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Remediating 1,4-dioxane-contaminated water with slow-release persulfate and zerovalent iron

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Highlights

- Fe⁰-activated persulfate was used to treat 1,4-dioxane.
- Excess Fe²⁺ from Fe⁰ can hinder dioxane degradation.
- Adding Fe⁰ in increments improves dioxane degradation.
- Slow-release persulfate and Fe⁰ formulations effectively treated dioxane.
- ¹⁴C-labeled dioxane was used to track mineralization.

Abstract

1,4-dioxane is an emerging contaminant that was used as a corrosion inhibitor with chlorinated solvents. Metal-activated persulfate can degrade dioxane but reaction kinetics have typically been characterized by a rapid decrease during the first 30 min followed by either a slower decrease or no further change (i.e., plateau). Our objective was to identify the factors responsible for this plateau and then determine if slow-release formulations of sodium persulfate and Fe⁰ could provide a more sustainable degradation treatment. We accomplished this by conducting batch experiments where Fe⁰-activated persulfate was used to treat dioxane. Treatment variables included the timing at which the dioxane was added to the Fe⁰-persulfate reaction (T = 0 and 30 min) and including various products of the Fe⁰-persulfate reaction at T = 0 min (Fe²⁺, Fe³⁺, and SO₄²⁻). Results showed that when dioxane was spiked into the reaction at 30 min, no degradation occurred; this is in stark contrast to the 60% decrease observed when added at T = 0 min. Adding Fe²⁺ at the onset (T = 0 min) also severely halted the reaction and caused a plateau. This indicates that excess ferrous iron produced from the Fe⁰-persulfate reaction scavenges sulfate radicals and prevents further dioxane degradation. By limiting the release of Fe⁰ in a slow-release wax formulation, degradation plateaus were avoided and 100% removal of dioxane observed. By using ¹⁴C-labeled dioxane, we show that ~40% of the dioxane carbon is mineralized within 6 d. These data support the use of slow-release persulfate and zerovalent iron to treat dioxane-contaminated water.

Keywords: Chlorinated solvents, TCE, Dioxane, Persulfate, Slow-release oxidants

1. Introduction

Water quality is one of the most important environmental issues in the United States. For most U.S. states, one of the biggest threats to groundwater quality has been contamination from industrial solvents. Chlorinated solvents such as trichloroethene (TCE), tetrachloroethene (PCE), and 1,1,1-trichloroethane

(1,1,1-TCA) clearly represent some of the most prevalent groundwater contaminants observed worldwide (Schwartzbach et al., 1993). Another contaminant often associated with industrial solvent use is 1,4-dioxane (dioxane). Dioxane is a colorless, flammable liquid that was used as a stabilizer and corrosion inhibitor with chlorinated solvents such as TCE and 1,1,1-TCA (EPA, 2006). Recognized as a possible human carcinogen (Class B2),

improved analytical testing has now verified the presence of dioxane in groundwater, surface waters, wastewater and drinking water (Zenker et al., 2003). Removing 1,4-dioxane and its associated co-contaminants represents a serious challenge at many sites and the fate of its oxidative degradation products is largely unknown (Jackson and Dwarakanath, 1999). During the past decade, significant efforts have been devoted to developing innovative remedial technologies to treat contaminants at the source.

Examples of techniques that have successfully removed 1,4-dioxane from contaminated groundwater include biodegradation (Zhang et al., 2016; Steffan, 2007) and chemical oxidation (Schreier et al., 2006; Vescovi et al., 2010). Advanced oxidative processes (AOPs) have been implemented at multiple sites to treat extracted groundwater containing 1,4-dioxane. Mixing hydrogen peroxide with Fe^{2+} or UV has been shown to be effective in removing dioxane (Kiker et al., 2010; Vescovi et al., 2010). Bench scale experiments have also demonstrated the effective removal of 1,4-dioxane using ozone, ozone plus hydrogen peroxide, persulfate, sono-activated persulfate, permanganate, and UV based oxidation technologies (Eberle et al., 2016; Ikehata et al., 2016; Li and Zhu, 2016; Wang et al., 2015; Félix-Navarro et al., 2007; Waldemer and Tratnyek, 2006; Vescovi et al., 2010; Mohr et al., 2010; Schreier et al., 2006).

While AOPs appear to be an effective approach, *ex situ* approaches are energy consuming and generally not sustainable for long term treatment. As such, *in situ* chemical oxidation (ISCO) is considered the most promising approach to treat 1,4 dioxane (DiGuseppi and Whitesides, 2007). Previous research has confirmed that activated persulfate can degrade dioxane, with laboratory studies reporting half-lives ranging from minutes to hours (Félix-Navarro et al., 2007).

The use of transition metals to activate persulfate for contaminant destruction has been reported by a number of researchers. Examples include the use of Ag^+ and Fe^{2+} to activate persulfate to treat organic contaminants such as 2,4-dichlorophenol (Anipsitakis and Dionysiou, 2004a), trichloroethene (Liang et al., 2004a, 2004b), other chlorinated phenols and polychlorinated biphenyls (Rastogi et al., 2009a, 2009b). A common observation among many of these references is the rapid degradation of the contaminant followed by either a much slower degradation rate or sometimes an almost immediate plateau (i.e., no further decrease). Oh et al. (2010) activated persulfate with Fe^{2+} to treat 2,4-dinitrotoluene (DNT). By using different masses of Fe^{2+} they found that DNT decreased within the first 10 min but further degradation was generally not observed for the remainder of the experiment (300 min). Liang et al. (2004a) used Fe^{2+} with persulfate in several different molar ratios to treat TCE and observed an almost 50% decrease in TCE during the first 30 min followed by a plateau reaching ~40% of the original concentration (C/C_0).

As an alternative to Fe^{2+} , some researchers have switched to using zerovalent iron (Fe^0) as an activator for persulfate (Lee et al., 2010; Kambhu et al., 2012; Oh et al., 2010; Xiong et al., 2014; Zhong et al., 2015). Zerovalent iron has the advantage of being a solid that can serve as electron donor by itself as well as provide a longer term supply of Fe^{2+} for persulfate activation. Zhong et al. (2015) used iron-activated persulfate to treat dioxane and observed rapid decomposition during the first 30 min followed by a slower rate of decay. Kambhu et al. (2012) and Chokejaroenrat et al. (2015) also used Fe^0 to activate persulfate but did so by mixing persulfate and Fe^0 separately with wax to produce slow-release formulations (i.e., oxidant and iron candles).

Our objective was to identify the conditions responsible for the reaction kinetics previously reported for metal-activated persulfate (e.g., rapid decreased of contaminant followed by plateau) and then determine if slow-release formulations of persulfate

and Fe^0 could provide a more sustainable degradation treatment for 1,4-dioxane.

2. Materials and methods

2.1. Solution experiments: single versus multiple doses

Batch experiments were performed in 100-mL Erlenmeyer flasks. These experimental units received 50 mL of 500 mg L^{-1} dioxane (5.67 mM) and were treated with persulfate, Fe^0 and sodium hexametaphosphate (SHMP). The Fe^0 was commercial cast iron, aggregate size 50D, type USMD from Peerless Metal Powders and Abrasive (Detroit, MI). To be consistent with the chemical makeup of the persulfate candles, SHMP was included in the solution experiments. For the single dose experiment, each replicate ($n = 3$) received 0.75 g sodium persulfate, 0.1875 g Fe^0 (4:1 sodium persulfate:iron, w/w) and 0.0375 g SHMP at $T = 0$ min. By adding these chemicals masses to 50 mL of dioxane, the molar ratio of persulfate to iron was 1:1 (persulfate, 63mM; Fe^0 , 67mM) and 11:1 for persulfate to dioxane.

For multiple dose treatments, the original doses listed above were split into either one-fourth or one-eighth proportions and then added in four or eight sequential applications. The one-fourth doses were added every 30 min and the one-eighth doses every 15 min. Finally, we conducted one experiment where we added all the persulfate and SHMP at the start ($T = 0$ min) and then split the Fe^0 additions into eight, one-eighth doses that were added every 15 min. Additional control experiments were also performed and are presented in Supplementary Material (Fig. SM-1).

To determine the reasons for the observed plateau in the degradation of dioxane following a single dose of persulfate and Fe^0 , we singularly added products of the persulfate- Fe^0 reaction at $T = 0$ min. This included adding Fe^{2+} (as FeSO_4) in the initial reaction mix ($T = 0$ min) in molar ratios of 1:1, 2:1 and 4:1 ($\text{Fe}^{2+}:\text{Fe}^0$) of the initial Fe^0 used (0.033 mol). Likewise, Fe^{3+} ($\text{Fe}_2(\text{SO}_4)_3$) was added at $T = 0$ min in a 2:1 ratio ($\text{Fe}^{3+}:\text{Fe}^0$) and SO_4^{2-} (Na_2SO_4) in a 3:1 ratio ($\text{SO}_4^{2-}:\text{Fe}^0$).

Experimental units were consistently mixed at 200 rpm during treatment by placing them in a temperature-controlled orbital shaker (20 °C). Sampling occurred at $T = 0, 5, 10$ and every 10 min thereafter for 120 min. To sample, we removed 1 mL of solution at selected times and placed it into a 1.5-mL microcentrifuge tube where the reaction was quenched with 0.2 mL sodium thiosulfate (500 g L^{-1}) and then centrifuged at $12,000 \times g$ for 15 min (Kambhu et al., 2012). The supernatant was transferred to a glass vial and analyzed with high performance liquid chromatography (HPLC). Use of sodium thiosulfate to quench the persulfate and stop the reaction as previously shown by Kambhu et al. (2012).

2.2. Batch experiments with slow-release candles

2.2.1. Manufacturing persulfate and Fe^0 candles

Slow release persulfate candles were produced in the same manner as previously reported (Kambhu et al., 2012) with the exception that the sodium persulfate was ground to a fine powder before being mixed with wax. Comparative studies by our laboratory found that powdered persulfate lasted longer than ones made with un-ground persulfate. To grind the persulfate, we placed ~75 g of commercial sodium persulfate into an electrical grinder (A 11 basic analytic mill, IKA®, Wilmington, NC) and ground the chemical for approximately 5 s. The powdered persulfate was then used to make slow-release persulfate candles.

Persulfate candles were fabricated by mixing the persulfate powder with paraffin wax at a ratio of 3:1 (w/w). As an

experimental treatment, sodium hexametaphosphate (SHMP) was included in some of the persulfate candle formulations by adding SHMP at 5% of the sodium persulfate weight. Adding SHMP to permanganate candles was previously found to improve oxidant release rates (Christenson et al., 2016). The persulfate candles were molded into the shape of a cylinder with a diameter of 1.3 cm and the length of 2.4 cm.

Zerovalent iron candles were made by mixing Peerless 50D Type USMD cast iron with paraffin wax with the ration of 2.35:1. As with the persulfate candles, SHMP was included as a treatment by adding SHMP at 5% of the iron weight. The zerovalent iron candles had the same diameter as persulfate candles, but were one-third the length (0.8 cm). We also drilled a 0.5 cm hole in the middle of each Fe^0 candle to increase the surface area.

2.2.2. Candle batch experiments

Batch experiments that treated dioxane with slow-release candles were performed in 150-mL Erlenmeyer flasks. Each flask was filled with 100 mL of 500 mg L^{-1} dioxane. At $T = 0$ d, experimental units were placed inside a dark incubating orbital shaker at 20 °C and mixed at 200 rpm. At $T = 0$ d, each flask received one persulfate and one Fe^0 candle. Temporal sampling occurred by removing 1 mL of solution at selected times and quenching the reaction with 0.2 mL of sodium thiosulfate (500 g L^{-1}) in a 1.5-mL microcentrifuge tube and centrifuging for 15 min at 12,000 $\times g$. The supernatant was transferred to a glass vial and analyzed with HPLC.

To test the longevity of the candles to degrade dioxane, batch experiments were run in repeated cycles. In these experiments, candles added at $T = 0$ d were allowed to react for 7 d, then the solution was discarded and replenished with fresh dioxane solution (100 mL of 500 mg L^{-1}) and temporal sampling repeated for another 7 d (2nd cycle). Following this, the solution was again discarded and replaced to create a 3rd cycle of data.

To pinpoint why the oxidant candles were not performing as well (i.e., plateauing) after the 1st cycle, 2nd cycle persulfate candles were paired with a fresh Fe^0 candle (i.e., a 1st cycle Fe^0 candle), a 2nd cycle Fe^0 candle that had its outer layer removed by scrapping and 2nd cycle Fe^0 candle that was chopped into smaller pieces to create more surface area. Likewise, the 2nd cycle Fe^0 candles were paired with a fresh persulfate candle (1st cycle), a 2nd cycle persulfate candle that was scrapped, and a 2nd cycle persulfate candle that was chopped.

To track the carbon backbone of the 1,4-dioxane and quantify mineralization (i.e., $^{14}\text{CO}_2$ production), batch experiments were performed with ^{14}C -labeled dioxane. The 500 mg L^{-1} dioxane solutions used in the batch experiments were spiked with ^{14}C -dioxane (American Radiolabeled Chemicals, Inc., St. Louis, Mo, specific activity: 10 mCi mmol^{-1}). Our ^{14}C -dioxane stock was in a methanol matrix and had an activity of 1.79×10^6 dpm mL^{-1} . By adding 1 mL of this stock to 0.5 L of 500 mg L^{-1} of 1,4-dioxane, the initial activity of the solutions in our batch reactors was ~ 3500 dpm mL^{-1} . In addition to the 1 mL of solution removed for HPLC analysis at selected times, an additional 1 mL of solution was collected for ^{14}C analysis.

2.3. Chemical analysis

Temporal changes in 1,4-dioxane concentrations were analyzed by high performance liquid chromatography (HPLC) using a photo diode array detector (Shimadzu Scientific Instruments Columbia, MD). The HPLC method used was modified from Scalia et al. (1990). An isocratic mobile phase of 50:50 acetonitrile-water was used with an injection volume of 20 mL. Using a flow rate of 1 mL min^{-1} , samples were separated by an AQUASIL C18 column (Thermo scientific, dia. 250×4.6 mm, particle size 5 μ) that was coupled to a guard column. Sample peaks were quantified at

195 nm by an external calibration curve. Matrix blanks were analyzed with samples to ensure the absence of background peaks.

^{14}C -activity was determined by removing 1 mL subsamples from the batch reactors and mixing with 6 mL of Ultima Gold™ liquid scintillation cocktail (PerkinElmer, Inc., Waltham, MA, USA). Samples were then mixed on a vortex mixer and allowed to settle for 24 h in the dark before analyzing on a Packard 1900 TR liquid scintillation counter (LSC; Packard instrument Co., Downers Grove, IL). A blank consisting of 6 mL Ultima Gold liquid scintillation cocktail was analyzed prior to running the samples and used to correct sample activity (dpm) values.

To identify dioxane degradation products following treatment with persulfate and Fe^0 candles, solutions were analyzed by gas chromatography coupled with mass spectrometry (GC/MS) and ion chromatography (IC) for organic acids. For GC/MS analysis, batch reactions (250 mL, 0.5 M 1,4-dioxane in water, treated with iron and persulfate candles) were analyzed hourly or daily as follows: 1 mL reactions samples were removed by pipet, extracted with 2 mL dichloromethane, and the dichloromethane extract analyzed directly by GC/MS. The intermediates were identified by comparison of mass spectra. Mass spectra were obtained by a Hewlett Packard HP6890 GC equipped with autoinjector and a 15 m DBWAX (123-7013, USD168815A) capillary column (Agilent, Palo Alto, CA) and an HP 5973 mass spectral detector. The initial oven temperature (50 °C) was maintained for 2 min, then increased (13 °C/min) to 205 °C and held for 6 min.

To identify oxalic acid, batch reactors were kept in the dark during treatment and sampling to prevent photodegradation of Fe(III) -oxalate complexes (Li et al., 1997). The IC system consisted of a conductivity detector and an electrolytically regenerated suppressor (Dionex AERS 500, RFICTM, 4 mm). We used an anion exchange analytical column (Dionex IonPac™ AS11-HC, RFICTM, 4250 mm) that was coupled with a guard column (Dionex IonPac™ AG11-HC, RFICTM, 4 50 mm). An isocratic mobile phase of 20 mM NaOH was used at a flow rate of 1.0 mL min^{-1} .

3. Results and discussion

3.1. Solution experiments: single versus multiple doses

Batch experiments where persulfate, Fe^0 and SHMP were initially added to a dioxane solution showed that degradation occurred within the first 10 min but then rapidly plateaued and resulted in approximately 40% of the dioxane remaining (Fig. 1A). When the original dosage was split into four, one-quarter doses (Fig. 1B), small decreases in dioxane concentrations were observed after each dosage, but in the end, the amount of dioxane remaining was similar to that observed after one single dose ($C/C_0 = \sim 40\%$, Fig. 1A, B). By splitting the dosages into eight, one-eighth dosages, we observed a more exponential decrease in the dioxane concentration with less than 20% of the dioxane remaining after 120 min (Fig. 1C). Finally, by adding the persulfate and SHMP at the beginning ($T = 0$ min) and then distributing only the Fe^0 as eight, one-eighth dosages, we achieved even higher destruction rates with less than 5% of the dioxane remaining (Fig. 1D).

Two possible reasons the dioxane concentration plateaued after a single dose include: (1) one or more degradation products produced from the treatment of dioxane quenched the reaction; or (2) products of the persulfate + Fe^0 reaction quenched the reaction.

The plateauing of contaminant degradation following treatment with metal-activated persulfate has been observed in earlier studies. Oh et al. (2010) activated persulfate with Fe^{2+} to treat 2,4-dinitrotoluene (DNT). By using different Fe^{2+} masses they found that DNT decreased within the first 10 min but little change was observed for the remainder of the experiment (300

Fig. 1. Effects of dosages on dioxane degradation. **A.** One dose application demonstrating rapid degradation followed by plateau, **B.** Quarter dose applications; **C.** Eighth dose applications; **D.** Eighth dose application of Fe⁰.

min). Liang et al. (2004a) activated persulfate with Fe²⁺ in several different molar ratios to treat TCE and observed an almost 50% decrease in TCE during the first 30 min followed by a plateau at ~40% (C/C₀) (180 min).

Given that this pattern of a rapid decrease followed by no change (i.e., plateau) has been observed with a variety of organic contaminants (e.g., 1,4-dioxane, TCE, 2,4-dinitrotoluene), the termination of the degradation reaction does not appear to be tied to a specific contaminant. While we acknowledge that some similar low molecular weight oxidation products could form from these contaminants and possibly act as radical scavengers, addition experiments we performed show that the reason the kinetic rate plateaued is not tied to dioxane.

We performed a control experiment where persulfate and Fe⁰ were allowed to react for 30 min before dioxane was spiked into the solution. Results from this experiment showed no degradation of dioxane when spiked in at 30 min. This was in stark contrast to the 60% decrease we observed when dioxane was added at T = 0 min (Fig. 2A). These results indicate that the persulfate + Fe⁰ reaction can terminate on its own (in the absence of an organic contaminant).

With regard to which products of the persulfate + Fe⁰ reaction were causing the plateau, there are only a few possibilities. Persulfate activation can proceed through direct electron transfer from Fe⁰ [Eqn (1)] or electron transfer from the subsequently produced Fe²⁺, which may be surface bound or in solution [Eqn (2)] (Oh et al., 2010).

Products that would be in solution as the reaction proceeds include the persulfate radical (SO₄^{·-}), Fe²⁺, Fe³⁺ and SO₄²⁻. Oh et al. (2010) explained the reason DNT only decreased from the persulfate/Fe²⁺ treatment during the first few minutes was due to abundance of Fe²⁺ in solution, which can act as a scavenger of the sulfate radical (Eqn. (3)).

Results from our experiments (Fig. 1D) and others (Liang et al., 2004a) showed that adding Fe⁰ in smaller, more frequent doses results in better destruction rates. This lends credence to the explanation that products of the Fe⁰ - persulfate reaction (i.e., Fe²⁺) are terminating the reaction and responsible for the plateau.

To demonstrate that Fe²⁺ can consume sulfate radicals, as previously recognized (Liang et al., 2004a; Oh et al., 2010; Xiong et al., 2014), we included Fe²⁺ in the initial reaction mix (T = 0 min) and added Fe²⁺ in molar ratios of 1:1, 2:1 and 4:1 to Fe⁰. Results from these experiments showed that as the concentration of Fe²⁺ increased, less dioxane degradation occurred (Fig. 2B) and the reaction plateaued at higher C/C₀ values (Fe²⁺:Fe⁰, 1:1, C/C₀ ~ 0.6; 2:1 C/C₀ ~ 0.8; 4:1 C/C₀ ~ 0.90). These results indicate

that Fe^{2+} can indeed suppress persulfate radical activity and reduce overall destruction rates. Therefore care must be taken to prevent excess Fe^{2+} from forming. Our additional control experiments showed that including Fe^{3+} and SO_4^{2-} at $T = 0$ min in the reaction had no effect (Fig. SM-2).

It is important to note that while 1 mol of Fe^0 could conceivably react with 3 mol of persulfate (Eqns. (1) and (2)), zerovalent iron will also react with any initially dissolved oxygen present in the water (Eqn. (4)) or eventually with water itself (Eqn. (5)) through aerobic/anaerobic corrosion to liberate Fe^{2+} . Thus, excess Fe^{2+} could easily form when zerovalent iron is used as the activator for persulfate.

To prevent excess Fe^{2+} from forming and scavenging the sulfate radical, we controlled the release of iron by incorporating it into a slow-release formulation (i.e., iron candle) and pairing it with different ratios of persulfate candles.

3.2. Treatment of dioxane with slow-release oxidants

The chemical properties of 1,4-dioxane (i.e., miscible, low Henry's Law constant, 4.9×10^{-6} atm m³/mol) allowed for batch experiments to be conducted in shake flasks. Our preliminary experiments with miniature persulfate candles confirmed that 1,4-dioxane (2 mM) could be degraded by persulfate alone but

activated persulfate (i.e., persulfate + zerovalent iron (ZVI) candles) clearly produced the fastest kinetics and persulfate and Fe^0 candles were used in the remainder of the experiments. The purpose of the oxidant candles was to provide a slow release of persulfate into solution; this necessitated that the experiments be run longer than the solution experiments where single and multiple doses of the persulfate chemical were added to the batch reactors (i.e., Sec. 3.1).

To test the longevity of the candles to degrade dioxane, we ran the experiments in three cycles, where after the first 7 d (1 cycle), the dioxane solution was discarded and replaced with a fresh dioxane solution (2 cycle); this was repeated again for a third cycle. Results showed that when the persulfate and Fe^0 candles were paired together in a one to one combination, dioxane was degraded within 2 d during the first cycle but concentrations plateaued during the 2nd and 3rd cycles (Fig. 3A).

We originally suspected that some oxide coatings may be covering the candles and preventing them from working. To counteract this, we tried a number of manipulations, such as scraping the candles, chopping them into smaller pieces and pairing the used (2nd cycle) persulfate and Fe^0 candles with fresh Fe^0 and persulfate candles. Results from these experiments simply proved the iron was not the limiting factor in degrading the dioxane but the nonlinear release of persulfate from the candles with subsequent cycles was likely allowing Fe^{2+} to become present in abundance (Fig. SM-3).

By using the results from our initial experiments without candles (Figs. 1 and 2), it became clear that the problem with our candle experiments was that the release rates of the persulfate

Fig. 2. A. Effect of timing on dioxane degradation by persulfate and Fe^0 (dioxane added at $T = 0$ vs. 30 min); B. Effect of adding Fe^{2+} at $T = 0$ min on dioxane degradation by persulfate and Fe^0 .

Fig. 3. Dioxane degradation by slow-release persulfate and Fe^0 candles during 1st, 2nd, and 3rd cycle experiments. A. One persulfate candle paired with one Fe^0 candle; B. Two persulfate candles paired with one Fe^0 candle.

and Fe^0 candles were not consistent between cycles and the Fe^0 candles were likely releasing too much Fe^{2+} into solution during the 2nd and 3rd cycles. By pairing two persulfate candles with one Fe^0 candle, results showed that the plateau was avoided and consistent dioxane degradation occurred throughout the experiments for all three cycles (Fig. 3B). To determine if the 2:1 ratio was optimal, we subsequently used persulfate to Fe^0 candle ratios of 1:1 to 4:1. Results showed that after the first cycle, the higher persulfate to Fe^0 candle ratio of 4:1 produced slightly faster initial dioxane degradation but changes in dioxane concentrations after 4 d were similar to the 3:1 and 2:1 ratios (Fig. SM-4). This indicates that using lower masses of Fe^0 candles with persulfate candles could improve long-term performance.

Finally, to aid in the release of the persulfate and Fe^0 from the wax matrix, we included SHMP in the formulations. Previous results using SHMP with permanganate candles showed that it greatly minimized the formation of oxide coatings on the candle surface and facilitated a more consistent release of the oxidant from the candle (Christenson et al., 2016). Moreover, Chokejaroenrat et al. (2013) found that SHMP also helped the oxidant penetrate low permeable zones in a series 2D-flow box experiments. For consistency we included SHMP in both the persulfate and Fe^0 candle formulations and compared results. We found the dioxane degradation was more complete and consistent among cycles when SHMP was included in the persulfate candle formulations (Fig. 4). This is logical considering our results show that best results are obtained when Fe^{2+} does not become in excess and the added SHMP likely facilitated oxidant release from the persulfate candles.

Fig. 4. Effect of including SHMP in persulfate and Fe^0 candle formulations. Batch reactors received one persulfate and one Fe^0 candle.

3.3. Treatment of ^{14}C -labeled dioxane

By including ^{14}C -labeled dioxane in our batch experiments, we will be able to ultimately track the carbon backbone of the parent structure and determine its fate upon treatment with the oxidant candles. Results showed that the persulfate- Fe^0 candles could mineralize 40–50% of the dioxane carbon (Fig. 5, Fig. SM-5). Because our commercial source of ^{14}C -labeled dioxane was in methanol and we could not remove it completely from our experiments, we acknowledge that dioxane mineralization rates could be higher in a pure aqueous system. Methanol is a known quenching agent for sulfate radicals (Rastogi et al., 2009a; Oh et al., 2010) and details of persulfate decomposition in methanol have been previously described (Bartlett and Cotman, 1949). Even though the ^{14}C -spiked dioxane used in the batch experiments contained small volumes of methanol (i.e., 1 mL ^{14}C -dioxane to 500 mL dioxane in H_2O), the effects of methanol were evident. Results showed that batch reactors spiked with ^{14}C -dioxane plateaued at ~20% (C/C_0) following treatment, whereas 100% removal of dioxane was observed when methanol was not present in the batch reactor (Fig. SM-5). As previously observed, better dioxane removal rates were observed when two persulfate candles were combined with one Fe^0 candle.

3.4. Dioxane degradation and product formation

By considering the chemistry of dioxane and the oxidants involved (persulfate, and sulfate radical), we believe the mechanism by which persulfate or the sulfate radical (Ox) attacks

Fig. 5. Temporal changes in dioxane concentration and ^{14}C activity following treatment with persulfate (PS) and Fe^0 candles. Experimental units were kept in the dark during treatment.

Fig. 6. Proposed degradation scheme of 1,4-dioxane by persulfate and Fe^0 candles. Structures in boxes have been identified.

dioxane will likely fall into one of three initial pathways (Fig. 6). These include: the oxidant removes an electron (Pathway 1); a hydrogen atom (H atom + 1 electron) (Pathway 2); or a hydride ion (H atom + 2 electrons) (Pathway 3) from the dioxane molecule. Each pathway likely produces a highly unstable and reactive oxonium ion (Fig. 6).

In aqueous solution, the oxonium ion will be quickly hydrolyzed to 1,4-dioxane-2-ol, which we identified by GC/MS (Fig. SM-6) and then to 2-hydroxyethoxy-2-acetaldehyde. This aldehyde is then transformed to 2-hydroxyethoxy-2-acetic acid (2HEAA) (Pathway 4, Fig. 6) and is the same product Steffan (2007) found in their research that investigated the biodegradation of dioxane. But unlike Steffan (2007) findings where bacteria had a difficult time further degrading 2HEAA, chemical oxidants are not as limited. For instance, primary alcohols are known to be oxidized to acids by chemical oxidants (Jefford and Wang, 1988) and through a series of several pathways, the oxidation and hydrolysis of 2HEAA leads to oxalic acid (Pathway 5, Fig. 6). While oxygen-saturated organic acids, like oxalic acid have been shown to be resistant to OH radical attack (e.g., Fenton Reaction, Bigda, 1995; Li et al., 1997), we found oxalic acid to be a product of the Fe^0 -persulfate candle treatment of dioxane and that further oxidation to CO_2 was possible. Interestingly, we found that by

keeping the experimental unit shielded from light allowed us to more easily detect the production of oxalate and higher ^{14}C -activity but upon exposure to light, the oxalate disappeared and ^{14}C decreased. This is explained by Li et al. (1997) who similarly found oxalate to be a product of TNT treated by the Fenton reaction. They demonstrated that the oxalate produced complexes with the Fe (III) in solution and upon exposure to light, further degrades to CO_2 .

4. Conclusions

We found that zerovalent iron activated persulfate could effectively degrade 1,4-dioxane but care must be taken to avoid excess production of Fe^{2+} . This can be accomplished by adding multiple, smaller doses of Fe^0 throughout the reaction or using slow-release formulations of Fe^0 and persulfate. Adding SHMP to the persulfate candles can also facilitate persulfate release. Our results also show that mineralization of dioxane is possible with persulfate and Fe^0 candles and that oxalic acid is an end product of the reaction.

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Appendix A. Supplementary data — Supplementary data related to this article follows the references.

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Remediating 1,4-dioxane-contaminated water with slow-release persulfate and zerovalent iron

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Supplementary Material (SM)

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6 Figures

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2. Materials and methods

2.1 Control experiments: wax and iron-wax coated flasks

To complement the solution experiments where single versus multiple doses were tested (Section 2.1, main manuscript), we ran control experiments where wax was introduced into experiment by coating the bottom of the batch reactor with either wax or a melted Fe^0 candle. To these experimental units, single versus multiple one-fourth doses were applied.

2.2 Effects of Fe^{3+} and SO_4^{2-} on dioxane degradation by persulfate and Fe^0

To determine reasons for the observed plateau in the degradation of dioxane following a single dose of persulfate and Fe^0 , we singularly added products of the persulfate- Fe^0 reaction at $T = 0$ min. This included adding Fe^{2+} in the initial reaction mix ($T = 0$ min) in molar ratios to Fe^0 (0.033 moles) of 1:1, 2:1 and 4:1. Likewise, Fe^{3+} was added at $T = 0$ min in a 2:1 ratio and SO_4^{2-} in a 3:1 ratio.

2.3 Pairing of 2nd cycle candles

To pinpoint why the oxidant candles were not performing as well after the 1st cycle (e.g., Fig. 3A, main manuscript), 2nd cycle persulfate candles were paired with a fresh Fe^0 candle (i.e., a 1st cycle Fe^0 candle), a 2nd cycle Fe^0 candle that had its outer layer scrapped off (scraped) and 2nd cycle Fe^0 candle that was chopped into smaller pieces to create more surface area. Likewise, the 2nd cycle Fe^0 candles were paired with a fresh persulfate candle (1st cycle), a 2nd cycle persulfate candle that was scrapped, and a 2nd cycle persulfate candle that was chopped.

3. Results

3.1 Control experiments: wax and iron-wax coated flasks

Results showed that the presence of wax had no effect on dioxane degradation but the flasks that were coated with Fe^0 -wax showed a linear (zero-order) rate of degradation (Fig. SM-1).

3.2 Effects of Fe^{3+} and SO_4^{2-} on dioxane degradation by persulfate and Fe^0

To complement and complete the experiments identifying which species were causing the dioxane degradation rates to halt (plateau), we singularly added products of the persulfate- Fe^0 reaction at $T = 0$ min. Although results showed that Fe^{2+} halted the reaction (Fig. 2B), we observed no effect of Fe^{3+} or SO_4^{2-} on the degradation of dioxane (Fig. SM-2) as results were very similar to results obtained when Fe^{3+} or SO_4^{2-} were not included (Fig. 1A). These results point to the presence of Fe^{2+} as the main reason for the reaction kinetics observed (i.e., plateau).

3.3 Pairing of 2nd cycle candles

Results using the 2nd cycle persulfate candles showed that regardless of which type of iron candle it was paired with, a plateau in the degradation of dioxane was achieved. By contrast, when 2nd cycle iron candles were paired with new, scrapped or chopped up persulfate candles, more complete degradation was achieved (Fig. SM-3). This indicates that when the release rate of persulfate decreases, persulfate can become limiting and the abundance of Fe^{2+} present can quench the persulfate radicals formed. As shown in the main manuscript, preventing this can be accomplished by increasing the ratio of persulfate candles to iron candles (Fig. 3B, Fig. SM-4) and by including SHMP in the persulfate formulation (Fig. 4B).

LIST OF FIGURES

- Figure SM-1.** Control experiments with wax-coated and iron-wax-coated flasks. A. wax-coated: one dose application, B. wax-coated: quarter dose application; C. iron-wax coated: one dose application; D. iron-wax coated: quarter dose applications.
- Figure SM-2.** Effect of adding Fe^{3+} (as $\text{Fe}_2(\text{SO}_4)_3$) and SO_4^{2-} (as Na_2SO_4) at $T = 0$ min on dioxane degradation by persulfate and Fe^0 .
- Figure SM-3.** Effect of pairing 2nd cycle persulfate and Fe^0 candles with new, scrapped, and chopped candles.
- Figure SM-4** Dioxane degradation by slow-release persulfate and Fe^0 candles combined in 1:1 to 4:1 ratios during 1st, 2nd and 3rd cycle experiments. A. 1st Cycle; B. 2nd Cycle; C. 3rd Cycle.
- Figure SM-5** Temporal changes in dioxane concentration and ^{14}C activity following treatment with persulfate (PS) and Fe^0 candles. Top: Effects of methanol on dioxane degradation; Bottom: Temporal changes in ^{14}C -activity. Experimental units were exposed to light.
- Figure SM-6** GC/MS confirming identification of 1,4-dioxane-2-ol formed during treatment of 1,4-dioxane with persulfate and zerovalent iron candles.

Figure SM-1

Figure SM-2

Figure SM-3

Figure SM-4

Figure SM-5

Figure SM-6