



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.

ARTICLE INFO

Article history:

Received 28 October 2016

Received in revised form

30 January 2017

Accepted 7 February 2017

Available online 8 February 2017

Handling Editor: W. Mitch

Keywords:

Chlorinated solvents

TCE

Dioxane

Persulfate

Slow-release oxidants

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.

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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

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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 (Schreiber 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; Schreiber 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 chemical masses to 50 mL of dioxane, the molar ratio of persulfate to iron was 1:1 (persulfate, 63 mM; Fe^0 , 67 mM) 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

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