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The destruction of benzene by calcium peroxide activated with Fe(II) in water

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Abstract

The ability of Fe(II)-activated calcium peroxide (CaO_2) to remove benzene is examined with a series of batch experiments. The results showed that benzene concentrations were reduced by 20 to 100% within 30 min. The magnitude of removal was dependent on the $\text{CaO}_2/\text{Fe(II)}/\text{Benzene}$ molar ratio, with much greater destruction observed for ratios of 4/4/1 or greater. An empirical equation was developed to quantify the destruction rate dependence on reagent composition. The presence of oxidative hydroxyl radicals ($\text{HO}^\bullet$) and reductive radicals (primarily $\text{O}_2^{\bullet-}$) was identified by probe compound testing and electron paramagnetic resonance (EPR) tests. The results of the EPR tests indicated that the application of $\text{CaO}_2/\text{Fe(II)}$ enabled the radical intensity to remain steady for a relatively long time. The effect of initial solution pH was also investigated, and $\text{CaO}_2/\text{Fe(II)}$ enabled benzene removal over a wide pH range of 3.0–9.0. The results of radical scavenging tests showed that benzene removal occurred primarily by $\text{HO}^\bullet$ oxidation in the $\text{CaO}_2/\text{Fe(II)}$ system, although reductive radicals also contributed. The intermediates in benzene destruction were identified to be phenol and biphenyl. The results indicate that Fe(II)-activated CaO_2 is a feasible approach for treatment of benzene in contaminated groundwater remediation.

Keywords

calcium peroxide; benzene; ferrous iron; reactive oxygen species

1. Introduction

Low molecular weight aromatic hydrocarbons such as BTEX (benzene, toluene, ethylbenzene, and xylenes), which account for nearly 20% volume fraction in gasoline and other fuels [1–2], continue to be of great concern for environmental and human-health issues. BTEX contaminants have been widely detected in soil and groundwater due to discharges from chemical industries, accidental spills, and pipe/tank leaks. Numerous

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studies have reported on the potential risks to microorganisms, animals, plants [2–5] and humans [6–8] derived from exposure to BTEX contaminants. As a result, development and application of methods for remediation of BTEX contamination remains a focus of research.

The use of in-situ bioremediation for treatment of BTEX-contaminated sites has been well established, with both aerobic and anaerobic degradation approaches [9–13]. However, bioremediation is generally slow, and both aerobic and anaerobic technologies require strict redox conditions that limit their applications [14]. While aerobic biodegradation is typically more effective, the flux of oxygen in subsurface systems is often not adequate to support biodegradation, and supplementation is required.

Chemical oxidation is an alternative method to in-situ bioremediation that may be more time- and cost-effective in certain situations. Fenton's reagent (a mixture of hydrogen peroxide (H_2O_2) and ferrous salt) has attracted much attention as an oxidant for in-situ use due to its strong, non-selective oxidation capability and low environmental impact. The Fenton reaction generates hydroxyl radical ($\text{HO}^\bullet$), which possesses a high oxidation potential (2.76 V) [15], and many studies have concluded that $\text{HO}^\bullet$ is a strong and relatively indiscriminate oxidant that can react with most contaminants [16–17]. Several Fenton's oxidation based technologies have been adapted for soil and groundwater remediation [18–20]. The results of many studies have shown that the traditional Fenton oxidant is relatively ineffective for subsurface applications due to the instability of H_2O_2 and issues with Fe availability. Therefore, solid H_2O_2 sources that can slow and control the release of H_2O_2 are of interest for in-situ applications.

Calcium peroxide (CaO_2) is one effective solid-phase source of hydrogen peroxide, releasing H_2O_2 and $\text{Ca}(\text{OH})_2$ when dissolved in water via:

releasing a maximum of 0.47 g H_2O_2 /g CaO_2 [21]. Compared to traditional liquid H_2O_2 , the H_2O_2 liberated from CaO_2 is auto-regulated by the dissolution of CaO_2 , thus reducing the decomposition loss of H_2O_2 . Ndjou'ou and Cassidy [22] observed that CaO_2 -based oxidation produced at least 20% greater degradation of contaminants compared to liquid H_2O_2 . Several studies have reported the use of CaO_2 for removal of various contaminants. Xu et al. [23] studied chemical oxidation of cable oil with solid CaO_2 , and the highest cable oil removal efficiency for CaO_2 was 18% at pH 1.8; Goi et al. [24] applied CaO_2 for the treatment of soil contaminated by polychlorinated biphenyls-containing electrical insulating oil, which resulting in nearly complete ($96 \pm 2\%$) oil removal; Zhang et al. [25] reported CaO_2 alone was also effective for removing six phenolic endocrine disrupting compounds from waste activated sludge over the wide pH range of 2 to 12; and Li et al. [26] have demonstrated CaO_2 can remove refractory organic contaminants effectively, which are non-biodegradable under ordinary anaerobic conditions. In addition, the removal of a wide variety of pollutants, including 2,4,6-trinitrotoluene (TNT) [27], total petroleum hydrocarbons (TPHs) [22], polycyclic aromatic hydrocarbons (PAHs) [28], trichloroethene (TCE) [29], and tetrachloroethene (PCE) [30] have been also reported.

To date there has been minimal investigation of CaO_2 for oxidative treatment of BTEX compounds. The reaction mechanisms and the dominant reactive oxygen radicals responsible for contaminant removal have yet to be studied. Therefore, the objectives of this research are to (1) evaluate the destruction of benzene in a $\text{CaO}_2/\text{Fe(II)}$ oxidation system; (2) identify the main reactive species contributing to benzene removal by using probe compounds, free-radical scavenging reagents, and electron paramagnetic resonance (EPR) tests; (3) establish an empirical mathematical model to quantify the reaction; (4) assess the impacts of solution pH; and (5) propose the mechanism of benzene destruction in the $\text{CaO}_2/\text{Fe(II)}$ system. It is anticipated that these experiments will provide fundamental support for BTEX-contaminated groundwater remediation using Fe(II) -activated CaO_2 .

2. Experiments

2.1 Materials

Ultrapure water (Milli-Q Classic DI, ELGA, Marlow, UK) was used for preparing the aqueous solutions. Benzene (99.7%) and calcium peroxide (CaO_2 , 75%) were provided by the Aladdin Reagent Co. Ltd. (Shanghai, China). Carbon tetrachloride (CT, 99.5%), methanol (CH_3OH , 99.9%), n-hexane (C_6H_{14} , 97%), and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.5%) were purchased from the Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Isopropanol ($\text{C}_3\text{H}_8\text{O}$, IPA, 99.5%), trichloromethane (CHCl_3 , 99.0%), and nitrobenzene (NB, 99.0%) were purchased from the Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Sigma (Shanghai, China). H_2SO_4 (0.1 M) or NaOH (0.1 M) was used for solution pH adjustment.

2.2 Experiment design

The experiments were conducted using custom glass vessels with a fluid capacity of 250 mL and a jacket for temperature control at $20 \pm 0.5^\circ\text{C}$. The solutions were mixed with a magnetic stirrer at moderate speed. Pure benzene was equilibrated with Milli-Q water and then diluted to the desired concentration. The initial concentration of benzene in all tests was set at 1.0 mM. All chemicals involved in the reactions (such as benzene, ferrous sulfate, etc.) except for CaO_2 were completely dissolved in the reactor, and the reaction started as soon as the predetermined CaO_2 dosage was added. Control reactors with no CaO_2 added were used for each experiment treatment. The initial solution pH in all tests was unadjusted except for the specific experiment that investigated the influence of solution pH. For this case, the pH was adjusted before addition of Fe(II) and CaO_2 . 2.5-mL samples were collected from the reactor at the desired time and added to a headspace vial containing 1.0 mL methanol solution to stop further reaction and sealed for immediate analysis by headspace-gas chromatography (HS-GC).

Radical probe tests were performed to identify the reactive species involved in the reactions. For these tests, benzene was replaced by either NB ($\text{HO}^\bullet$ probe) [31–32] or CT ($\text{O}_2^{\bullet-}$ probe) [33–34]. Additional details of the probe test are presented in the Supplementary Materials. EPR detection was conducted to confirm the primary radicals present in the $\text{CaO}_2/\text{Fe(II)}$ system. This test used DMPO to trap the radicals in solution. At the desired time intervals,

samples (1.0 mL) were collected from the benzene destruction reactors and thoroughly mixed with 1.0 mL DMPO solution (8.84 mM) for 1 min. The mixed sample was then analyzed with the EPR instrument. In addition, radical scavenger tests were conducted to help characterize the dominant reactive species. The compounds IPA ($\text{HO}^\bullet$ scavenger) [32] and CHCl_3 ($\text{O}_2^{\bullet-}$ scavenger) [34] were used as radical scavengers and added to the benzene destruction solution to assess the impacts of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals. Ethyl acetate was used in extracting products formed in benzene destruction, and the concentrated ethyl acetate was then analyzed by GC/MS. Additional details of the scavenger test are presented in the Supplementary Materials.

Central composite designs (CCD) are multivariable, multilevel experimental procedures that analyze the interactions between variables and produce response equations. If the two variables are evaluated and represented on the x and y axis of a coordinate system, the results can be described by a response surface [e.g., 35]. To determine the optimum conditions for the $\text{CaO}_2/\text{Fe(II)}$ system, a CCD with two factors was applied in the present study (Table 1). Two variables (CaO_2 concentration and Fe(II) concentration) were investigated in the $\text{CaO}_2/\text{Fe(II)}$ system for oxidation of benzene using CCD experiments. The variables X_i are coded as x_i according to Eq. 2:

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \quad (2)$$

where X_i is the real value of the input variable, X_{i0} is the value of X_i at the center point of the investigated area and the ΔX_i is the step change. The response variable is fitted by a quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^2 \beta_i x_i + \sum_{i=1}^2 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} x_i x_j \quad (3)$$

where Y is the response variable (the benzene destruction efficiency), x_i and x_j are the code values of the input variables, and β_0 , β_i , β_{ii} and β_j are the model coefficients.

2.3 Analytical methods

Benzene extract was analyzed using an Agilent HS-GC (Agilent 6890N, Palo Alto, CA, USA) with a flame ionization detector (FID), an HP-5 column (30-m length, 0.32-mm I.D., 0.25- μm thickness), and an auto-sampler (COMBI-PLA, CTC, Switzerland). The CT and NB extracts were analyzed using an Agilent gas chromatograph (Agilent 7890A, Palo Alto, CA, USA) with an electron capture detector (ECD), an auto-sampler (Agilent 7693), and a DB-VRX column (60 m length, 250 μm i.d., and 1.4 μm thickness). The intermediates formed in benzene destruction were identified by GC/MS (Agilent 6890/5973N). The free radicals were identified by EPR (EMX-8/2.7C, Bruker, Germany) using DMPO as a spin trap. The instrumental settings were as follows: field sweep: 100 G, microwave frequency: 9.866 GHz, microwave power: 2.016 mW, modulation amplitude: 1 G, conversion time: 40.96 ms, time constant: 163.84 ms, receiver gain: 3.17×10^4 , and number of scans: 1. The

pH was measured with a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland). The other specific conditions for the analyses can be found in our previously published paper [36].

The benzene destruction data were used to develop regression equations and modeled by using the software MINITAB. The analysis of variance (ANOVA) was used to assess the model. The resulted regression equations were plotted response surfaces using MINITAB software.

3. Results and Discussion

3.1 Effectiveness of $\text{CaO}_2/\text{Fe(II)}$ process for benzene destruction

The experiments were performed with a fixed benzene concentration (1.0 mM) at various $\text{CaO}_2/\text{Fe(II)}/\text{Benzene}$ molar ratios ranging from 1/1/1 to 10/10/1, and the results are presented in Fig. 1. The results from the control tests (absence of CaO_2) showed less than 7% benzene loss, likely by volatilization. CaO_2 or Fe(II) alone did not remove benzene in this study, which indicates that only Fe(II) -catalyzed CaO_2 can generate the reactive species responsible for benzene destruction (Supplementary material, Fig. S1).

As shown in Fig. 1, 26%, 48%, 89%, 100% and 98% of benzene was removed in 30 min at $\text{CaO}_2/\text{Fe(II)}/\text{benzene}$ molar ratios of 1/1/1, 2/2/1, 4/4/1, 8/8/1, and 10/10/1, respectively. It is clear that benzene destruction was enhanced with increasing dosages of CaO_2 and Fe(II) . The magnitude of benzene destruction approximately doubles with a doubling of the reactant concentrations up to a molar ratio of 4/4/1, at which point close to complete destruction is attained.

In addition, rapid benzene destruction was observed within the first 5 min, and the destruction became much slower in the remaining reaction time. This may be due to the fast generation of reactive species after CaO_2 was added into the reactor. The decomposition of CaO_2 produced H_2O_2 and this supported the rapid reaction with Fe(II) for generating reactive species within a short time period. Once CaO_2 was induced by Fe(II) along with the generation of reactive species, Fe(II) was oxidized into Fe(III) , which soon caused a shortage of Fe(II) . A rapid accumulation of Fe(III) accelerated the precipitation of Fe(OH)_3 , and the lack of Fe(II) impeded the radical propagation cycle, thus slowing down the benzene destruction.

Tawabini reported that benzene could be degraded more than 95% within 5 min by a $\text{UV}/\text{H}_2\text{O}_2$ process [37]; Daifullah and Mohamed also reported over 90% benzene degradation in 10 min of UV irradiation with the presence of H_2O_2 [38]; Liang et al. [39] reported the activated persulfate (PS) anion ($\text{S}^{2-}_2\text{O}_8^{2-}$) could remove nearly 70% benzene at $\text{PS}/\text{Fe(II)}/\text{benzene}$ molar ratio of 20/20/1 in 80 min. Compared to the above techniques, the $\text{CaO}_2/\text{Fe(II)}$ system is a feasible option in benzene destruction.

3.2 Detection of free radicals by EPR

To identify the reactive species, a series of tests were conducted with probes, scavenger compounds, and EPR for the detection of radicals. All of the experiments were designed and

performed based on the hypothesis that $\text{CaO}_2/\text{Fe(II)}$ is a Fenton-like process. The probe and scavenging experiment results are listed in Supplementary Materials. The acquired probe-tests results (Fig. S1) demonstrate the presence of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$, suggesting that CaO_2 is a viable alternative as a Fenton-like system. EPR detection was conducted to further confirm the radicals present in the $\text{CaO}_2/\text{Fe(II)}$ system. Fig. 2a shows the radical intensity variation and Fig. 2b presents the typical EPR spectrum of the $\text{CaO}_2/\text{Fe(II)}$ system.

A DMPO-OH adduct was observed in the EPR spectra. The EPR spectrum, which has a specific quartet spectrum with peak height ratios of 1:2:2:1, indicated the formation of $\text{HO}^\bullet$. The results are consistent with other research [40]. The EPR detection, together with the results of the scavenging tests (Fig. S2), indicated that $\text{HO}^\bullet$ is the predominant radical in the $\text{CaO}_2/\text{Fe(II)}$ system. However, the peaks of $\text{O}_2^{\bullet-}$ was not confirmed during the EPR analyses, which could be attributed to the low intensity of $\text{O}_2^{\bullet-}$ and the complicated solution composition in the $\text{CaO}_2/\text{Fe(II)}$ system.

3.3 Effect of CaO_2 and Fe(II) dosages on benzene destruction

The effect of CaO_2 and Fe(II) dosage corresponding to various $\text{CaO}_2/\text{Fe(II)}/\text{Benzene}$ molar ratios on benzene destruction performance was investigated, and the results are shown in Fig. 3. The first set of experiments was performed by fixing Fe(II) at 4 mM while varying the CaO_2 concentration from 2 to 8 mM in order to explore the effect of CaO_2 dosage on benzene removal (Fig. 3a). With the increase in the initial CaO_2 dosage from 2 to 4 mM, the benzene destruction rate increased from 80% to 89% in 30 min. However, excessive CaO_2 decreased the benzene destruction efficiency to 44% over the same reaction time when the initial CaO_2 concentration was increased to 8 mM.

With an increase in CaO_2 dosage, the generation of H_2O_2 was increased and thus the production of radicals was enhanced. As a result, benzene removal increased. However, an elevation in solution pH was observed; the final solution pH levels increased to 8.9 and 11.6 when the $\text{CaO}_2/\text{Fe(II)}/\text{Benzene}$ molar ratios were 4/4/1 and 8/4/1, respectively. It was also noted that the dissolution of CaO_2 could produce Ca(OH)_2 (Eq. 1) and then increase the solution pH, which imparts a negative effect on the Fenton reaction [41]. Moreover, the excessive CaO_2 generated excessive H_2O_2 , which in turn scavenged the reactive species via the reaction in Eq. 4 [15]:

It is clear that the solution pH was a significant factor in the $\text{CaO}_2/\text{Fe(II)}$ system and will be discussed in a later section of this study.

The second set of experiments was performed by fixing CaO_2 at 4 mM while varying the Fe(II) concentration from 2 to 8 mM to explore the effect of Fe(II) dosage on benzene removal (Fig. 3b). It is apparent that the increase in Fe(II) dosage accelerated the oxidation of benzene. The benzene removal increased from 36% to 89% when the initial Fe(II) dosage increased from 2 to 4 mM. Conversely, an increase in the Fe(II) concentration to 8 mM did not enhance efficiency anymore. This result could be due to the reactions shown in Eqs. 5

and 6. Although an increased Fe(II) dosage could lower the solution pH (the final solution pH was 4.8 at the molar ratio of 4/8/1) and benefit benzene destruction, excessive Fe(II) could also scavenge HO[•] (Eq. 6) [42] and result in reduced removal.

Northup [30] also reported that the yield of H₂O₂ and the dissolution rate of CaO₂ increased with the decreasing of solution pH. The increased Fe(II) dosage could lower the solution pH and accelerated the release of H₂O₂ from CaO₂. Therefore, Fe(II) not only participated in the reaction with H₂O₂, but also promoted the release of H₂O₂ from CaO₂ by decreasing the solution pH. At an optimal molar ratio of CaO₂/Fe(II), the iron could accelerate the release of H₂O₂ as well as activate the released H₂O₂, thereby enhancing HO[•] radicals generation at a steady rate as shown in Fig. 2.

3.4 A mathematical model for the CaO₂/Fe(II) system

To better understand the influence of the identified variables on the destruction of benzene in the CaO₂/Fe(II) system, benzene removal was used as the response variable for the RSM. By fitting the values of benzene removal in Table S1, a quadratic polynomial model was derived as Eq. 7:

$$Y = -0.159 + 0.0340 * [\text{CaO}_2] + 0.2391 * [\text{Fe(II)}] - 0.01342 * [\text{CaO}_2] * [\text{CaO}_2] - 0.02143 * [\text{Fe(II)}] * [\text{Fe(II)}] + 0.01886 * [\text{CaO}_2] * [\text{Fe(II)}] \quad (7)$$

The analysis of variance (ANOVA) for Eq. 7 is shown in Table S2. The P-value of the model is less than 0.05, indicating that the model is significant. A high correlation coefficient (R²) of 0.980 suggests a good agreement between the experimental values and the model predicted values. The ANOVA revealed a significant interaction effect of the concentration of CaO₂ and Fe(II) on the destruction kinetics of benzene (F = 33.67; P < 0.05). Fig. 4 is the response surface graph of removal values of benzene showing the influence of the concentration of CaO₂ and Fe(II). It can be seen that the optimum molar ratio of CaO₂ and Fe(II) close to 1:1. The response surface shows that the optimum conditions for benzene destruction were 8.0 mM CaO₂ and 8.0 mM Fe(II) in this study.

3.5 Effect of initial solution pH on benzene treatment

Benzene destruction in the CaO₂/Fe(II) system for a pH range of 3.0~11.0 is shown in Fig. 5. Benzene removal surpassed 80% within 5 min when the initial solution pH ranged from 3.0 to 9.0, whereas the destruction was less than 60% when the initial solution pH was 11.0. Therefore, pH appears to have a significant impact on benzene destruction in the CaO₂/

Fe(II) system when it exceeds ~9. Greater destruction at lower solution pH is consistent with existing literature [25, 36, 43].

The Fe(II) and H₂O₂ speciation are strongly influenced by the solution pH in the conventional Fenton reaction. The elevation of solution pH facilitates the precipitation of Fe(III) in the form of Fe(OH)₃, thus impeding radical propagation. This drawback was also observed for the CaO₂/Fe(II) system. In addition, CaO₂ dissolution is significantly influenced by the solution pH [30–31], thus the generation of H₂O₂ in the CaO₂/Fe(II) system was constrained by the solution pH, resulting in the decrease of HO• generation and benzene destruction. When the pH was less than 10.0, CaO₂ mainly released H₂O₂ via Eq. 1; but when the pH increased to 11.0, CaO₂ mainly produced Ca(OH)₂ and O₂ through Eq. 8 [29–30].

Hence, the release of H₂O₂ in the CaO₂/Fe(II) system can be regulated by adjusting the pH. These results suggest that CaO₂-based radical generation is viable over a wide range of pH, which is a significant advantage compared to the conventional Fenton reaction.

Based on the benzene removal pattern, benzene destruction is treated as a second-order reaction [44], which can be described as follows:

$$-dC_i/dt = k_{\text{obs}} * C_i^2 \quad (9)$$

It can then be modified as:

$$1/C_i = 1/C_0 + k_{\text{obs}} * t \quad (10)$$

where C₀ is the initial benzene concentration in solution (mM); C_i is the benzene concentration at time t (mM); and t is the reaction time (min); k_{obs} is the second-order reaction rate constant that represents the overall rate of benzene destruction by a variety of oxidizing or reducing species (e.g., HO• and O₂^{•-}) generated in the system (M⁻¹ min⁻¹) under various initial solution pH levels, and the R² values are summarized in Table 2. It is observed that k_{obs} increased from 0.042 to 0.21 M⁻¹ min⁻¹ (0.0007 to 0.0035 M⁻¹ s⁻¹) with a decrease in the initial solution pH from 11.0 to 3.0. Due to the complicated composition of groundwater, the impact of changes in pH on benzene destruction should be investigated in more detail. This will be a focus in a future study.

3.6 The mechanism of benzene destruction

Phenol and biphenyl were identified to be the major intermediates in benzene destruction. As shown in Fig. S1, benzene removal was significantly inhibited when IPA was present. The final benzene removal decreased from 89% to 22% when IPA was added, indicating that

HO• is the dominant reactive species in the CaO₂/Fe(II) system. As for scavenging O₂^{•−}, the benzene removal decreased from 89% to 77% in the presence of chloroform. The inhibition of benzene destruction indicated that a certain amount of O₂^{•−} was generated in the reactions and contributed to benzene destruction to some extent. Based on the experimental results, HO• is the dominant reactive species, and possible benzene destruction pathways are shown in Fig. 6.

CaO₂ released H₂O₂ when dissolved in water, and the liberated H₂O₂ reacted with Fe²⁺ producing HO•. The produced HO• immediately abstracted hydrogen atom from benzene ring to form an unstable intermediate, which is presumed to be phenyl radical [45–46]; then phenol was produced through dehydration, and biphenyl formed after dimerization and dehydration. Other possible intermediates [45] were not identified by GC/MS.

4. Conclusions

This is an initial study that investigated the efficiency of benzene destruction by Fe(II)–activated CaO₂ in aqueous solution. The experimental results indicated that the CaO₂/Fe(II) system has the ability to remove benzene. Benzene destruction performance was related to the molar ratio of CaO₂/Fe(II)/Benzene whose optimum ratio was found to be 4/4/1. An empirical equation was developed based on the experimental data. The probe compound experiments clearly identified the generation of the reactive species, namely, HO• and O₂^{•−}, in the CaO₂/Fe(II) system. Furthermore, free radical scavenger tests further demonstrated that HO• was the dominant active species responsible for benzene removal and that O₂^{•−} partly contributed to the destruction. EPR tests also indicated that the application of CaO₂/Fe(II) enabled the radical intensity to remain steady for a relatively long time. The effect of the initial solution pH was investigated, and the results showed that CaO₂ enabled a high degree of benzene removal at a pH range of 3.0–9.0, with reduced degree of destruction at higher pH. Phenol and biphenyl were identified as the major intermediate products in benzene destruction. In summary, the CaO₂/Fe(II) system is a feasible technique for the destruction of benzene.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Benzene destruction in the CaO₂/Fe(II) system at different CaO₂/Fe(II)/Benzene molar ratios ([Benzene]₀ = 1.0 mM).

Fig. 2.

(a) The intensity of $\text{HO}^\bullet$ versus reaction time in the $\text{CaO}_2/\text{Fe(II)}$ system; (b) EPR spectra at the reaction time of 90 s ($[\text{CaO}_2]_0 = 4.0$ mM, $[\text{Fe(II)}]_0 = 4.0$ mM; peaks associated with the presence of DMPO-OH are indicated with $\downarrow$).

Fig. 3. Effect of (a) CaO₂ dosage and (b) Fe(II) dosage on benzene destruction ($[\text{Benzene}]_0 = 1.0$ mM). Values in the legend represent different CaO₂/Fe(II)/Benzene molar ratios.

Fig. 4. Response surface for benzene destruction in the $\text{CaO}_2/\text{Fe(II)}$ system (Isoresponselines represent percent oxidation).

Fig. 5. Effect of initial solution pH on benzene destruction in the $\text{CaO}_2/\text{Fe(II)}$ system ($[\text{Benzene}]_0 = 1.0 \text{ mM}$, $[\text{CaO}_2]_0 = 4.0 \text{ mM}$, $[\text{Fe(II)}]_0 = 4.0 \text{ mM}$, initial solution pH = 3.0, 5.0, 7.0, 9.0, 11.0).

Fig. 6.
Proposed benzene destruction pathway in the $\text{CaO}_2/\text{Fe(II)}$ system.

Table 1

Ranges and levels of the variables tested in the CCD

Independent variables	Symbol	Actual values of the coded variable levels				
		-1.41421	-1	0	1	1.41421
CaO ₂ /mM	X1	2	3.17	6.00	8.83	10
Fe(II)/mM	X2	2	3.17	6.00	8.83	10

Table 2

Kinetic parameters in benzene destruction under various pHs

pH	Operational conditions	k_{obs} ($\text{M}^{-1} \text{s}^{-1}$)	R^2
3.0	CaO ₂ /Fe(II)/Benzene = 4/4/1 ([Benzene] ₀ = 1.0 mM)	0.0035	0.9667
5.0		0.0025	0.8885
7.0		0.0022	0.9254
9.0		0.0023	0.9525
11.0		0.0007	0.7676