Published in final edited form as:

Water Air Soil Pollut. 2016 December ; 227: . doi:10.1007/s11270-016-3146-y.

Influence of groundwater constituents on 1,4-dioxane degradation by a binary oxidant system

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Abstract

The influence of groundwater on the degradation of 1,4-dioxane (dioxane) by siderite-activated hydrogen peroxide coupled with persulfate was investigated through a series of batch experiments. The degradation of dioxane was considerably slower in groundwater compared to the tests conducted with ultrapure water. Additional tests were conducted to examine potential inhibitory effects of selected ions in isolation. The inhibition effect of anions on dioxane degradation, from strongest inhibition to weakest, was: bicarbonate (HCO_3^-) > sulfate (SO_4^{2-}) > chloride (Cl^-). The inhibition effect of cations on dioxane degradation, from strongest inhibition to weakest, was: calcium (Ca^{2+}) > potassium (K^+) > magnesium (Mg^{2+}). Bicarbonate and calcium ions, which are the most abundant ions in the groundwater used herein, resulted in the greatest decrease in dioxane degradation rate compared to the other constituents. The results of experiments conducted to evaluate their impact over a range of concentrations showed that dioxane degradation was reduced asymptotically with the increase in their concentrations. The results of this study reveal a potential inhibitory effect caused by groundwater constituents during the application of activated binary H_2O_2 -persulfate for in-situ treatment of organic contaminants in groundwater. This effect is attributed to radical scavenging, and its impact should be considered during the evaluation of total oxidant demand (TOD) prior to application.

Keywords

1,4-Dioxane; in-situ chemical oxidation; ionic composition; radical scavenging

1 Introduction

1,4-Dioxane (dioxane) in surface and groundwaters continues to attract considerable attention due to its widespread occurrence and potential negative effects on human-health. Dioxane has been classified as a suspected human carcinogen (B2) (EPA 2000). As a widely

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used solvent stabilizer, dioxane commonly co-occurs with chlorinated contaminants, typically 1,1,1-trichloroethane (1,1,1-TCA), at contaminated sites (EPA 1995; IARC 1999; Adamson et al. 2014; Adamson et al. 2015). Dioxane is miscible in water, has low retardation, and generally low transformation potential, and thus is typically highly mobile in subsurface environments. Therefore, large groundwater contaminant plumes of dioxane often form, usually co-occurring with chlorinated-constituent plumes (Anderson et al. 2012; EPA 2013; Adamson et al. 2014; Adamson et al. 2015).

The remediation and management of groundwater contaminated by dioxane is challenging. It is generally resistant to biological treatment under both aerobic and anaerobic conditions (Adams et al. 1994; Raj et al. 1997; Beckett and Hua 2000). Standard above-ground treatment strategies such as GAC adsorption and air stripping are ineffective. Advanced oxidation processes (AOP) are now being used for above-ground treatment of dioxane-contaminated groundwater. However, alternative, in-situ treatment approaches that would hopefully be less costly than these pump-and-treat methods continue to be investigated. In-situ chemical oxidation (ISCO) is a promising direct treatment alternative for contaminated soil and groundwater.

The advantages and disadvantages of ISCO have been discussed (Watts and Teel 2006; Krembs et al. 2010; Tsitonaki et al. 2010; Brusseau et al. 2011). The effectiveness of ISCO for subsurface applications is known to be influenced by geochemical properties and conditions of the subsurface. For example, natural-occurring organic matter serves as a background oxidant demand. Groundwater temperature and pH can also influence ISCO reactions. It has also been shown that various inorganic constituents (e.g., salts) present in groundwater may influence ISCO through scavenger effects.

Salts can interact with and quench radicals or complex with a metal activator and thus reduce radical production, both of which would reduce contaminant degradation (Lipczynska-Kochany et al. 1995; Beltran et al. 1998; Valentine and Wang 1998; De Laat et al. 2004; Liang et al. 2006; Bennedsen et al. 2012). Furthermore, the presence of some anions (such as ClO_4^-) leads to acidification, which has been observed to inhibit some oxidation reactions (Barbeni et al. 1987; Peyton 1993; Lipczynska-Kochany et al. 1995; Liang et al. 2006; Bennedsen et al. 2012). While the influence of anions (e.g., Cl^- , CO_3^{2-} , HCO_3^{2-}) on the degradation of selected contaminants (e.g., trichloroethene) during ISCO have been reported, minimal research has focused on the inhibition effect of cations. To our knowledge, the influence of groundwater constituents on dioxane degradation has not yet been reported.

The objective of this study is to investigate the influence of groundwater and selected constituents on the degradation of dioxane. A promising binary oxidant system, siderite-activated hydrogen peroxide (H_2O_2) coupled with persulfate, was used as a representative ISCO reagent for our experiments due to its high oxidation potential and moderate oxidant decomposition rate (Block et al. 2004; Huang et al. 2012; Ko et al. 2012; Yan et al. 2013; Yan et al. 2015; Zhang et al. 2015). Batch experiments were conducted to determine dioxane oxidation rates in ultrapure water and groundwater. The influence of selected anions and cations on the oxidative degradation of dioxane was also explored.

2 Materials and methods

2.1 Chemicals

All solutions used in this study were prepared using ultrapure (filtered, distilled, deionized) water (Millipore Model Milli-Q Academic A10), except where noted. All of the reagents were reagent grade or higher. Siderite was purchased from the Wuhan Iron and Steel (Group) Corporation, China; hydrogen peroxide (H_2O_2 , ~30 wt. % in water), 1,4-dioxane ($\text{C}_4\text{H}_8\text{O}_2$, 99%), ascorbic acid, sodium chloride (NaCl , 99.8%), sodium sulfate (Na_2SO_4 , 95%), sodium bicarbonate (NaHCO_3 , 99.8%), potassium chloride (KCl , 99.8%), calcium chloride (CaCl_2 , 96%), magnesium chloride (MgCl_2 , 97%) were obtained from Beijing Chemical Works, China; sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98%) was purchased from the Xilong Chemical Co., Ltd, China.

The following reagent concentrations were used for all of the experiments. Oxidant concentrations were selected based on the results of previous studies employing persulfate and H_2O_2 (Yan et al. 2013; Yan et al. 2015). For dioxane, 10 μL of dioxane was added to each vial for the relevant experiments. This quantity is equivalent to 11.69 mM (1,030 mg/L) in solution. Concentrations of persulfate, H_2O_2 , and siderite in the final solutions were 6.3 mM (1,500 mg/L), 150 mM (5100 mg/L), and 11,450 mg/L respectively for all experiments. The oxidant concentrations are much lower than the concentrations typically used for standard field ISCO applications. Thus, use of these concentrations will produce conservative results.

2.2 Experiment setup

Batch experiments (in triplicate) were conducted at 20 ± 1 °C with 20 mL borosilicate vials fitted with PTFE septum caps. Two sets of control experiments were set up. One set comprised only ultrapure water and dioxane, and was used to evaluate the loss of dioxane through any potential mass-loss processes during the study. Another control group contained oxidant and contaminant to determine whether dioxane could be degraded in the absence of activator. The control test with ultrapure water and dioxane is under neutral pH condition. The pH of the control group containing oxidant and contaminant is ~3.

Three sets of treatment reactors were used. One set of reactors was designed to compare dioxane degradation efficiency in ultrapure water and groundwater. The groundwater was collected from a monitoring well located in the China University of Geosciences (Beijing), China. The chemical composition of the groundwater is shown in Table 1. The estimated mineralization of the studied groundwater is 412.45 mg/L by solving Eq. (1), which indicates the groundwater used herein was a relatively low mineral content.

$$M = \sum M_{\text{cation}} + \sum M_{\text{anion}} \quad (1)$$

Ultrapure water or groundwater was used to create the solutions of $\text{Na}_2\text{S}_2\text{O}_8$, and H_2O_2 . Then dioxane was added to the vial. The total solution volume was 10 mL. Each vial contained 0.1145 g siderite.

The second reaction group was designed to evaluate the influence of anions on dioxane degradation by the binary oxidant system. Three common anions (Cl^- , SO_4^{2-} , HCO_3^-) were tested. Solutions of 0.6 mM NaCl or NaSO_4 or NaHCO_3 , 6.3 mM $\text{Na}_2\text{S}_2\text{O}_8$, and 150 mM H_2O_2 were added to the vial. Then dioxane was added to the vial. The total solution volume was 10 mL. Each vial contained 0.1145 g siderite.

The third reaction group was designed to evaluate the influence of cations on dioxane degradation by the binary oxidant system. Three common cations (K^+ , Ca^{2+} , Mg^{2+}) were tested. Solutions of 0.6 mM KCl or CaCl_2 or MgCl_2 , 6.3 mM $\text{Na}_2\text{S}_2\text{O}_8$, and 150 mM H_2O_2 were added to the vial. Then dioxane was added into the vial. The total solution volume was 10 mL. Each vial contained 0.1145 g siderite.

Another reaction group was designed to evaluate the influence of ion concentrations on dioxane degradation by the binary oxidant system. Two ions (HCO_3^- and Ca^{2+}) were tested. Solutions of 0.2/0.6/1/2 mM NaHCO_3 or CaCl_2 , 6.3 mM $\text{Na}_2\text{S}_2\text{O}_8$, and 150 mM H_2O_2 were added to the vial. Then dioxane was added to the vial. The total reaction volume was 10 mL. Each vial contained 0.1145 g siderite.

After preparation, the vials were maintained at 20 ± 1 °C in an air bath for the experiments. At selected time-points, samples were collected and ascorbic acid was added to quench further oxidation. The pH of the siderite-activated binary H_2O_2 -persulfate system is ~3. $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ is expected to be the dominant carbonate species at equilibrium in the system.

2.3 Analytical methods

Dioxane was analyzed using gas chromatography (Agilent GC6820) equipped with a headspace autosampler, a flame ionization detector (FID), and a 30 m $\times$ 0.53 mm DB-5 capillary column (film thickness was 1.5 μm). External standards were used for quantification. The temperatures of the injection port and detector were 200 and 250 °C, respectively. 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.

3 Results and discussion

3.1 Influence of groundwater chemistry on dioxane degradation

Both control tests showed that the mass-loss of dioxane was ~4% for the ultrapure water and dioxane group, and ~10% for the oxidant and dioxane group in 48 hours (Fig. 1a). The results for dioxane degradation by siderite-activated persulfate- H_2O_2 in ultrapure water and groundwater are presented in Fig. 1b. There was approximately 35% dioxane loss for the system in the presence of groundwater at 48 hours. In contrast, approximately 50% degradation was attained for the system with ultrapure water. The results indicate considerable impact of the background groundwater constituents on the removal of dioxane. Dioxane degradation was essentially identical in ultrapure water (~31%) and groundwater (~29%) after 4 hours of reaction. However, the degradation rates deviated greatly thereafter.

Dioxane degradation exhibited a two-stage reaction pattern, with a high rate of degradation in the first 4 hours followed by a relatively slow rate of degradation. Pseudo-first-order reaction rate constants for dioxane degradation with and without groundwater are 0.064 ± 0.001 and $0.068 \pm 0.001 \text{ h}^{-1}$ for the initial degradation stage, indicating similar degradation efficiency during this period. Conversely, the rate constants were 0.006 ± 0.001 and $0.016 \pm 0.001 \text{ h}^{-1}$ for the later stage. The results indicate that the presence of groundwater resulted in approximately 3 times slower degradation after the first 4 hours.

The reduction of the rate of dioxane degradation in the presence of groundwater was most likely caused by activation inhibition and/or the radical scavenging effect. As shown in Table 1, several ions are abundant in the groundwater sample used herein. They are typical constituents for most groundwaters. Specific experiments were conducted to illuminate the impact of specific ions on dioxane degradation, the results of which are presented in the following sections.

3.2 Influence of selected anions on the degradation of dioxane

Chloride (Cl^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-) ions were studied, since they are the most abundant anions in the groundwater used in the previous section. They are also three typical anionic constituents in groundwater. The degradation of dioxane in the presence of chloride, sulfate, and bicarbonate, respectively, is illustrated in Fig. 2a. The addition of chloride ion produced no significant impact on dioxane degradation. However, dioxane removal was significantly inhibited with the addition of sulfate and bicarbonate ions, with degradation reduced by ~35% and 66%, respectively, compared to ultrapure water.

It is hypothesized that the inhibition effect observed is related to the scavenging of hydroxyl and sulfate radicals by the added ions. The scavenging ability is expected to decrease in the following order (for equal concentration): bicarbonate > sulfate > chloride (Kochany and Lipczynska-Kochany 1992; Lipczynska-Kochany et al. 1995; Liang et al. 2006). It is also reported that chloride might have a greater impact on Fenton processes than bicarbonate and sulfate (Riga et al 2011). However, a chloride concentration of 100 mM (3.5 g/L) was used in that study, higher than what is typical for most groundwaters.

Additional experiments were conducted with different concentrations of bicarbonate ion. The inhibition effect increased with the increase of bicarbonate concentrations from 0 to 2 mM (Fig. 2b). Moreover, dioxane degradation efficiency was significantly inhibited with as low as 0.2 mM bicarbonate present. No further significant increase in inhibition was observed above 0.2 mM bicarbonate. Further inhibition was limited due to the limited amount of radicals present.

3.3 Influence of selected cations on the degradation of dioxane

The degradation of dioxane in the presence of potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), respectively, is illustrated in Fig. 3a. Dioxane degradation was inhibited with the addition of potassium, calcium, and magnesium ions, with degradation reduced by ~35%, 59%, and 28%, respectively. It is noteworthy that the observed inhibition is particularly strong for calcium.

One possibility is that potassium, calcium, and magnesium ions might consume oxidant without generation of effective radicals, and lead to less oxidant available for the oxidative degradation of dioxane. For example, calcium might consume persulfate to generate CaSO_4 without the generation of sulfate radicals. Calcium is a typical cationic constituent in groundwater, and its concentration can reach hundreds of milligram per liter in high salinity groundwater. Additional experiments were conducted with different concentrations of calcium ion. The inhibition effect increased with the increase of calcium concentrations from 0 to 2 mM (Fig. 3b). There was a considerable decrease in degradation efficiency when calcium concentration increased from 0 to 0.2 mM. However, the decrease in efficiency was more modest when the concentration exceeded 0.2 mM.

4 Conclusion

Dioxane was successfully degraded by the siderite-activated binary H_2O_2 -persulfate system. However, the rate of degradation was slower in the presence of groundwater and typical groundwater constituents compared to ultrapure water. Chloride, sulfate, bicarbonate, potassium, calcium, and magnesium ions that are present in groundwater inhibited the oxidative degradation of dioxane. The inhibition was particularly strong for bicarbonate and calcium ions.

Traditional factors considered during calculation of the total oxidant demand (TOD) usually include: 1) stoichiometric demand of contaminant (dissolved phase, sorbed phase, and free phase), 2) soil mineral (dissolved and solid phase) consumption, 3) organic carbon (dissolved and sorbed phase) consumption, and 4) oxidant decomposition (Haselow et al., 2003). The results of this work indicate that the scavenging effect of ions may be another contributor to TOD that should be considered. This may be especially critical for bicarbonate and calcium, which are typically present in groundwater at concentrations higher than 0.2 mM (usually 1–2 mM).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC) (41272268), the NIEHS Superfund Research Program (ES04940), and the Strategic Environmental Research and Development Program (ER-2302). The first author acknowledges support by the China Scholarship Council.

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Fig. 1.

(a) The loss of dioxane in the control test; (b) dioxane degradation by the siderite-activated persulfate and H_2O_2 in ultrapure water and groundwater. Bars represent standard error.

Fig. 2. Dioxane degradation by the siderite-activated persulfate and H₂O₂ after 48 h reaction (a) the effects of Cl⁻, SO₄²⁻, and HCO₃⁻ on the degradation efficiency; (b) the influence of HCO₃⁻ concentration on the degradation efficiency. Bars represent standard error.

Fig. 3. Dioxane degradation by the siderite-activated persulfate and H₂O₂ after 48 h reaction (a) the effects of K⁺, Ca²⁺, and Mg²⁺ on the degradation efficiency; (b) the influence of Ca²⁺ concentration on the degradation efficiency. Bars represent standard error.

Table 1

The chemistry compositions of the groundwater

Major ions detected in the groundwater (mg/L)									
K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Fe ³⁺	Fe ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
2.22	18.38	80.75	38.18	ND ^a	ND	52.94	17.19	74.89	255.8

Trace elements detected in the groundwater (µg/L)									
Co	Cr	Cu	Mn	Mo	Ni	Ti	Sr	V	Zn
0.24	6.44	2.75	0.52	4.38	0.65	0.82	2733	1.19	3.31
As	Ba	Be	Cd	Ga	Li	Pb	Rb	Sc	U
0.65	81.9	0.12	0.13	0.02	3.21	0.14	0.94	0.76	2.58

^aNot detected

Table 2

Pseudo-first-order reaction rate constant k and half-life $t_{1/2}$ for dioxane degradation in siderite-activated H_2O_2 and persulfate

Aqueous phase	Rate constant k (h^{-1})		Half-life $t_{1/2}$ (h)	
	Rapid ^a	Slow ^b	Rapid	Slow
Ultrapure water	0.068	0.016	10.2	43.3
Groundwater	0.064	0.006	10.8	115.5

^aRate constant k for siderite-activated binary oxidant system was calculated by rapid reaction period

^bRate constant k for siderite-activated binary oxidant system was calculated by slow reaction period