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Treatment of 1,4-dioxane and trichloroethene co-contamination by an activated binary persulfate-peroxide oxidation process

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Abstract

The efficacy of a binary oxidant system, hydrogen peroxide (H₂O₂) and persulfate, was investigated for treatment of 1,4-dioxane (dioxane) and trichloroethene (TCE) co-contamination. Batch experiments were conducted to examine the catalytic efficiency of Fe²⁺ and NaOH based activation, oxidant decomposition rates, contaminant degradation effectiveness, and competitive degradation effects. For NaOH-activation, the oxidant decomposition rate was moderate and sustained during the entire test period of 96 hours. However, dioxane degradation was limited (~33%). Conversely, the oxidants were depleted within 24 hours for the Fe²⁺-activated system, and dioxane degradation was complete within 4 hours. The activation and radical generation processes were different between Fe²⁺ and NaOH activation. Both dioxane and TCE underwent complete degradation in the co-contaminant experiment. The results of this study indicate that the Fe²⁺-catalyzed binary hydrogen peroxide-persulfate oxidant system is effective for oxidation of the tested contaminants separately and as co-contaminants.

Keywords

1,4-Dioxane; Trichloroethene; Co-contamination; Advanced oxidation; Activation mechanism

1. Introduction

1,4-Dioxane (dioxane), a prior commonly used chlorinated solvent stabilizer, has become an environmental concern due to its widespread occurrence and potential negative effects on human health. It has been classified as a suspected carcinogenic compound by the United State Environmental Protection Agency (U.S. EPA) and by the International Agency for Research on Cancer (IARC) (IARC 1999). Dioxane has been detected frequently in both surface and subsurface water bodies throughout the world (Abe 1999; Mohr et al. 2010; Zenker et al. 2003). The results of a recent survey of sites with groundwater contamination

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indicated a median maximal concentration of dioxane of 365 µg/L (Adamson et al. 2014). Field data has shown that dioxane is present along with trichloroethylene (TCE) and other chlorinated-solvent compounds in groundwater at some sites (Adamson et al. 2014; Anderson et al. 2012; EPA 2013). One example is the Tucson International Airport Area (TIAA) Superfund site in Tucson, AZ (Figure S1).

Groundwater extraction with subsequent above-ground treatment (pump and treat) is one of the most widely used groundwater remediation technologies. It is typically used to remediate groundwater contaminated by chlorinated-solvent compounds and dioxane. As a hydrophilic compound (water solubility=4.4×10⁵ mg/L, vapor pressure=29 mmHg; 20°C), dioxane cannot be treated cost-effectively by traditional methods such as granular activated carbon adsorption and air stripping. It is also generally resistant to biological treatment (EPA, 2018). Thus, advanced oxidation processes (AOPs) are being used for above-ground treatment of dioxane contaminated groundwater as well as wastewaters (e.g. Adams et al. 1994; Chitra et al. 2012; Felix- Navarro et al. 2013; Ghosh et al. 2010; Merayo et al. 2014; Mohr et al. 2010; Vescovi et al. 2010; Zhao et al. 2014). However, it is well established that site closure will likely require many decades or longer using pump-and-treat based remediation methods (e.g. EPA 2003; NRC 2013). The significant costs associated with long-term operation of pump-and-treat systems results in an enormous financial burden for site remediation. Thus, alternatives based on in-situ treatment and management of groundwater contaminant plumes are being investigated.

In-situ chemical oxidation (ISCO) has been demonstrated to be a relatively effective treatment method for subsurface systems. Ozone (O₃), permanganate (MnO₄⁻), hydrogen peroxide (H₂O₂), and persulfate (S₂O₈²⁻) have been used as ISCO reagents due to their high oxidation potentials (e.g. Krembs et al. 2010; Tsitonaki et al. 2010; Watts and Teel 2006). Each of the oxidants have their advantages and disadvantages, which are discussed in detail in the preceding references. The use of persulfate has some advantages for subsurface applications, and it has been proven to be effective for the treatment of TCE (e.g., Liang et al. 2004a; Liang et al. 2004b) and dioxane (Zhong et al., 2015; Eberle et al. 2016; Yan et al., 2016).

A promising binary oxidant reagent, catalyzed persulfate coupled with hydrogen peroxide, has been shown to be effective for treatment of chlorinated-solvent compounds (Huang et al. 2012; Ko et al. 2012; Yan et al. 2013,2015,2017). Compared to the traditional Fenton reaction (Fe²⁺-catalyzed hydrogen peroxide), the addition of persulfate can moderate the decomposition rate of hydrogen peroxide (e.g. Yan et al. 2013; Yan et al. 2015). Also, the heat released by hydrogen peroxide decomposition can accelerate the activation of persulfate. In this manner, the binary oxidant system overcomes the disadvantage of using one oxidant alone, thus enhancing treatment effectiveness.

The effectiveness of catalyzed hydrogen peroxide-persulfate for dioxane degradation has not been investigated significantly. Furthermore, its potential for treatment of dioxane-TCE co-contamination has also not been explored. The objective of this study is to investigate the efficiency of the catalyzed hydrogen peroxide-persulfate binary oxidant system for dioxane degradation alone and as a co-contaminant with TCE. Heat (Lee et al. 2012; Johnson et al.

2008; Ghauch et al. 2012), base (Furman et al. 2010; Liang et al. 2007; Liang and Guo 2012), and transition metals (Li et al. 2017; Cheng et al. 2016; Barndok et al. 2016) are commonly used activators for ISCO. This study will focus on two activators practical for in-situ applications, ferrous ion (Fe^{2+}) and base (NaOH).

2. Materials and Methods

2.1. Materials

All of the reagents used in this study are reagent grade or higher. Trichloroethene (TCE, > 99.4%), hydrogen peroxide (H_2O_2 , ~35 wt % in water), potassium iodide (KI, > 99.4%) and sodium bicarbonate (NaHCO_3 , powder), were obtained from Sigma- Aldrich Corp., St. Louis, MO; sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98%) was obtained from Acros Organics, NJ; 1,4-dioxane ($\text{C}_4\text{H}_8\text{O}_2$, class 1B) was obtained from Fisher Scientific Inc., NJ; ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, granular) was obtained from J.T.Baker Inc., Phillipsburg, NJ; ferrous iron and ferover reagent powder pillows were obtained from Hach Corp., Loveland, CO, USA.

The experiments were conducted using one of two solution matrices, ultrapure (filtered, distilled, deionized) water (Barnstead NANOpure water system) or a synthetic groundwater solution. The latter was composed of MgSO_4 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, NaHCO_3 , and NaCl , at concentrations of 124 mg/L, 85 mg/L, 9 mg/L, 171 mg/L, and 20 mg/L, respectively (Johnson et al. 2003). No natural organic carbon was added, to allow focus on reactions associated with the target contaminants.

For reactors with TCE present, 40 μL of pure TCE was added to each vial, equivalent to 11.15 mM (1,500 mg/L) in solution. This equivalent concentration exceeds the aqueous solubility of TCE, reflecting the presence of TCE liquid. The following reagent concentrations were used for all of the experiments. Dioxane: 0.57 mM (50.2 mg/L), persulfate: 6.3 mM (1,500 mg/L), hydrogen peroxide: 150 mM (5,100 mg/L), FeSO_4 : 0.8 mM (121.6 mg/L), NaOH : 31.50 mM (1,260 mg/L). The selected dioxane concentration is representative of the upper range of groundwater concentrations reported for contaminated sites (Mohr et al. 2010; Adamson et al. 2014), and was used to present a conservative case of higher concentrations. The oxidant concentrations are relatively low compared to typical concentrations used for field applications. Thus, this study will produce conservative results.

2.2. Experiment setup

Batch experiments (in triplicate) were conducted at 25 ± 1 °C with 40 mL borosilicate vials fitted with PTFE septum caps. Experiments were conducted to examine dioxane degradation alone and in the presence of TCE in the catalyzed coupled hydrogen peroxide/persulfate system. Multiple experiment control sets were conducted. The B group (blank group) contained only ultrapure water or synthetic groundwater and the contaminant (dioxane alone, TCE alone, or dioxane + TCE), and was used to evaluate the loss of TCE and/or dioxane through volatilization or other mass-loss mechanisms. The C-1 group (control group 1) contained oxidant and contaminant (dioxane alone, TCE alone, or dioxane + TCE) but no catalyst, to determine if and to what extent the contaminant could be degraded under non-catalyzed conditions. The R group (reaction group) contained ultrapure water or synthetic

groundwater, binary oxidant, contaminant (dioxane alone, TCE alone, or dioxane + TCE), and catalyst, which were added in that order. The C-2 group (control group 2) contained ultrapure water, the single oxidant (peroxide or persulfate), contaminant, and catalyst, which were added in that order. The latter control group was conducted to delineate the comparative effects of single versus binary oxidant systems.

The vials were sealed after the addition of all the chemicals. The vials were shaken to ensure the solutions were well mixed, and then kept quiescent for the remainder of the experiment. Subsamples (0.5 ml) were collected over the course of the experiment. Each set of samples were extracted into hexane and then analyzed immediately.

2.3. Analytical methods

Dioxane and TCE were analyzed using gas chromatography (Shimadu GC-14A, Columbia, MD) equipped with a 30m×0.53 mm SPB™-624 capillary column (film thickness was 3 μm), and a flame ionization detector (FID). External standards were used for quantification. The temperatures of the injection port and detector were 200 and 250 °C, respectively. For samples with only dioxane, the initial oven temperature was 50 °C, maintained 2 minutes, and then heated at a rate of 10 °C/min to a final temperature of 110 °C. For samples with only TCE, the initial oven temperature was 40 °C and heated at a rate of 10 °C/min to a final temperature of 140 °C. For TCE- dioxane co-contaminant samples, the initial oven temperature was 40 °C and heated at a rate of 13 °C/min to a final temperature of 131 °C. The detection of hydrogen peroxide and persulfate concentrations were based on iodide spectrophotometry method (Liang et al. 2008). For the hydrogen peroxide-persulfate system, the concentrations of the oxidants were determined as the sum of the two oxidants. The Fe²⁺ and total iron were analyzed with a Hach DR2800 spectrophotometer using 1,10-phenanthroline-based method (HACH module No.8146) and FerroVer method (HACH module No.8008) respectively. The concentration of ferric iron (Fe³⁺) was calculated by the difference of total iron concentration and Fe²⁺ concentration. Sample pH was measured by Orion model 290A pH meter. The presence of degradation products was evaluated using gas chromatography mass spectrometry (Agilent GC-6890/MS-5975).

3. Results and Discussion

3.1. Dioxane degradation in the catalyzed hydrogen peroxide-persulfate system

The degradation of dioxane by the binary hydrogen peroxide-persulfate system for Fe²⁺ and NaOH activation is shown in Figure 1a for the experiments conducted using ultrapure water. The control test showed minimal loss of dioxane. There was ~10% dioxane loss for the non-activated hydrogen peroxide-persulfate system. Complete degradation of dioxane was attained for the Fe²⁺-catalyzed system in 4 h. Conversely, dioxane degradation was much slower in the NaOH-catalyzed system, with 33% degradation in 96 h. During the reaction, the pH decreased slightly for the Fe²⁺- catalyzed system as persulfate decomposed to generate sulfuric acid, while it increased slightly for the NaOH-catalyzed system (Figure 1b). As the pH typically does not change in the base-activated persulfate system (Furman et al. 2010), the increase of pH for the NaOH-catalyzed system is likely due to the generation OH⁻ from hydrogen peroxide decomposition. The results for dioxane degradation by Fe²⁺-

activated hydrogen peroxide-persulfate in the synthetic groundwater solution were essentially identical to those obtained for the ultrapure water system (Figure 2). This indicates that the impact of inorganic background species was minimal for this system.

The results obtained for dioxane degradation using the single oxidant systems are presented in Figures S2 and S3 for peroxide and persulfate, respectively. Complete degradation of dioxane was attained for the Fe^{2+} -catalyzed peroxide system in almost 4 h. This is very similar to the results obtained for the binary oxidant system. However, degradation of TCE was much more limited for the peroxide-alone system compared to the binary system. This is likely due to the fact that oxidant levels remained significantly higher in the binary system, meaning oxidant use was more efficient. Complete degradation of dioxane required more than 24 hours for the Fe^{2+} -catalyzed persulfate system, much longer than either the peroxide or peroxide-persulfate systems. These results illustrate the greater effectiveness of the binary oxidant system compared to either of the single oxidant systems.

The degradation of dioxane in the hydrogen peroxide-persulfate system followed first-order kinetics. Table 1 presents the rate constants (k_{obs}) for the degradation of dioxane under NaOH and Fe^{2+} activation conditions. The k_{obs} for Fe^{2+} activation is approximately 1000 times larger than for NaOH activation. The comparatively slow kinetics observed for the alkaline system is consistent with the results from prior studies for BTEX and MTBE oxidation (Crimi and Taylor 2007; Deng et al.). The k_{obs} for the Fe^{2+} -activated persulfate experiment (no peroxide) is 0.13 h^{-1} , almost 30 times smaller than the value obtained for the Fe^{2+} activated hydrogen peroxide-persulfate system.

Prior research using ion chromatography has shown that organic acids, such as glycolic acid, acetic acid, and oxalic acid, are observed as degradation products of dioxane treatment by activated-hydrogen peroxide or activated-persulfate (Chitra et al. 2012; Felix-Navarro et al. 2013; Stefan and Bolton 1998). Rather than repeating the same analysis for this study, we employed GC-MS analysis to supplement the prior research. This allowed further investigation of potential additional degradation products. No measurable compounds were detected (Figure S4), suggesting that the organic acids are the primary byproducts.

Oxidant decomposition results are presented in Figure 3. The results show that oxidant decomposition was essentially identical for Fe^{2+} -activation (~32%) and NaOH- activation (~35%) up to 4 h of reaction. However, the decomposition rates deviated greatly thereafter, with complete loss of oxidant occurring after 23 hours for the Fe- activated system, whereas ~97 hours were required for the NaOH-activated system. The first-order rate constants for oxidant decomposition are presented in Table 2.

A comparison of dioxane degradation to oxidant decomposition is presented in Figure 3. The results show that while oxidant decomposition was essentially identical for Fe^{2+} -activation and NaOH-activation up to 4 h of reaction, dioxane degradation differed significantly, with complete degradation after 4 h for the Fe^{2+} -activated system but only 8% degraded in the NaOH-activated system. As noted, the rate constant for dioxane degradation is ~1000 times greater for Fe activation versus NaOH activation. Conversely, the rate constant for oxidant decomposition is only ~6 times larger for the Fe-activated system.

These contrasting results indicate that Fe^{2+} activation apparently generated more sulfate radical ($\text{SO}_4^{\cdot-}$, $E^0=2.6$ V) and hydroxyl radical ($\text{HO}^{\cdot}$, $E^0=2.7$ V) per oxidant consumed compared to NaOH activation. Based on these results, it is hypothesized that different reaction mechanisms are involved in dioxane degradation for the two activation methods.

3.2. Activation process analysis

There appears to have been no prior report on activation processes for the NaOH-catalyzed binary hydrogen peroxide-persulfate system. However, processes for NaOH activation of persulfate alone have been reported (Furman et al. 2010), described by (Eq. 1–2):

While NaOH has been demonstrated to be an effective activator for persulfate by previous researchers, there is no reported evidence of its effectiveness for hydrogen peroxide activation. Hence, it is presumed that NaOH interacts primarily with persulfate. In addition, it has been shown that $\text{SO}_4^{\cdot-}$ can convert to $\text{HO}^{\cdot}$ via electron transfer reaction in highly alkaline conditions (Hayon et al. 1972):

Previous investigators hypothesized that hydrogen peroxide may be generated in base-activated persulfate systems. The generated hydrogen peroxide could react with the hydroperoxide anion (HO_2^-), shown by (Eq. 4), or convert into HO_2^- under alkaline conditions (Eq. 5) (Corbin III 2008; Zhao et al. 2013).

Based on the preceeding, we propose (Eq. 1–5) as the hypothesized primary activation process for the NaOH-catalyzed binary hydrogen peroxide-persulfate system.

The process for Fe^{2+} activation of the hydrogen peroxide-persulfate system is more straightforward. Electron paramagnetic resonance (EPR) spin-trapping was used by Yan et al. (2015) to characterize the radical species formed in the iron-activated hydrogen peroxide-persulfate system. They determined that $\text{HO}^{\cdot}$ and $\text{SO}_4^{\cdot-}$ are the primary species generated.

This is consistent with the numerous prior studies conducted using the individual oxidants. This is described as:

Both $\text{HO} \cdot$ and $\text{SO}_4 \cdot^-$ are effective radicals for oxidation of a wide variety of organic contaminants. The proposed process for NaOH activation of the binary oxidant system involves indirect generation of $\text{HO} \cdot$ and $\text{SO}_4 \cdot^-$, which is limited by the generation rate of HO_2^- . These conditions are in contrast to the direct generation of radicals achieved for Fe activation of both hydrogen peroxide and persulfate.

The significant loss of oxidant compared to the minimal degradation of dioxane observed for the NaOH-based system (Figure 3) indicates that not all of the oxidant consumed was used to generate reactive radicals ($\text{HO} \cdot$ and $\text{SO}_4 \cdot^-$) and/or that there are other mechanisms of radical consumption beyond dioxane degradation. Thus, there must be additional sources of oxidant or radical consumption. It was reported that under alkaline conditions, the amount of conjugate base HO_2^- increases (Eq. 8) and the self-decomposition rate of hydrogen peroxide also increases (Eq. 9).

Although the production of HO_2^- can promote the generation of $\text{HO} \cdot$ according to (Eq. 4), HO_2^- can also react with another molecule of $\text{HO} \cdot$ via (Eq. 10). Therefore, the productivity of $\text{HO} \cdot$ decreases with decreasing amount of hydrogen peroxide. At the same time, high solution pH also depletes $\text{HO} \cdot$ according to (Eq. 10–11) (Chu et al. 2011; Kasiri et al. 2008), with the generation of weaker radicals (superoxide ($\text{O}_2 \cdot^-$) and $\text{HO}_2 \cdot$) (Ciotti et al. 2009).

The consumption of radical to generate $O_2^{\cdot -}$ and $HO_2^{\cdot}$ would result in a lower availability of $HO^{\cdot}$ for oxidation of dioxane, although some $HO^{\cdot}$ could be “re-generated” according to (Eq. 12).

Additionally, in the Fe^{2+} -activated system, the combination of Fe^{2+} and hydrogen peroxide is Fenton reagent, which generates large quantities of $HO^{\cdot}$. The radical generation efficiency per unit of hydrogen peroxide consumption is higher in the Fenton reaction compared to the NaOH-catalyzed hydrogen peroxide-persulfate reaction.

3.3. Degradation behavior of dioxane and TCE co-contamination

A set of experiments was conducted to investigate the degradation of dioxane in the presence of TCE co-contamination. Fe^{2+} was selected as the preferred activation reagent for the subsequent co-contamination experiments based on the prior results. The degradation of dioxane and TCE in the controls and the Fe^{2+} -activated binary oxidant systems are presented in Figure 4a, b, and c, respectively. The presence of TCE significantly reduced the rate of dioxane degradation for the specific conditions employed. However, complete degradation of dioxane occurred within 48 hours.

4. Conclusion

The ability of the binary hydrogen peroxide-persulfate oxidant system to degrade dioxane was investigated. Activation by Fe^{2+} and NaOH was explored, and Fe^{2+} was significantly more effective. Activation processes were delineated by analyzing dioxane degradation efficiency and oxidant decomposition rates, along with incorporation of prior research results. The degradation of dioxane-TCE co-contamination was also examined. Complete degradation of dioxane and TCE was observed. The results of the study indicate that the activated binary oxidant system is generally effective for treating dioxane and TCE.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

a) Dioxane degradation by catalyzed $H_2O_2-S_2O_8^{2-}$ in ultrapure water (the insert presents the first 4 hours of reaction for higher resolution); b) pH change in the system.

Fig. 2.
Comparison of dioxane degradation by Fe²⁺-H₂O₂-S₂O₈²⁻ in ultrapure water and synthetic groundwater.

Fig. 3.

The comparison of dioxane degradation with oxidant decomposition in activated H₂O₂-S₂O₈²⁻ system.

Fig. 4. Comparison of dioxane and TCE degradation under single or co-contaminant condition in $\text{Fe}^{2+}\text{-H}_2\text{O}_2\text{-S}_2\text{O}_8^{2-}$ system system: a) control experiments without activation; b) dioxane degradation; c) TCE degradation.

Table 1

Kinetic equations for the degradation of dioxane

Activator	FeSO ₄ (mM)	NaOH (mM)	Na ₂ S ₂ O ₈ (mM)	H ₂ O ₂ (M)	Regression equation	R ²	k _{obs} ^a (h ⁻¹)
Fe (UW ^b)	0.8		6.3	0.15	$y = -3.46x + 0.33$	0.97	3.5
Fe (SG ^c)	0.8		6.3	0.15	$y = -3.45x - 0.28$	0.98	3.4
NaOH (UW)		31.5	6.3	0.15	$y = -0.004x - 0.08$	0.97	0.004

^ak_{obs} is the first-order rate constant^bUW is ultrapure water^cSG is synthetic groundwater

Table 2

Kinetic equations for the decomposition of oxidants

Activator	R.T. ^a (h)	FeSO ₄ (mM)	NaOH (mM)	Na ₂ S ₂ O ₈ (mM)	H ₂ O ₂ (M)	Regression equation	R ²	k _{obs} (h ⁻¹)
Fe	0–36 ^b	0.8		6.3	0.15	$y = -0.17x + 0.255$	0.93	0.17
NaOH	0–98		31.5	6.3	0.15	$y = -0.03x - 0.234$	0.95	0.03

^aR.T. is the reaction time^bThe total length of the experiment. The time interval used is less than 98 h for the treatment that attained complete decomposition prior to the end of the experiment.