

Research Article

Heat-Activated Persulfate Oxidation of Chlorinated Solvents in Sandy Soil

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Heat-activated persulfate oxidative treatment of chlorinated organic solvents containing chlorinated ethenes and ethanes in soil was investigated with different persulfate dosages (20 g/L, 40 g/L, and 60 g/L) and different temperatures (30°C, 40°C, and 50°C). Chlorinated organic solvents removal was increased as persulfate concentration increase. The persulfate dosage of 20 g/L with the highest OE (oxidant efficiency) value was economically suitable for chlorinated organic solvents removal. The increasing temperature contributed to the increasing depletion of chlorinated organic solvents. Chlorinated ethenes were more easily removed than chlorinated ethanes. Moreover, the persulfate depletion followed the pseudo-first-order reaction kinetics ($k_{ps} = 0.0292 [PS]_0 + 0.0008$, $R^2 = 0.9771$). Heat-activated persulfate appeared to be an effective oxidant for treatment of chlorinated hydrocarbons.

1. Introduction

The chlorinated organic solvents such as trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), 1,1,1-trichloroethane (TCA), and 1,2-dichloroethane (1,2-DCA) have been widely used for decades as a degreasing agent, a cleaning agent, and organic synthesis intermediates in chemical, pharmaceutical, electronic, tanning, printing, and other industries [1–3]. The chlorinated organic solvents were considered as priority toxic pollutants and associated risks to humans representing a public health threat. Historically, the improper disposal of these chlorinated organic solvents has resulted in extensive contamination of soils and groundwater. Due to the high density and low water solubility, the chlorinated organic solvents sink beneath the water table, do not pool, and rather continue to migrate downward in the aquifer, displacing the water until reaching a formation of sufficient impermeability to prevent further migration. That is, it will last a long time, once subsurface medium was contaminated. Therefore, it is urgent to find a fast and efficient method to remediate chlorinated solvents in soils.

In situ chemical oxidation (ISCO) is a remediation technology used to clean up contaminated soils and groundwater

in-place. It has been greatly recognized and widely applied in many contaminated field sites. The typical oxidants used for ISCO are potassium permanganate, hydrogen peroxide (Fenton's reagent), and ozone [4]. Each oxidant has its limitations (e.g., persistence, reactivity, etc.) within a soil matrix [5]. Recently, persulfate ($Na_2S_2O_8$, PS) emerged as an efficient oxidant for ISCO applications with the properties of high water solubility, no odor, effectiveness of oxidation over a wide range of pH, and lower affinity for soil organics [6]. The use of persulfate for soil and groundwater treatment holds a lot of promise as persulfate can combine the strength of hydrogen peroxide with the stability of permanganate [4]. Persulfate can be thermally [2, 7–9], chemically [10–12], or photochemically [13] activated to generate the powerful oxidant known as the sulfate free radical ($SO_4^{\cdot-}$), with a redox potential of 2.6 V [14], which can be instrumental in the destruction of most organic contaminants commonly present in soil and groundwater including trichloroethylene [5, 6, 15], naphthalene [11], and phenol [8, 13, 16]. Compared with other activations, heat activation is the most effective activation technology. Thermally activated persulfate oxidation of chlorinated organic solvents such as TCE has been quite successful in remediating groundwater contaminant.

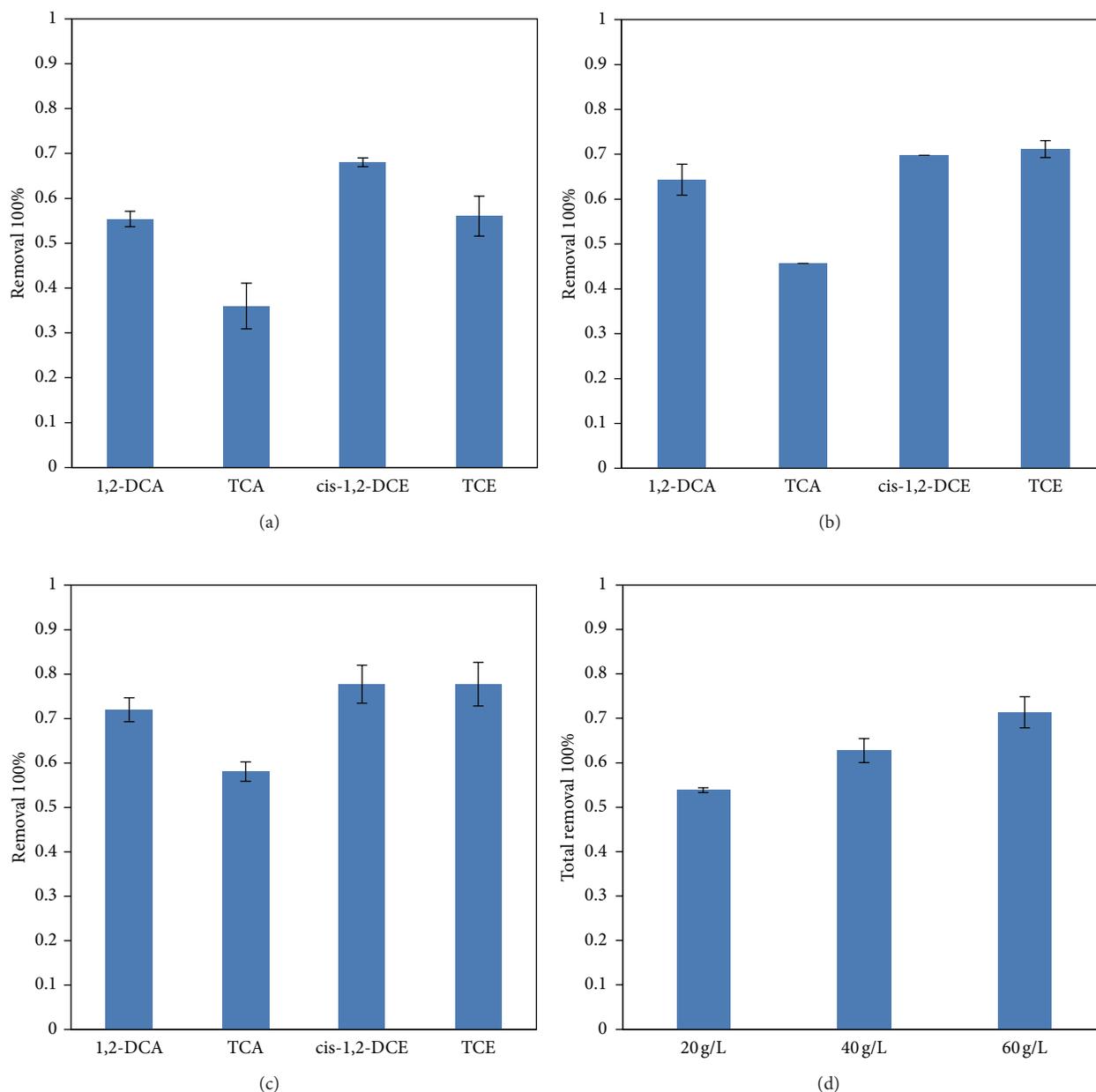


FIGURE 1: The depletion of chlorinated organic solvents by activated persulfate at 30°C with different persulfate dosages: (a) 20 g/L, (b) 40 g/L, and (c) 60 g/L, and (d) the total removal of chlorinated organic solvents.

However, most studies focus on the treatment of single contaminants, such as TCE or TCA, and focus on the treatment of groundwater rather than soils.

In this study, research focuses on the heat-activated persulfate oxidative treatment of organic compounds containing chlorinated ethenes and ethanes in the subsurface medium. The most suitable persulfate dosage for chlorinated organic compounds depletion was determined and the influence of activated persulfate oxidative chlorinated organic compounds under different temperature was investigated.

2. Materials and Methods

2.1. Materials. All chemicals were of analytical grade except for methanol (CH_3OH , >99.5%, Sinopharm Chemical Reagent Co., Ltd.) which was of HPLC grade. Persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd, and used as oxidizer. The pure trichloroethene (TCE, >99.0%), cis-1,2-dichloroethene (cis-1,2-DCE, >99.0%), 1,1,1-trichloroethane (TCA, >94.0%), and 1,2-dichloroethane (1,2-DCA, >99.0%) were purchased from

Sinopharm Chemical Reagent Co., Ltd, and diluted to the certain concentration for each experiment. Methanol was used to extract the organic contaminants from soil slurry samples and to quench the oxidation reaction. Sodium bicarbonate (NaHCO_3 , >99.0%) and potassium iodide (KI, >99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd, and used for persulfate analysis. Mixed standard solutions ($10 \mu\text{g/mL}$) of trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), 1,1,1-trichloroethane (TCA), and 1,2-dichloroethane (1,2-DCA) in purge and trap grade methanol were purchased from Sinopharm Chemical Reagent Co., Ltd, and used as an internal standard for gas chromatography analysis. Ultrapure water from a Millipore system was used in the experiments.

Coarse sandy soil (0.5–2 mm) was prepared.

2.2. Laboratory Experiments. The mixed solution of TCE, cis-1,2-DCE, TCA, and 1,2-DCA was prepared as stock solution and diluted to the certain concentration (81.8, 71.2, 75.0, and 70.6 mg/L of TCE, cis-1,2-DCE, TCA, and 1,2-DCA, resp.) for each experiment. And a series of 30 mL brown reaction bottles equipped with Agilent caps and TFE liners were used for all tests. For each test, 25 mL water and 25 g soil were sequentially added to the reaction bottle with the solid-water ratio of 1:1 and mixed followed by injection of $7 \mu\text{L}$ mixed contaminated solution and a predetermined amount of persulfate solution. Finally, a predetermined amount of water was added via a syringe to make sure the reaction bottle filled with no air bubbles. All the reaction bottles were shaken continuously on a ZWY-240 thermostatic reciprocating shaker at 100 r/min. At each time interval, $50 \mu\text{L}$ sample was collected via a syringe from each reaction bottle for persulfate analysis and $50 \mu\text{L}$ sample was collected with methanol addition for organic compounds analysis. All experiments were conducted in duplicate. Control tests in the absence of persulfate were also carried out.

2.3. Analysis. Persulfate anion concentration was determined using a spectrophotometric method with potassium iodide [17]. The organic compounds (TCE, DCE, TCA, and DCA) were quantified using HP7890A gas chromatography equipped with a column HP-5MS ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) capillary column.

3. Results and Discussion

3.1. Influence of Persulfate Dosage. The depletion of chlorinated organic solvents by activated persulfate at 30°C was illustrated in Figure 1. The low TCA removal was obtained at the persulfate concentration of 20, 40, or 60 g/L. The high removal was up to 79.5%, 74.0%, 69.7%, and 54.8% of TCE, cis-1,2-DCE, 1,2-DCA, and TCA, respectively, while the persulfate concentration of 60 g/L was carried out. The phenomenon showed that chlorinated ethenes (TCE and cis-1,2-DCE) were more easily removed than chlorinated ethanes (TCA and 1,2-DCA). Chlorinated organic solvents removal was increased as persulfate concentration increased (shown in Figure 1(d)), but meanwhile, more persulfate could

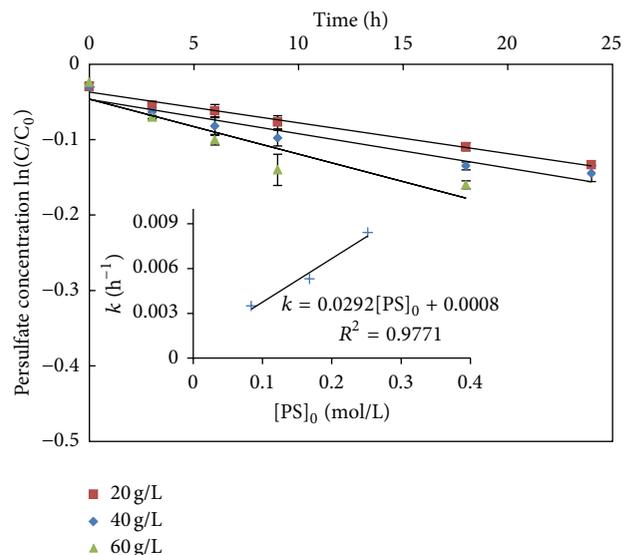


FIGURE 2: The decomposition of persulfate in the reactive system.

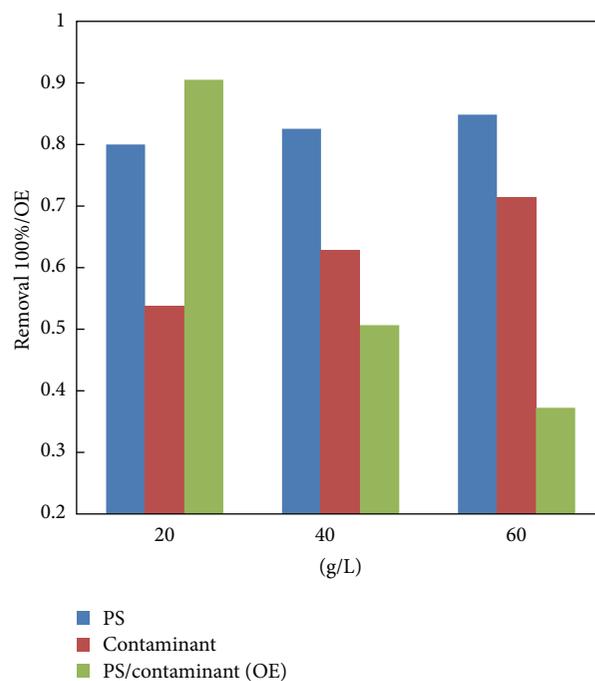


FIGURE 3: The decomposition of persulfate and contaminants after 72 h reaction time and the oxidant efficiency in the reactive system.

be decomposed (shown in Figure 2). The semilogarithmic graphs of $[\text{PS}]/[\text{PS}]_0$ under different initial persulfate concentration as a function of reaction time were shown in Figure 2. Results demonstrated that the depletion rate was pseudo-first-order with respect to the initial persulfate concentration, and a similar result was described by Deng et al. [9]. For a given $[\text{PS}]_0$, the depletion rate constant k_{ps} decreased from 0.0035 to 0.0084 h^{-1} with increasing initial persulfate concentration ($[\text{PS}]_0$) from 20 to 60 g/L. As shown in the

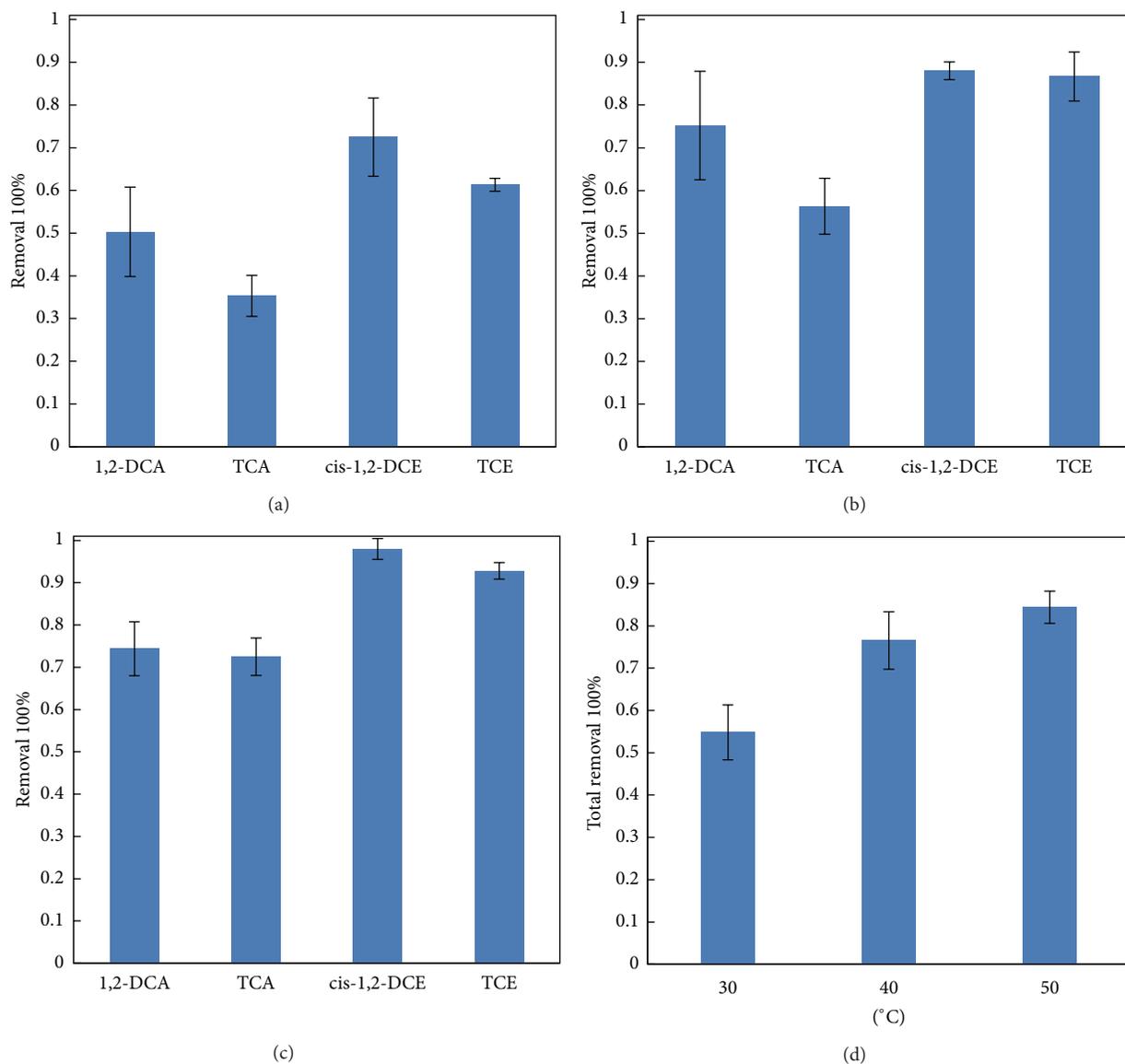


FIGURE 4: The depletion of chlorinated organic solvents by activated persulfate at different temperatures: (a) 30°C, (b) 40°C, and (c) 50°C after 72 h reaction time.

insert image of Figure 2, the depletion rate constant exhibits a linear trend ($k_{ps} = 0.0292 [\text{PS}]_0 + 0.0008$, $R^2 = 0.9771$). Therefore, the test with increasing persulfate dosage resulted in more decomposed persulfate. Moreover, the test with 20 g/L persulfate concentration resulted in the highest OE value (the oxidant efficiency (mmol of contaminant depletion per g of persulfate decomposition)) [18], shown in Figure 3. Thus, the persulfate dosage of 20 g/L was economically suitable for chlorinated organic solvents removal.

3.2. Influence of Temperature. The depletion of chlorinated solvents by thermal activated persulfate at different temperatures was illustrated in Figure 4. Results showed that cis-1,2-DCE obtained the highest removal by activated persulfate, followed by TCE, 1,2-DCA, and TCA at 30°C, 40°C, or 50°C.

The test with 30°C resulted in the low 1,2-DCA, TCA, cis-1,2-DCE, and TCE removal of 50.3%, 35.3%, 72.5%, and 61.3%, respectively. Compared with TCA and TCE, 1,2-DCA and cis-1,2-DCE obtained higher removal which related to the active molecular structure. The highest TCE, cis-1,2-DCE, 1,2-DCA, and TCA removal was up to 79.5%, 74.0%, 69.7%, and 54.8%, respectively, while the test with temperature 50°C was carried out. In general, the depletion of chlorinated solvents was increased with increasing temperature. First, the increasing temperature resulted in higher activation energy, which is in favor of generating the significant oxidant ($\text{SO}_4^{\cdot-}$). Second, the high temperature can accelerate the reaction of chlorinated organic solvents with persulfate. Moreover, heat can also accelerate desorption from soil phase to aqueous phase, which contributes to the further destruction of chlorinated organic solvents.

4. Conclusion

In this study, heat-activated persulfate appeared to be the most effective oxidant for treatment of chlorinated organic solvents. Chlorinated organic solvents removal was increased as persulfate concentration increased. The persulfate dosage of 20 g/L with the highest OE (oxidant efficiency) value was economically suitable for chlorinated organic solvents removal. The increasing temperature contributed to the increasing depletion of chlorinated organic solvents. Chlorinated ethenes (TCE and cis-1,2-DCE) were more easily removed than chlorinated ethanes (TCA and 1,2-DCA). Moreover, the persulfate depletion followed the pseudo-first-order reaction kinetics ($k_{ps} = 0.0292 [PS]_0 + 0.0008$, $R^2 = 0.9771$).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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