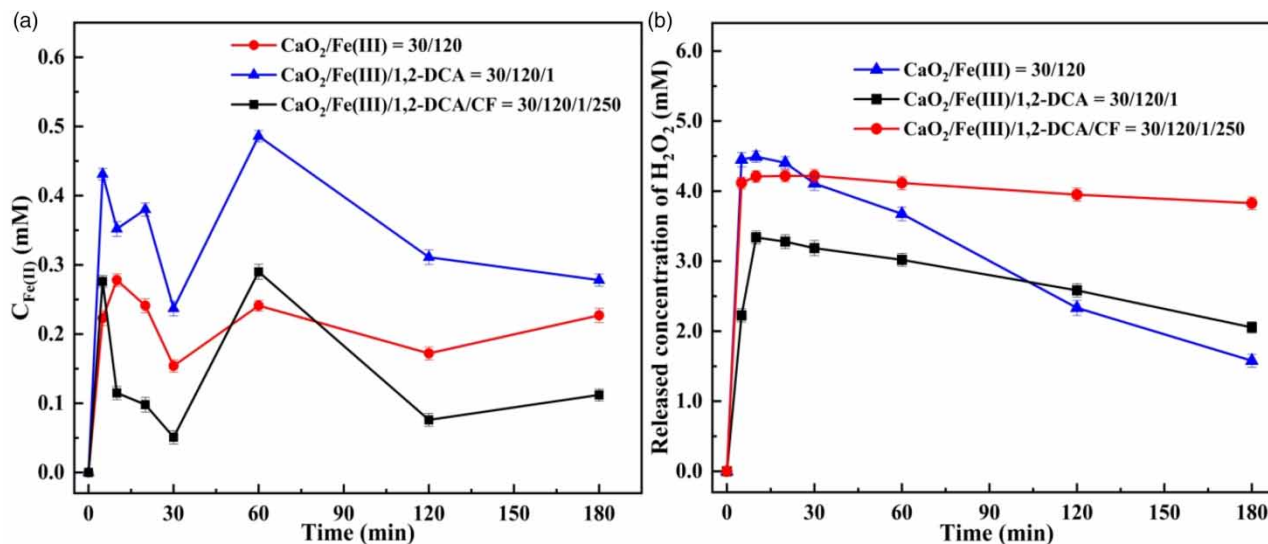


Figure 2 | (a) The concentrations of Fe(II) and (b) the released concentrations of H₂O₂ in various systems ([CaO₂]₀ = 6.0 mM, [Fe(III)]₀ = 24 mM, [1,2-DCA]₀ = 0.2 mM, [CF]₀ = 50 mM).

24, 0.2, and 50 mM, respectively. In the CaO₂/Fe(III) system, the fluctuation of Fe(II) was small and the Fe(II) concentration was maintained at 0.2 mM. The concentration of Fe(II) in the CaO₂/Fe(III)/1,2-DCA system was higher than that in the CaO₂/Fe(III) system in this work, indicating that reductive intermediates were produced during the reaction. Similarly, Xue *et al.* (2019) compared CaO₂/Fe(II) systems with and without benzene, and they also found that the concentration of Fe(II) increased in the CaO₂/Fe(II)/benzene system. In addition, the same trend of Fe(II) concentration variation in CaO₂/Fe(III)/1,2-DCA and CaO₂/Fe(III)/1,2-DCA/CF systems was observed, but the concentration of Fe(II) in the CaO₂/Fe(III)/1,2-DCA system was higher than that in the CaO₂/Fe(III)/1,2-DCA/CF system, suggesting that the addition of CF could hinder Fe(II) recovery by scavenging O₂⁻ (Equation (6)) (Neyens & Baeyens 2003).

The concentration of released H₂O₂ is an important factor concerning the degradation performance of contaminants in Fenton-like systems. As shown in Figure 2(b), the released concentrations of H₂O₂ in CaO₂/Fe(III), CaO₂/Fe(III)/1,2-DCA, and CaO₂/Fe(III)/1,2-DCA/CF systems were investigated. The initial concentrations of 1,2-DCA, CaO₂, Fe(III), and CF were 0.2, 6.0, 24, and 50 mM, respectively. The maximum released concentrations of H₂O₂ were 4.49, 4.20, and 3.34 mM in CaO₂/Fe(III), CaO₂/Fe(III)/1,2-DCA, and CaO₂/Fe(III)/1,2-DCA/CF systems, respectively. These results indicated that 1,2-DCA could consume H₂O₂ released by CaO₂ in aqueous solution. Compared with the CaO₂/Fe(III)/1,2-DCA system, the concentration of H₂O₂ in CaO₂/Fe(III)/1,2-DCA/CF was maintained at a relatively higher concentration, showing that the existence of CF could inhibit the reaction between 1,2-DCA and H₂O₂, resulting in the decreased consumption of H₂O₂.

The amount of HO[•] produced in the CaO₂/Fe(III) system was further determined to illustrate the relationship between the 1,2-DCA degradation rate and the generation of HO[•] when the CaO₂/Fe(III) molar ratio was controlled at 1/4 (Figure 3). The generation of HO[•] was divided into two stages. The generated amount of HO[•] increased to 1.58 mM within 60 min, while it rapidly decreased to 0.01 mM after 60 min when CaO₂ was 6.0 mM, which was consistent with the degradation performance of 1,2-DCA. The amount of generated HO[•] increased from 0.12 mM to 1.59 mM with the CaO₂ dosage increasing from 4 to 6 mM, suggesting that increasing the CaO₂ dosage would significantly enhance the generated HO[•] amount as well as 1,2-DCA removal. However, when the CaO₂ dosage further increased to 12 mM, the generated HO[•] concentration increased only a little bit, because the numerous generated HO[•] could be consumed by itself.

3.2. Effects of experimental parameters on 1,2-DCA degradation

The influence of Fe(III) dosage on 1,2-DCA degradation in the CaO₂/Fe(III) system was investigated and the initial concentrations of CaO₂ and 1,2-DCA were fixed at 6.0 and 0.2 mM, respectively. As shown in Figure 4(a), with the concentration of Fe(III) increasing from 6.0 to 24 mM, the 1,2-DCA removal increased from 2.5% to 83.3%, indicating that the degradation efficiency of 1,2-DCA could be enhanced by the augmentation of Fe(III) dosage. On one hand, the addition of Fe(III) could lower the pH, which prevented the formation of iron precipitation and maintained the soluble iron ions in solution.

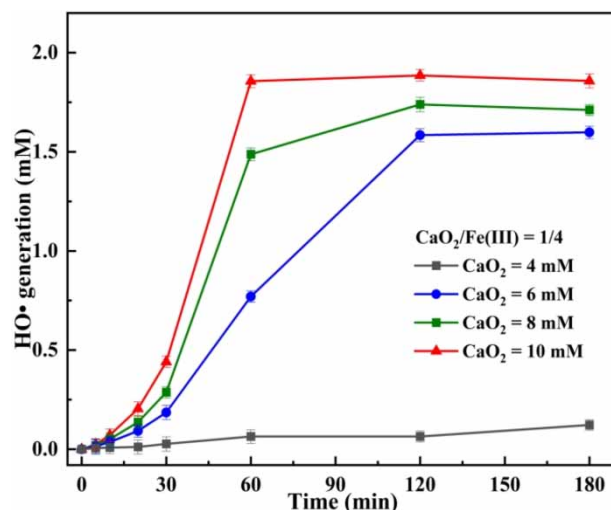


Figure 3 | HO[•] generation in CaO₂/Fe(III) system (the molar ratio of [CaO₂]₀/[Fe(III)]₀ = 1/4).

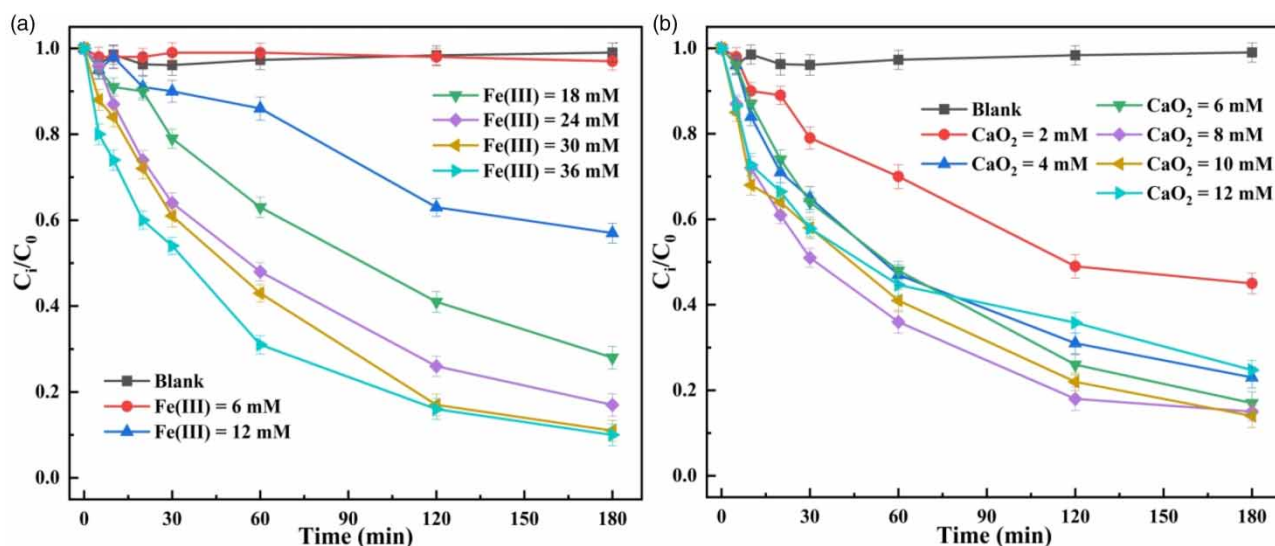


Figure 4 | Effects of (a) Fe(III) dosage ([CaO₂]₀ = 6.0 mM, [1,2-DCA]₀ = 0.2 mM) and (b) CaO₂ dosage ([Fe(III)]₀ = 24 mM, [1,2-DCA]₀ = 0.2 mM) on 1,2-DCA degradation in the CaO₂/Fe(III) system.

In addition, massive Fe(III) could promote the regeneration of Fe(II) and further facilitate the activation of CaO₂ (Equations (4) and (6)). However, when the dosage of Fe(III) increased from 24 to 36 mM, the removal of 1,2-DCA only increased by 6.2%, thus the Fe(III) concentration was controlled at 24 mM in the subsequent experiments.

The amounts of Fe(III) and 1,2-DCA were fixed at 24 mM and 0.2 mM to further investigate the influence of the CaO₂ amount on 1,2-DCA degradation. As illustrated in Figure 4(b), the removal of 1,2-DCA increased from 54.7% to 83.3% within 180 min when the concentration of CaO₂ increased from 2 to 6 mM. This consequence indicated that appropriately increasing the CaO₂ dosage could produce more ROS and promote the degradation of 1,2-DCA in the CaO₂/Fe(III) system. With the CaO₂ concentration further increasing from 6 to 10 mM, 1,2-DCA removal increased just from 83.3% to 85.2%. When the dosage of CaO₂ further increased to 12 mM, the degradation of 1,2-DCA was slightly inhibited. Over-concentrated CaO₂ in aqueous solution could increase the pH, which in turn accelerated the formation of iron precipitation and was not conducive to 1,2-DCA removal. Similarly, Xue *et al.* (2018a) reported that BTEX removal was suppressed in the CaO₂/Fe(II) system when the concentration of CaO₂ increased from 2.5 to 20 mM. In consideration of the practical application and the chemical cost-saving, the optimal concentration of CaO₂ was set as 6.0 mM.

3.3. Mechanisms of 1,2-DCA degradation

Probe compounds and EPR detection were used to confirm the ROS generated in the 1,2-DCA degradation process. In the probe experiments, NB and CT were used to detect the existence of HO^\bullet and $\text{O}_2^{\bullet-}$, and the initial concentrations of CaO_2 , Fe(III) , NB and CT were 6.0, 24, 0.2 and 0.2 mM, respectively. As shown in Figure 5, NB was completely removed within 10 min, demonstrating that a large amount of HO^\bullet was generated in the $\text{CaO}_2/\text{Fe(III)}$ system, and 32.3% of CT was degraded in the $\text{CaO}_2/\text{Fe(III)}$ system, accounting for the presence of $\text{O}_2^{\bullet-}$. Moreover, the signal of DMPO- HO^\bullet peaks was detected in the $\text{CaO}_2/\text{Fe(III)}$ system, and the result proved the generation and presence of HO^\bullet (Figure 6). Unfortunately, no DMPO- $\text{O}_2^{\bullet-}$ peak was found in the $\text{CaO}_2/\text{Fe(III)}$ system due to the instability of $\text{O}_2^{\bullet-}$.

To confirm the generated ROS and their contribution to 1,2-DCA degradation in the $\text{CaO}_2/\text{Fe(III)}$ system, scavenging tests were implemented. TBA and CF were used as HO^\bullet and $\text{O}_2^{\bullet-}$ scavengers, respectively, and the initial concentrations of CaO_2 , Fe(III) , TBA, and CF were 6.0, 24, 100, and 50 mM, respectively. As shown in Figure 7, the removal of 1,2-DCA decreased from 83.3% to 3.3% with the addition of 100 mM TBA, which revealed that HO^\bullet played a crucial role in 1,2-DCA degradation. Notably, 1,2-DCA removal decreased from 83.3% to 3.5% when 50 mM CF was added before the reaction started, confirming

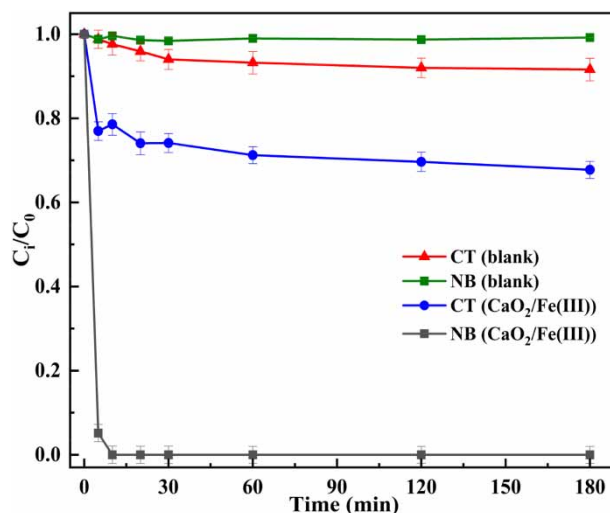


Figure 5 | Degradation performance of probe compounds in the $\text{CaO}_2/\text{Fe(III)}$ system ($[\text{CaO}_2]_0 = 6.0$ mM, $[\text{Fe(III)}]_0 = 24$ mM, $[\text{1,2-DCA}]_0 = [\text{NB}]_0 = [\text{CT}]_0 = 0.2$ mM).

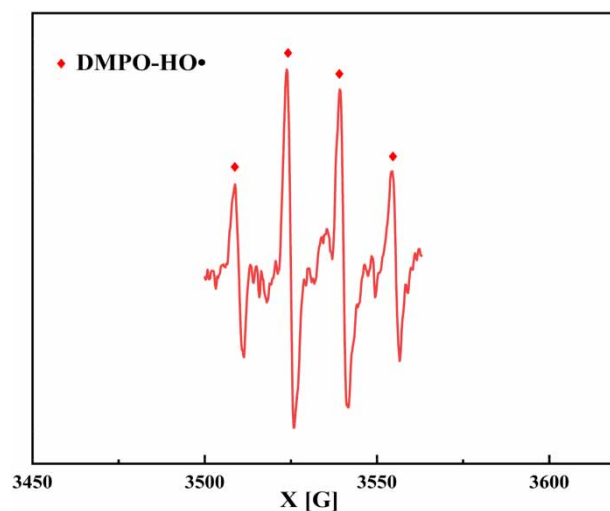


Figure 6 | EPR spectra at the reaction time of 60 min in the $\text{CaO}_2/\text{Fe(III)}$ system (DMPO as radical trap).

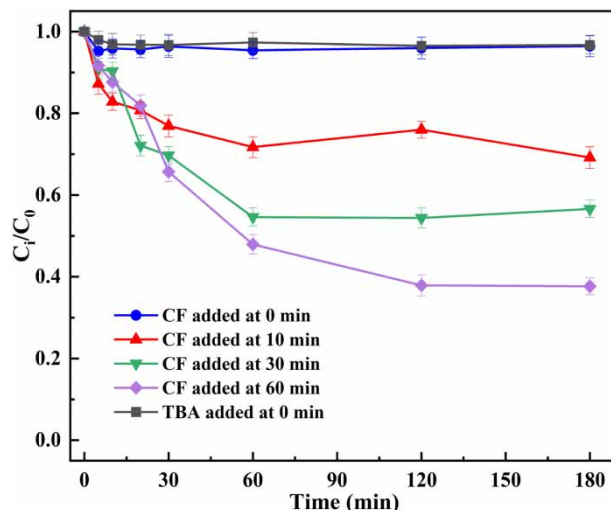


Figure 7 | Effect of scavengers on 1,2-DCA degradation in the $\text{CaO}_2/\text{Fe(III)}$ system ($[\text{CaO}_2]_0 = 6.0 \text{ mM}$, $[\text{Fe(III)}]_0 = 24 \text{ mM}$, $[\text{1,2-DCA}]_0 = 0.2 \text{ mM}$, $[\text{TBA}]_0 = 100 \text{ mM}$, $[\text{CF}]_0 = 50 \text{ mM}$).

that O_2^- also played an important role in 1,2-DCA degradation. Differently, Zhang *et al.* (2016) reported the degradation performance of trichloroethene (TCE) in a $\text{CaO}_2/\text{Fe(III)}$ /citric acid system and they found that HO^\cdot was the dominant ROS for TCE degradation, while the contribution of O_2^- to TCE removal could be negligible. Hence, the contribution of various ROS could be different due to the properties and structures of target contaminants. Experiments of adding CF at different reaction times were carried out to further investigate the contribution of ROS to 1,2-DCA removal. The 1,2-DCA removal decreased to 3.5%, 30.8%, 43.4%, and 62.7% when CF was added at 0, 10, 30, and 60 min, respectively (Figure 7). The result indicated that 1,2-DCA degradation was significantly inhibited in the presence of CF and O_2^- played an important role in 1,2-DCA degradation.

3.4. Effects of water matrices on 1,2-DCA degradation

To evaluate the application prospect of the $\text{CaO}_2/\text{Fe(III)}$ system in actual groundwater remediation, the effects of complex water matrices (pH, Cl^- , HCO_3^- , NO_3^- , and SO_4^{2-}) on 1,2-DCA degradation were investigated. The initial concentrations of CaO_2 , Fe(III) , and 1,2-DCA were 6.0, 24, 0.2 mM, respectively. As shown in Figure 8, 89.6%, 87.2%, 85.3%, 84.2%, and

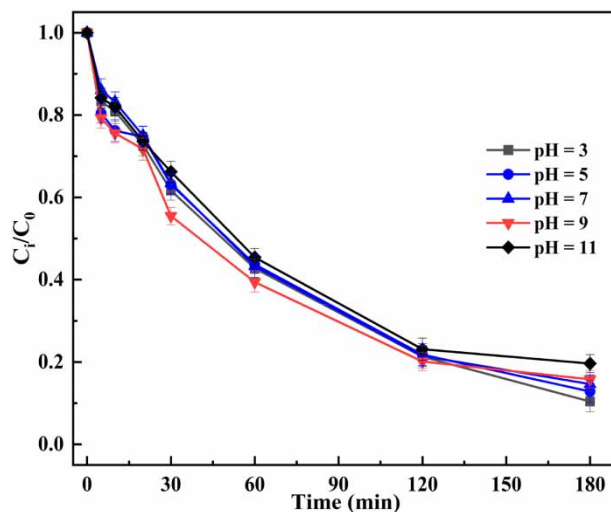


Figure 8 | Effect of initial solution pH on 1,2-DCA degradation in the $\text{CaO}_2/\text{Fe(III)}$ system ($[\text{CaO}_2]_0 = 6.0 \text{ mM}$, $[\text{Fe(III)}]_0 = 24 \text{ mM}$, $[\text{1,2-DCA}]_0 = 0.2 \text{ mM}$).

80.3% of 1,2-DCA were degraded at the initial solution pH of 3.0, 5.0, 7.0, 9.0, and 11.0, respectively. It is worth noting that 1,2-DCA could be removed effectively in the CaO₂/Fe(III) system in the pH range of 3–11 and acidic solution was conducive for 1,2-DCA removal. Northup & Cassidy (2008) reported that the dissolution of CaO₂ and the release of H₂O₂ were promoted in an acidic environment, which could enhance pollutant degradation. The CaO₂/Fe(III) system was still effective for 1,2-DCA removal in alkaline conditions because a large amount of Fe(III) was hydrolyzed, resulting in an acidic condition (Table 3).

The influences of inorganic anions (Cl⁻, HCO₃⁻, NO₃⁻, and SO₄²⁻) on 1,2-DCA degradation were further investigated. As illustrated in Figure 9(a), 1,2-DCA removal decreased from 83.3% to 78.2%, 36.4%, and 37.4% when the Cl⁻ concentration increased from 0 to 1, 10, and 100 mM. The inhibition of 1,2-DCA removal caused by the presence of Cl⁻ could be attributed to the scavenging effects of HO[•] and O₂^{-•} through Equations (7) and (8) (Walling 1975; Xu *et al.* 2017):



Table 3 | Parameter values under various experimental conditions

Experimental conditions	1,2-DCA removal (%)	pH (Initial/final)
pH = 3 ^a	89.6	3.02/2.62
pH = 5 ^a	87.1	5.01/2.68
pH = 7 ^a	85.3	7.05/2.73
pH = 9 ^a	84.2	9.00/2.75
pH = 11 ^a	80.4	10.98/2.76
CaO ₂ /Fe(III)/1,2-DCA = 10/40/1	29.3	2.56/2.72
CaO ₂ /Fe(III)/1,2-DCA = 20/80/1	63.4	2.39/2.42
CaO ₂ /Fe(III)/1,2-DCA = 30/120/1	83.3	2.26/2.35
CaO ₂ /Fe(III)/1,2-DCA = 40/160/1	89.9	2.16/2.36
CaO ₂ /Fe(III)/1,2-DCA = 60/240/1	93.3	2.06/2.21
[Cl ⁻] = 1 mM	78.2	2.21/2.44
[Cl ⁻] = 10 mM	36.4	2.22/2.42
[Cl ⁻] = 100 mM	37.4	2.23/2.44
[HCO ₃ ⁻] = 1 mM	82.4	2.22/2.43
[HCO ₃ ⁻] = 10 mM	82.2	2.58/2.50
[HCO ₃ ⁻] = 100 mM	4.3	6.58/7.05
[NO ₃ ⁻] = 1 mM	88.5	2.24/2.42
[NO ₃ ⁻] = 10 mM	86.7	2.24/2.43
[NO ₃ ⁻] = 100 mM	87.9	2.19/2.35
[SO ₄ ²⁻] = 1 mM	87.0	2.22/2.43
[SO ₄ ²⁻] = 10 mM	84.4	2.29/2.50
[SO ₄ ²⁻] = 100 mM	73.0	2.60/2.65
CaO ₂ /Fe(III)/1,2-DCA = 20/80/1 ^b	32.1	2.68/2.53
CaO ₂ /Fe(III)/1,2-DCA = 30/120/1 ^b	42.1	2.49/2.40
CaO ₂ /Fe(III)/1,2-DCA = 40/160/1 ^b	47.6	2.31/2.33
CaO ₂ /Fe(III)/1,2-DCA = 60/240/1 ^b	63.1	2.17/2.28
CaO ₂ /Fe(III)/1,2-DCA = 100/400/1 ^b	73.4	2.01/2.23

^aAdjusting pH before adding other agents.

^bUsing actual groundwater instead of Milli-Q water.

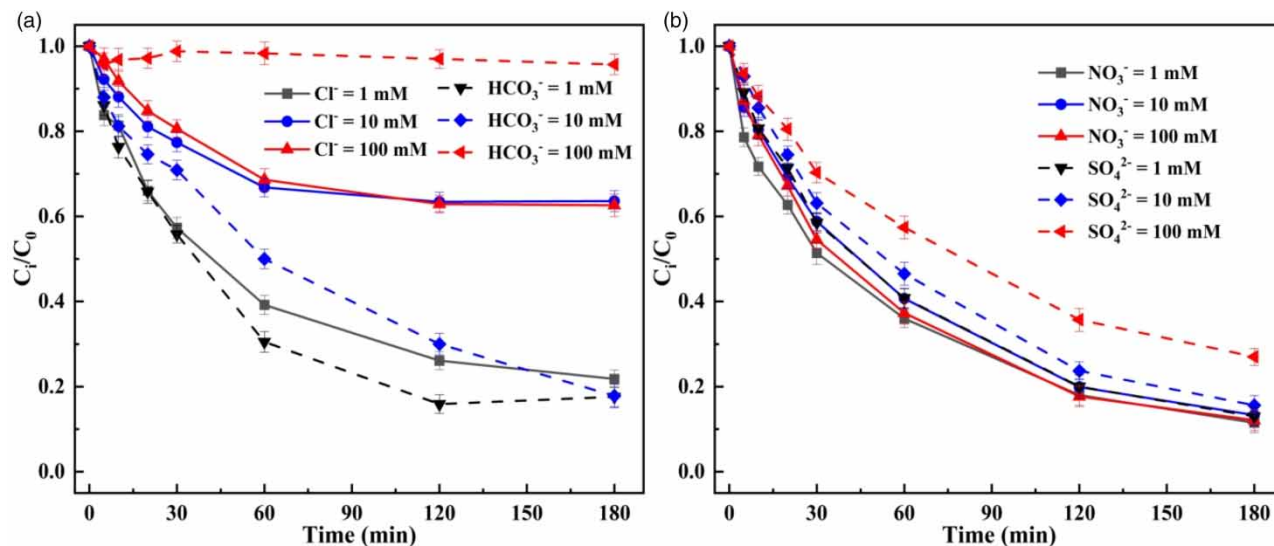


Figure 9 | The influences of (a) Cl^- and HCO_3^- , (b) NO_3^- and SO_4^{2-} on 1,2-DCA degradation in the $\text{CaO}_2/\text{Fe(III)}$ system ($[\text{CaO}_2]_0 = 6.0 \text{ mM}$, $[\text{Fe(III)}]_0 = 24 \text{ mM}$, $[\text{1,2-DCA}]_0 = 0.2 \text{ mM}$).

The removal of 1,2-DCA decreased from 83.3% to 82.4%, 82.2%, and 4.3% with the concentration of HCO_3^- increasing from 0 mM to 1, 10, and 100 mM, respectively. The inhibition effect of HCO_3^- could be negligible when the concentration of HCO_3^- was 1 or 10 mM, but it was significant when the concentration of HCO_3^- was 100 mM. This is because the initial pH increased from 2.22 to 6.58 with the concentration of HCO_3^- increasing from 1 to 100 mM (Table 3), which was not conducive for 1,2-DCA removal. Yang *et al.* (2021) also found that the presence of HCO_3^- had an obvious inhibition on naphthalene degradation in an $\text{H}_2\text{O}_2/\text{Fe(II)}$ system when the concentration of HCO_3^- was 100 mM. Moreover, the presence of HCO_3^- could scavenge the generated O_2^- through Equations (9) and (10) (Schmidt 1972). Furthermore, the effect of NO_3^- addition on 1,2-DCA degradation was negligible (Figure 9(b)). The addition of 1 and 10 mM SO_4^{2-} had little effect on the degradation of 1,2-DCA, but when the concentration of SO_4^{2-} increased to 100 mM, the 1,2-DCA removal decreased from 83.3% to 73.0%, which could be attributed to the quenching of HO^\bullet by SO_4^{2-} (Tang *et al.* 2020).



To further assess the applicability of the $\text{CaO}_2/\text{Fe(III)}$ system in practice, actual groundwater was used to replace the ultra-pure water in preparing the 0.20 mM 1,2-DCA aqueous solution. The main parameters of the actual groundwater used in this work are shown in Table 4. As shown in Figure 10, when the concentrations of CaO_2 and Fe(III) were 4 and 16 mM, respectively, only 32.7% of 1,2-DCA was removed within 180 min in the $\text{CaO}_2/\text{Fe(III)}$ system due to the scavenging effect of high Cl^- and HCO_3^- concentrations on HO^\bullet and O_2^- . However, 1,2-DCA removal increased to 73.4% with the concentrations of CaO_2

Table 4 | The main characteristics of the actual groundwater

Parameter	Value	Parameter	Value
pH	7.91	SO_4^{2-}	32.7 mg L ⁻¹
TOC	7.89 mg L ⁻¹	Total Fe	<0.010 mg L ⁻¹
Cl^-	117 mg L ⁻¹	Ca^{2+}	21 mg L ⁻¹
HCO_3^-	332 mg L ⁻¹	Mg^{2+}	12 mg L ⁻¹
NO_3^-	2.44 mg L ⁻¹	Mn^{2+}	<0.010 mg L ⁻¹

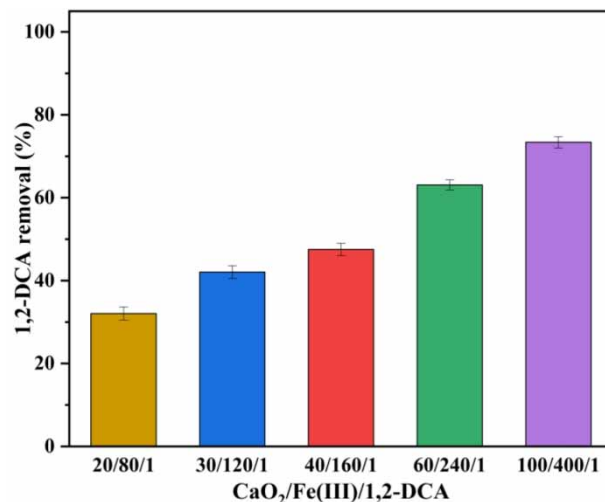


Figure 10 | 1,2-DCA degradation performance in actual groundwater in the CaO₂/Fe(III) system ([1,2-DCA]₀ = 0.2 mM).

and Fe(III) increasing to 20 and 80 mM, respectively. This result revealed that increasing the chemical amounts could enhance 1,2-DCA removal in the CaO₂/Fe(III) system in actual groundwater.

3.5. Possible 1,2-DCA degradation pathway

The dechlorination performance of 1,2-DCA in the CaO₂/Fe(III) system was investigated. Theoretically, 2 M Cl⁻ would be released from 1 M 1,2-DCA when being dechlorinated completely. As shown in Figure 11, the released amount of Cl⁻ reached 70% in the CaO₂/Fe(III) system, demonstrating that most of the chlorine in the 1,2-DCA could be dechlorinated to Cl⁻.

Furthermore, the degradation intermediates of 1,2-DCA in the CaO₂/Fe(III) system were analyzed by GC-MS. The GC-MS spectrum of the intermediates is supplied in Figure 12. Based on the above analytical results, a degradation pathway of 1,2-DCA was proposed in the CaO₂/Fe(III) system (Figure 13). Firstly, O₂^{•-} attacked 1,2-DCA and generated vinyl chloride (VC). Then VC was transformed to 2-chloroethanol or 1-chloroethanol through an HO[•] addition reaction, resulting in the generation of ethylene glycol and 1,1-ethanediol. Moreover, the ethylene glycol and 1,1-ethanediol were unstable and were converted to acetaldehyde. Finally, the acetaldehyde was oxidized by HO[•] and transformed to H₂O and CO₂.

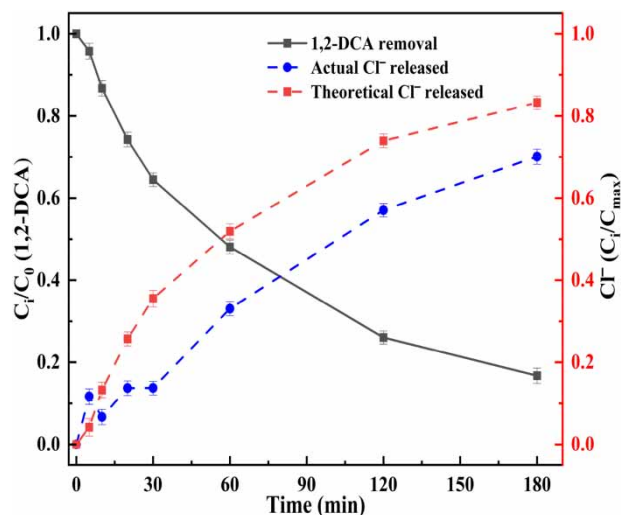


Figure 11 | The dechlorination performance of 1,2-DCA in the CaO₂/Fe(III) system ([CaO₂]₀ = 6.0 mM, [Fe(III)]₀ = 24 mM, [1,2-DCA]₀ = 0.2 mM).

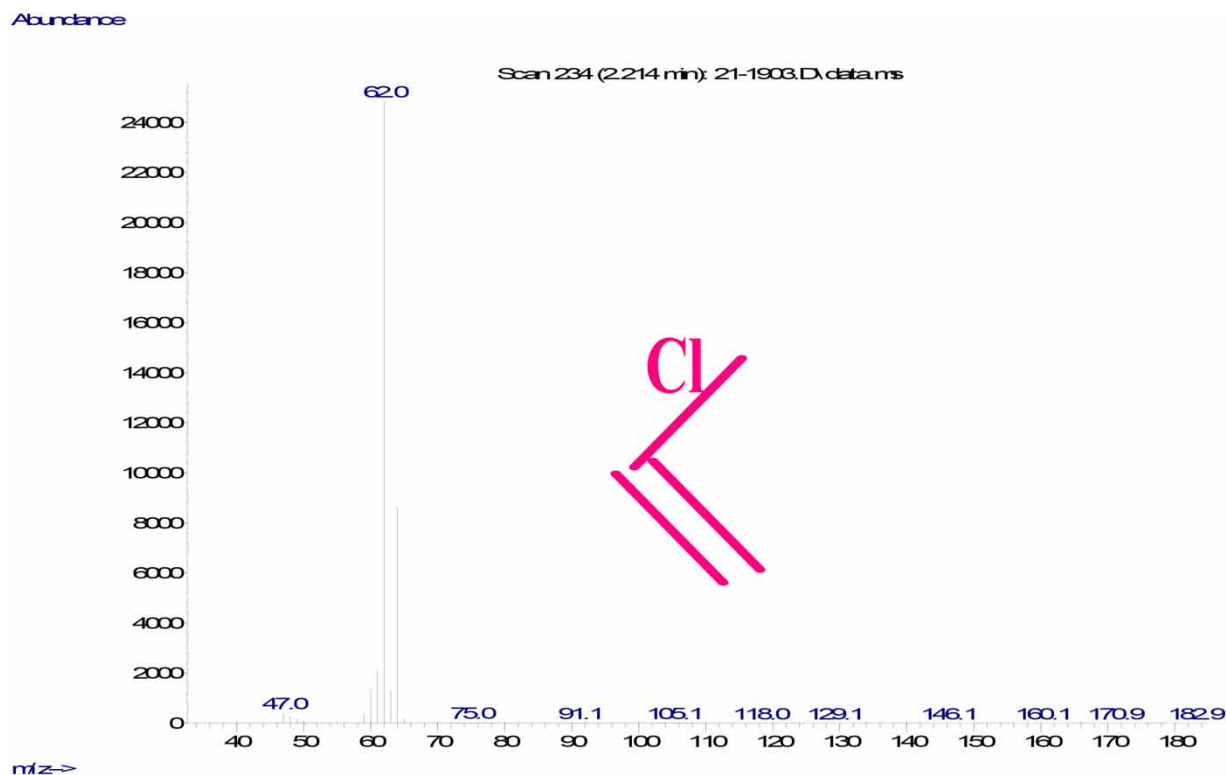


Figure 12 | GC-MS chromatogram of 1,2-DCA degradation intermediates at the reaction time of 60 min in the $\text{CaO}_2/\text{Fe(III)}$ system ($[\text{CaO}_2]_0 = 6.0 \text{ mM}$, $[\text{Fe(III)}]_0 = 24 \text{ mM}$, $[\text{1,2-DCA}]_0 = 0.2 \text{ mM}$).

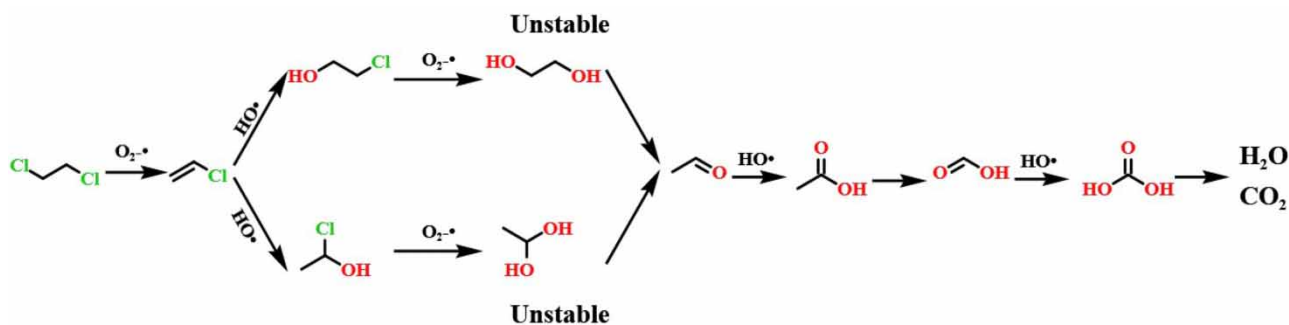


Figure 13 | Proposed 1,2-DCA degradation pathway in the $\text{CaO}_2/\text{Fe(III)}$ system ($[\text{CaO}_2]_0 = 6.0 \text{ mM}$, $[\text{Fe(III)}]_0 = 24 \text{ mM}$, $[\text{1,2-DCA}]_0 = 0.2 \text{ mM}$).

4. CONCLUSIONS

- (1) A total of 83.3% of 1,2-DCA could be effectively degraded in the $\text{CaO}_2/\text{Fe(III)}$ system when the molar ratio of $\text{CaO}_2/\text{Fe(III)}/\text{1,2-DCA}$ was 30/120/1, and both HO^\bullet and $\text{O}_2^{\bullet-}$ contributed to the 1,2-DCA removal.
- (2) The 1,2-DCA could be efficiently removed in the $\text{CaO}_2/\text{Fe(III)}$ system in the initial pH range of 3–11, and the negative effect of anions followed the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$.
- (3) The released concentration of Cl^- (84.1%) revealed that most of the chlorine in 1,2-DCA could be dechlorinated. Based on the detection results of GC-MS, 1,2-DCA was firstly reduced to VC and later oxidized to CO_2 and H_2O .
- (4) The degradation performance of 1,2-DCA in actual groundwater was not as efficient as that in ultrapure water due to the buffering and coexistence of ions in the actual groundwater, but increasing chemical dosages could overcome this shortcoming, demonstrating that the $\text{CaO}_2/\text{Fe(III)}$ system has a remarkable prospect in 1,2-DCA-contaminated groundwater remediation.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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