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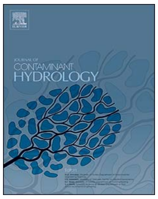

Spectroscopic methods for aqueous cyclodextrin inclusion complex binding measurement for 1,4-dioxane, chlorinated co-contaminants, and ozone

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ABSTRACT

Recalcitrant organic contaminants, such as 1,4-dioxane, typically require advanced oxidation process (AOP) oxidants, such as ozone (O_3), for their complete mineralization during water treatment. Unfortunately, the use of AOPs can be limited by these oxidants' relatively high reactivities and short half-lives. These drawbacks can be minimized by partial encapsulation of the oxidants within a cyclodextrin cavity to form inclusion complexes. We determined the inclusion complexes of O_3 and three common co-contaminants (trichloroethene, 1,1,1-trichloroethane, and 1,4-dioxane) as guest compounds within hydroxypropyl-β-cyclodextrin. Both direct (ultraviolet or UV) and competitive (fluorescence changes with 6-p-toluidine-2-naphthalenesulfonic acid as the probe) methods were used, which gave comparable results for the inclusion constants of these species. Impacts of changing pH and NaCl concentrations were also assessed. Binding constants increased with pH and with ionic strength, which was attributed to variations in guest compound solubility. The results illustrate the versatility of cyclodextrins for inclusion complexation with various types of compounds, binding measurement methods are applicable to a wide range of applications, and have implications for both extraction of contaminants and delivery of reagents for treatment of contaminants in wastewater or contaminated groundwater.

1. Introduction

1,4-Dioxane (1,4-D) was previously used as a solvent stabilizer mixed with chlorinated solvents (Mohr et al., 2010), mainly 1,1,1-trichloroethane (TCA) and trichloroethene (TCE) (Adamson et al., 2015; Anderson et al., 2012; Zenker et al., 2003). 1,4-D is released as a by-product of polyester production and disposal of various consumer products (DiGuiseppi and Whitesides, 2007; Mohr et al., 2010; Zenker et al., 2003). The solvent stabilizer, 1,4-D, has emerged in the environmental remediation arena as an unexpected and recalcitrant wastewater and groundwater contaminant even though it is not currently classified as a U.S. EPA priority pollutant, and it does not have a maximum contaminant level for drinking water (Mohr et al., 2010). Toxicological studies suggest that 1,4-D may be harmful, and it has been designated as a probable human carcinogen (Anderson et al., 2012; Coleman et al., 2007; EPA, 2013; IARC, 1999; Mohr et al., 2010).

The properties of 1,4-D that make it useful for solvent stabilization, such as the high polarity, which results in its high aqueous solubility and low adsorption and volatilization (DiGuiseppi and Whitesides, 2007; Mohr et al., 2010; Zenker et al., 2003), have resulted in extensive wastewater and groundwater contaminant plumes that are often as large as those associated with the chlorinated solvents and make it a challenge for water treatment. Despite the co-disposal and coincidence of plumes, 1,4-D is not effectively removed from groundwater through sorption or volatilization technologies typically used for chlorinated co-contaminant treatment (DiGuiseppi et al., 2016; DiGuiseppi and Whitesides, 2007; Zenker et al., 2003; Zhang et al., 2017), and the cleanup targets being proposed for 1,4-D are potentially as low as, or lower than, those for most chlorinated solvents. For example, biological methods have been shown to be inhibited for 1,4-D in the presence of chlorinated co-contaminants (Mahendra et al., 2013; Hand et al., 2015; Zhang et al., 2016; Zhang et al., 2017). In terms of treatment using chemical oxidation, mineralization of 1,4-D typically requires strong oxidants (i.e., advanced oxidation processes or AOP) that have a standard redox potential greater than two electron volts (DiGuiseppi et al., 2016; DiGuiseppi and Whitesides, 2007; Zenker et al., 2003). Currently, the most common method used to remediate 1,4-D involves ex situ treatment using AOP (e.g., ozone or O_3 and H_2O_2) (DiGuiseppi et al., 2016; DiGuiseppi and Whitesides, 2007; Zenker et al., 2003). O_3 ($E^o = 2.07\ V$) is widely used for AOP of recalcitrant emerging water contaminants (Bhuyan and Latin, 2012; Clayton et al., 2011; Huling and Pivetz, 2006a). Chemical oxidation processes can be used to treat

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1,4-D either in situ or ex situ (Huling and Pivetz, 2006b; Zenker et al., 2003). A key limitation to implement AOP wastewater treatment of recalcitrant contaminants is the short half-lives (i.e., up to 1 h for aqueous O_3 depending on aqueous chemistry) (Dettmer et al., 2017; Huling and Pivetz, 2006a).

Oxidant stabilizers have been proposed to increase oxidant longevity (Huling and Pivetz, 2006a), and these typically include the complexation of the oxidant. Stabilizers have been developed mainly for iron (i.e., chelators) and H_2O_2 (i.e., phosphates or organic acids) (Watts et al., 2007). These modified-Fenton reaction methods use a facilitated-transport approach to apply the Fenton reaction for in situ chemical oxidation (ISCO) of organic contaminants (Lee and Lee, 2010; Lewis et al., 2009; Lindsey et al., 2003; Wang and Brusseau, 1998). Various organic acids have proven effective to enhance the lifespan of H_2O_2 in soil (Chang et al., 2013; Jung et al., 2013; Watts et al., 2007).

Cyclodextrins are cyclic D-glucopyranoses bonded through α-1,4-glucosidic linkages, the exterior is hydrophilic, and they also have a hydrophobic interior into which compounds can partition (Bender and Komiyama, 1978; French, 1957; Szejtli, J., 1998). Reviews have discussed inclusion complexation formation within cyclodextrins (Boving and McCray, 2000; Connors, 1997; Landy et al., 2012). The mechanism that is generally accepted for inclusion-complex formation within the HPβCD cavities is hydrophobic partitioning and displacement of water molecules from the cavity (Connors, 1997), and this partitioning is generally considered to be a weak attraction force that is generally reversible. Inclusion complex formation has long been an important area in cyclodextrin research (Bender and Komiyama, 1978; Connors, 1997; Saenger, 1980), which has had increased interest recently for contaminant remediation (Landy et al., 2012). Clathrates such as cyclodextrins have been shown to enhance the solubility, transport, and extraction of both organic and metal contaminants (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 for oxidation stabilization, preventing the consumption of H_2O_2 and precipitation of iron (Lindsey et al., 2003). Veignie et al., (2009) also demonstrated that various types of cyclodextrin increase contaminant solubility and its degradation by Fenton's reagent. A ternary complex between hydroxypropyl-β-cyclodextrin (HPβCD), Fe^{2+}, and pollutants has been proposed (Liang et al., 2007). Recently, Dettmer et al. (2017) have also documented the inclusion complexation of O_3 within HPβCD, which seems act as an oxidant stabilizer. Due to the relatively low solubility and hydrophilicity of O_3, it can partition into the HPβCD cavity. Dettmer et al. did observe partial oxidation of the HPβCD, whereas there was a portion of HPβCD that was not oxidized and a fraction of O_3 that partitioned into the cavity. The vast majority of the investigated guest compounds that complex with cyclodextrins have been organic, and prior work has not evaluated the inclusion constant of O_3 with cyclodextrin or the potential competitive complexation between O_3 and 1,4-D and/or chlorinated solvent co-contaminants.

A critical area of supramolecular chemistry includes the investigation of host-guest complex formation processes and the determination of complexation binding constants (K) values for aqueous systems (Connors, 1987), which is the equilibrium constant for the aqueous complex formation reaction as follows (e.g., Connors, 1997; Blyshak et al., 1991; Singer et al., 1991):

$$Guest + CD \overset{K}{\leftrightarrow} Guest - CD \tag{1}$$

here Guest (or G) is the activity of target compound in the aqueous phase, CD refers to the activity of cyclodextrin molecules, Guest-CD (or G-CD) is the activity of the inclusion complex when the guest compound has partitioned into the CD cavity, and the K is the equilibrium binding (i.e., or formation stability) constant, which can also be defined as:

$$K = \frac{[G - CD]}{[G][CD]} \tag{2}$$

NMR instruments are capable of obtaining high-quality spectra with sub-millimolar concentrations (routinely as low as $10^{-4}\,M^{-1}$) for measuring and determining complexation binding constants up to $106\,M^{-1}$ (Connors, 1987). Shirin et al. (2003) evaluated several β-cyclodextrins derivatives as agents for enhancement of the aqueous solubility of two major organic pollutants (e.g., TCE) using ^{1}H NMR. Yang et al. (2006) also reported inclusion constants for three different contaminants, including TCE, with two types of cyclodextrins using gas chromatography and partitioning relationships. Perhaps the most common method for supra-molecular titration experiments is UV-visible spectroscopy. With the right chromospheres, host concentrations in the sub micro molar ($10^{-7}\,M^{-1}$) can be used, making the determination of binding constants as high as $109\,M^{-1}$ in simple 1:1 systems (Connors, 1987). For example, Garcia-Rio et al. (2006) used UV-visible spectroscopy to examine competitive binding equilibrium and kinetics for 1,4-D in presence of α-cyclodextrin and β-cyclodextrin. Another analytical method that is often used is fluorescence spectroscopy that can determine binding constants with analytes at the micromolar or nanomolar (nM) ranges (Connors, 1987). However, few comparisons of these spectroscopic methods for determining binding constants and inclusion complex stoichiometries have been reported. In addition, use of these spectroscopic methods can be applied for direct measurement of the binding equilibria as well as indirectly by competition for complexation when more than one guest compound is present (Connors, 1987; Johnson and Reinsborough, 1992). Development and application of these competitive methods for K determination has been lacking compared to direct spectroscopic methods, and comparisons of these direct and competitive methods are needed for further understanding of method applicability.

Although 1,4-D has typically been released into the environment as a contaminant associated with either TCE or TCA, cyclodextrin complexation K values of 1,4-D and competitive complexation of 1,4-D with these compounds have not been reported. K values for O_3 with cyclodextrin have also not been reported, and a comparison of O_3 and contaminant K values would be needed for use of cyclodextrin for either oxidant delivery or contaminant solubilization. Also, enhanced solubilization of O_3 and contaminants via cyclodextrin complexation may also enhance AOP treatment of wastewater contaminated with 1,4-D and other recalcitrant contaminants. The purpose of this investigation was to measure and compare the inclusion binding constant values and complexation stoichiometies for 1,4-D, TCE, TCA, and O_3 with HPβCD using both direct and competitive spectroscopic methods. In addition, the impacts of aqueous chemistry variability (e.g., pH and ionic strength) on K values were examined to evaluate variability within natural water systems. In addition to the need for K measurement for these recalcitrant co-contaminants and O_3 to support water treatment, we also examine the applicability and comparability between multiple spectroscopic K measurement methods.

2. Materials and methods

2.1. Materials

Cyclodextrins (CDs) used herein included HPβCD (1460 g mol^{-1} from Sigma Aldrich with ≤7.0% loss on drying and ≤5.0% polypropylene glycol) and gamma cyclodextrin or γ-CD (1297 g mol^{-1} from Wacke Chemie AG.Company). These were selected as they are two of the most commonly used CDs, and γ-CD has a larger cavity and aqueous solubility. Reagent grade 1,4-D, TCA, and TCE were purchased from Sigma Aldrich with 99% purity. Reagent grade sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Sigma Aldrich with 99% purity. Reagent grade sodium chloride (EM Science;