Stabilization and prolonged reactivity of aqueous-phase ozone with cyclodextrin

Adam Dettmer [a], Raymond Ball [b], Thomas B. Boving [c], Naima A. Khan [a], Tanner Schaub [a], Nilusha Sudasinghe [a], Carlos A. Fernandez [d], Kenneth C. Carroll [a,*]

[a] New Mexico State University, MSC 3Q, P.O. Box 30003, Las Cruces, NM 88003, USA
[b] Enchem Engineering, Inc., 151 California Street, Newton, MA 02458, USA
[c] University of Rhode Island, Kingston, RI 02881, USA
[d] Pacific Northwest National Laboratory, Richland, WA 99354, USA

ARTICLE INFO

ABSTRACT

Recalcitrant organic groundwater contaminants, such as 1,4-dioxane, may require strong oxidants for complete mineralization. However, their efficacy for in-situ chemical oxidation (ISCO) is limited by oxidant decay and reactivity. Hydroxypropyl-β-cyclodextrin (HPβCD) was examined for its ability to stabilize aqueous-phase ozone (O_3) and prolong oxidation potential through inclusion complex formation. Partial transformation of HPβCD by O_3 was observed. However, HPβCD proved to be sufficiently recalcitrant, because it was only partially degraded in the presence of O_3. The formation of a HPβCD:O_3 clathrate complex was observed, which stabilized decay of O_3. The presence of HPβCD increased the O_3 half-life linearly with increasing HPβCD:O_3 molar ratio. The O_3 half-life in solutions increased by as much as 40-fold relative to HPβCD-free O_3 solutions. Observed O_3 release from HPβCD and indigo oxidation confirmed that the formation of the inclusion complex is reversible. This proof-of-concept study demonstrates that HPβCD can complex O_3 while preserving its reactivity. These results suggest that the use of clathrate stabilizers, such as HPβCD, can support the development of a facilitated-transport enabled ISCO for the O_3 treatment of groundwater contaminated with recalcitrant compounds.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Groundwater contamination with recalcitrant, anthropogenic, organic chemicals remains a common and significant risk to human-health and water-resource sustainability. These contaminants may be treated using in-situ chemical oxidation (ISCO), which involves the introduction of oxidants into the subsurface where contaminants are transformed, through oxidation, into benign by-products (e.g., Huling and Pivetz, 2006). However, some organic contaminants (e.g., 1,4-dioxane) may require strong oxidants (i.e., compounds that have a standard redox potential greater than two volts) to be completely mineralized (Huling and Pivetz, 2006). Such contaminants are currently remediated using ex situ chemical oxidation (Zenker et al., 2003). This does require extraction of contaminated groundwater to the surface before treatment, which is generally inefficient and costly. Although advanced oxidation would be the preferred ISCO remediation method for recalcitrant contaminants, there are significant limitations in the use of strong oxidants for in-situ treatment.

Because of its relatively high standard oxidation potential (2.07 V), ozone (O_3) is a proven ISCO reagent for contaminated soil and groundwater (Bhuyan and Latin, 2012; Clayton et al., 2011; Huling and Pivetz,

2006). However, a key limitation for implementation of O_3, and other strong oxidants, in the treatment of recalcitrant contaminants is the short half-live and high reactivity of the oxidant in the subsurface environment (Huling and Pivetz, 2006). Radical scavengers, such as transition metals and soil organic matter associated with the subsurface materials, both aqueous and solid, can impose a significant oxidant demand, which ultimately reduces the amount of oxidant available for reaction with contaminants and increases the cost of treatment (e.g., Brusseau et al., 2011; Crimi and Siegrist, 2003; Marble et al., 2010; Mumford et al., 2004; Urynowicz, 2008; Xu and Thomson, 2009). The oxidant demand, as well as the reactivity of the oxidants, provides a serious challenge for the development of ISCO in general, and the variability and potential controls of O_3 oxidant demand in ISCO systems remains subject to research (e.g., Clayton et al., 2011; Huling and Pivetz, 2006; Lim et al., 2002; Masten, 1991; Masten and Davies, 1997; Wang et al., 2012).

O_3 is only sparingly soluble (~208 μM or 10 mg/L) in typical groundwater systems, and for that reason has mainly been injected as a gas (Masten and Davies, 1997). The half-life for aqueous O_3 is typically < 1 h due to the reactivity of the hydroxyl radical (OH•). This severely limits O_3 delivery to contaminants residing at significant distances away from the oxidant injection point. O_3 transforms contaminants through either direct oxidation or through decomposition and production of hydroxyl radicals, which then react with contaminants. Clayton

et al. review the relatively selective direct O_3:contaminant reaction mechanisms and indirect contaminant oxidation by radicals generated by O_3 (Clayton et al., 2011). The reactions that produce radicals from O_3 are generally thought to follow either the Hoigne, Staehelin, and Bader model (Hoigne and Bader, 1983a; Hoigne and Bader, 1983b; Hoigne et al., 1985) or the Tomiyasu, Fukutomi, and Gordan model (Tomiyasu et al., 1985) mechanisms (Clayton et al., 2011). Although, indirect oxidation using radical formation is highly reactive, this pathway may be limited in the presence of radical scavengers.

Use of oxidant stabilizers has been considered for increased oxidant stability and transportability within the subsurface (Huling and Pivetz, 2006). Oxidant stabilization generally involves addition of a chemical that forms a complex with an oxidant, which limits oxidant reactivity. Stabilizers have been developed mainly for iron (i.e., chelators) and hydrogen peroxide (H_2O_2) (i.e., phosphates or organic acids) (Watts et al., 2007). These modified-Fenton reaction methods then utilize a facilitated-transport approach to deliver the oxidant to the organic contaminants (Lee and Lee, 2010; Lewis et al., 2009; Lindsey et al., 2003; Wang and Brusseau, 1998).

Clathrates such as cyclodextrins have been shown to enhance the solubility and transport of both organics and metals (e.g., Blanford et al., 2014; Boving and McCray, 2000; Boving et al., 1999; Brusseau et al., 1994; Brusseau et al., 1997; Carroll and Brusseau, 2009; Chatain et al., 2004; Fourmentin et al., 2007; Gao et al., 2013; McCray et al., 2000; Skold et al., 2007; Tick et al., 2003; Wang and Brusseau, 1995). Cyclodextrins have also been used to complex iron, preventing the consumption of H_2O_2 and precipitation of iron (Lindsey et al., 2003). A ternary complex between the specific cyclodextrin called hydroxypropyl-β-cyclodextrin (HPβCD), Fe^{2+}, and pollutants has been observed (Liang et al., 2007). Veignie et al. demonstrated that certain cyclodextrins increase contaminant solubility while simultaneously supporting their degradation by Fenton's reaction (Veignie et al., 2009). It has been hypothesized that the formation of a ternary complex (i.e., pollutant-cyclodextrin-iron) enhances contaminant degradation by increasing the proximity of the contaminant to the OH• radical (Lindsey et al., 2003; Veignie et al., 2009).

O_3 is relatively hydrophobic, and could potentially be attracted to the hydrophobic cavity of HPβCD. The oxidative transformation of glucose with O_3 is well known (Marcq et al., 2009), and therefore destruction of HPβCD (i.e., a ring of glucose molecules) would be expected. However, HPβCD is generally more recalcitrant than the glucose building blocks, e.g. they are resistant to biological decay for a period of at least a few months (Wang et al., 1998). Prior work has not examined the potential for O_3 or other strong oxidants to oxidize HPβCD. Thus, it is currently unknown if and to what extend O_3 can degrade HPβCD and what transformation products are formed in the process. Examination of the potential for O_3 to transform HPβCD and/or for HPβCD to form a complex with O_3 is examined herein.

It is hypothesized that aqueous-phase O_3 partitions into the cavity of the HPβCD molecule, and that the formation of a HPβCD:O_3 inclusion complex (i.e., one chemical compound forms a cavity in which molecules of a second "guest" compound are located) prolongs the reactivity of O_3 in groundwater solutions. The objective of this research was to examine the potential for complexation of O_3 by HPβCD, as suggested previously (Ball, 2011), and the resulting impact on the stabilization and prolonged reactivity of the O_3. Because HPβCD is a cyclic sugar,

consisting of glucose molecules, it must be expected that the HPβCD molecule is susceptible to oxidation. Therefore, the potential for O_3 to transform HPβCD was studied in aqueous-phase batch experiments. The ultimate goal was to provide insights into O_3 complexation by HPβCD and related facilitated transport processes that potentially extends the reactive lifetime and lateral reach of O_3 in subsurface environments. Such a technology could support ISCO remediation of groundwater contaminated with recalcitrant compounds.

2. Materials and methods

2.1. Materials

Hydroxypropyl-β-cyclodextrin, or HPβCD, (90% purity technical grade; average molecular weight: 1375 g mol^{-1}) was purchased from Sigma-Aldrich (Milwaukee, WI. Lot #BCBK6962V). A Barnstead NANOpure II (Series 550, Dubuque, Iowa) system was used to purify water used for all solutions to >18 MΩ-cm (termed DI). A synthetic groundwater solution (Table 1) containing 9 mg/L $Ca(NO_3)_2$, 85 mg/L $CaCl_2$, 124 mg/L $MgSO_4$, 171 mg/L $NaHCO_3$, and 20 mg/L NaCl prepared in DI was used for all experiments except when noted that DI was used. The synthetic groundwater represents the chemistry of the contaminated groundwater at Air Force Plant 44 (AFP44) in Tucson, Arizona, USA (Matthieu et al., 2013). All experiments were conducted at 20($\pm$1) °C. Gas-phase O_3 was generated using a G-series Pacific Ozone Generator (model #G1110101, Benicia, California), which was sparged through aqueous solutions to dissolve O_3 before each experiment.

2.2. Chemical analysis

Aqueous O_3 concentrations were determined by the indigo method (Bader and Hoigné, 1981) using a Milton Roy Spectronic 401 spectrophotometer, which has a reported precision to be 2% or 3 μg/L for O_3 analysis. Aqueous HPβCD samples were analyzed for concentration by fluorescence methods (Kondo et al., 1976) using a LS-55 Perkin Elmer spectrofluorometer. UV–Vis spectroscopy wavelength scans were also used to confirm HPβCD:O_3 complexation (SpectraMax M2, Molecular Devices). Additionally, HPβCD samples were analyzed for concentration and for identification of transformation products, by positive-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS), performed with a hybrid linear ion trap 7 T FT-ICR mass spectrometer (LTQ FT, Thermo, San Jose, CA). The mass spectrometer was equipped with a chip-based nano-electrospray ionization and sample-handling robot (Advion Triversa NanoMate) to produce positively- and negatively-charged ions. Prior to mass spectral analysis, samples were diluted 2-fold in methanol that contained 0.1% formic acid and 0.3 μM reserpine as an internal standard for signal normalization. Mass spectra were collected at a mass range of 300–2000 m/z and at mass resolving power of m/Δm$_{50\%}$ = 400,000 (m/z 400). Internal mass calibration of FT-ICR mass spectra produces sub-part-per-million mass measurement accuracy, and enables the direct determination of elemental composition from measured mass to charge ratios. Thus, compounds were identified at the level of elemental composition based on accurate mass measurement by FT-ICR MS and linear ion trap mass spectra were used for relative quantitation. Peak lists generated from linear ion trap mass spectra were normalized to the internal

Table 1
Characteristics of synthetic groundwater used for all experiments.

Description	pH	TDS (mg/L)	Conductivity (μS/cm)	Eh (mV)
Synthetic groundwater	7.9	379	565	212

Hydrogeochemistry	Major cation	Concentration (mg/L)	Major anion	Concentration (mg/L)
	Na	54.7	Cl	66.5
	Ca	32.9	HCO_3:	99.0
	Mg	25.0	SO_4:	124.0