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Studies of hydrophobic organic pollutant interactions with cyclodextrin: implication for groundwater remediation

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STUDIES OF HYDROPHOBIC ORGANIC POLLUTANT INTERACTIONS WITH CYCLODEXTRIN: IMPLICATION FOR GROUNDWATER REMEDIATION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
In

The Department of Civil and Environmental Engineering

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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................................................................. ii

LIST OF TABLES ......................................................................................................... vi

LIST OF FIGURES ................................................................................................. vii

ABSTRACT ................................................................................................................ viii

CHAPTER 1 INTRODUCTION ..................................................................................... 1
  1.1 Background ......................................................................................................... 1
  1.2 Objectives ......................................................................................................... 1
  1.3 Dissertation Organization .................................................................................. 3

CHAPTER 2 LITERATURE REVIEW AND EXPERIMENTAL BACKGROUND ......... 4
  2.1 Aquifer Remediation ......................................................................................... 4
    2.1.1 Aquifer Contamination and Remediation Techniques .................................. 4
    2.1.2 Chemically-Enhanced Flushing (CEF) Techniques ........................................ 4
  2.2 Cyclodextrin-enhanced In-situ Flushing ............................................................ 5
    2.2.1 Cyclodextrin ................................................................................................. 5
    2.2.2 Environmental Application of HPβCD .......................................................... 6
    2.2.3 Pilot-scale Field Studies on Cyclodextrin-enhanced In-situ Flushing ............... 9
    2.2.4 Key Knowledge Gaps ................................................................................... 10
  2.3 Measurement of Henry’s Law Constant ............................................................. 10
    2.3.1 Ratio of Vapor Pressure and Solubility ......................................................... 11
    2.3.2 Equilibrium Partitioning in Closing System Methodology ............................... 12
    2.3.3 Modified EPICS Methodology ...................................................................... 13
    2.3.4 Static Headspace Phase Ratio (SHPR) .......................................................... 13
  2.4 Distribution Model Development ....................................................................... 14
  2.5 Activated Carbon .............................................................................................. 15
  2.6 Sorption Isotherms from Batch Studies ............................................................ 16
  2.7 Column Studies and Fate and Transport Models ............................................... 19
  2.8 References ........................................................................................................ 20

CHAPTER 3 EFFECT OF CYCLODEXTRIN CONCENTRATION AND TEMPERATURE ON HENRY’S LAW CONSTANT OF ORGANIC POLLUTANTS .... 25
  3.1 Introduction ....................................................................................................... 25
  3.2 Material and Experimental Methods ................................................................. 25
    3.2.1 Chemicals and Supplies ............................................................................... 25
    3.2.2 Sample Preparation ..................................................................................... 26
    3.2.3 Static Headspace Parameters ...................................................................... 27
3.2.4 Gas Chromatograph................................................................. 27
3.2.5 Conductivity and pH Measurement........................................... 28
3.2.6 Incubation Time Determination................................................ 28
3.2.7 Henry’s Law Constants Determination....................................... 28
3.3 Results and Discussion............................................................. 30
3.3.1 Conductivity and pH.............................................................. 30
3.3.2 Incubation Time Determination................................................ 31
3.3.3 Accuracy and Reliable Analysis on Henry’s Law Constant
Determination.................................................................................. 32
3.3.4 Dependence of $K_{\text{at2}}$ on CD Concentration............................. 35
3.3.5 Dependence of $K_{\text{at2}}$ and $K_{\text{at2}}^\prime$ on Temperature....................... 37
3.4 References.................................................................................. 42

CHAPTER 4 THE PSEUDOPHASE APPROACH TO ASSESSING CHEMICAL
PARTITIONING IN AIR-WATER-CYCLODEXTRIN SYSTEMS......................... 45
4.1 Introduction............................................................................... 45
4.2 Materials and Experimental Methods.......................................... 46
4.3 Data Analysis............................................................................ 46
4.3.1 Mathematics Model of CD Pseudophase-water Partitioning Behavior... 46
4.3.2 Development of Solubility Enhancement Factor............................... 49
4.3.3 Mass Distribution of HOPs in Air-water-CD Systems......................... 50
4.4 Results and Discussion............................................................. 51
4.4.1 CD Pseudophase-Water Partitioning............................................ 51
4.4.2 Solubility Enhancement.......................................................... 55
4.4.3 Mass Distribution Among Phases................................................. 58
4.5 References.............................................................................. 60

CHAPTER 5 ADSORPTION OF ORGANIC POLLUTANTS TO GRANULAR
ACTIVATED CARBON IN THE PRESENCE OF CYCLODEXTRIN – RESULTS FROM
BATCH STUDIES............................................................................. 63
5.1 Introduction............................................................................... 63
5.2 Materials and Experimental Methods.......................................... 63
5.2.1 Chemicals.............................................................................. 63
5.2.2 Preliminary GAC Screening....................................................... 64
5.2.3 Batch Mode Adsorption Studies............................................... 66
5.3 Data Analysis............................................................................ 68
5.3.1 Adsorption Isotherms and Mass Distribution............................... 68
5.3.2 Statistical Analyses................................................................. 70
5.3.3 Correlation of Freundlich Adsorption Coefficient ($K_f$) with Solubility
Enhancement Factor ($E$).................................................................. 72
5.4 Results and Discussion............................................................. 72
5.4.1 Mass Distribution among Phases................................................ 72
5.4.2 Batch Mode Adsorption of TCE................................................ 74
5.4.3 Correlation of $K_f^\prime$, CD Concentration, and $E$......................... 79
5.5 Conclusions .................................................................................................................................................. 80
5.6 References .................................................................................................................................................. 80

CHAPTER 6 INTERACTIONS BETWEEN GRANULAR ACTIVATED CARBON, CYCLODEXTRIN, AND ORGANIC POLLUTANTS IN COLUMN STUDIES .... 83
6.1 Introduction .............................................................................................................................................. 83
6.2 Materials and Experimental Methods .................................................................................................... 83
  6.2.1 Chemicals and Suppliers .................................................................................................................... 83
  6.2.2 Column Setup and Experiments ....................................................................................................... 84
6.3 Temporal Moment Analysis .................................................................................................................... 86
6.4 Fate and Transport Modeling ................................................................................................................ 87
6.5 Results and Discussion ........................................................................................................................... 90
  6.5.1 Bromine Tracer Result ...................................................................................................................... 90
  6.5.2 Effect of CD Concentration ............................................................................................................ 93
  6.5.3 Effect of Flow Rate ......................................................................................................................... 95
  6.5.4 Mixtures Effects ............................................................................................................................ 98
6.6 Conclusions ............................................................................................................................................ 100
6.7 References ............................................................................................................................................. 100

CHAPTER 7 SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS ....103
7.1 Conclusions .............................................................................................................................................. 103
7.2 Future Research Directions .................................................................................................................. 104

APPENDIX AMERICAN CHEMICAL SOCIETY’S POLICY ON THESES AND DISSERTATIONS ................................................................. 106

VITA .............................................................................................................................................................. 108
LIST OF TABLES

Table 2-1: Various Henry’s constant definitions and units..................................................11

Table 2-2: Summarization of the four main shapes of isotherms reported by Giles et al. (1974)...........................................................................................................................................17

Table 3-1: Conductivities and pH values measured for CD solutions.................................30

Table 3-2: Dimensionless Henry’s law constants for TCE, PCE and BTEX (KA12, K'A12) determined at different temperatures and CD concentrations..................................................34

Table 3-3: Power law constants describing CD concentration dependence of 'A12.............37

Table 3-4: Van’t Hoff Parameters for TCE, PCE and BTEX for dimensionless Henry’s constants in water and CD solutions..............................................................................................40

Table 4-1: HPβCD solubility enhancement determined by McCray et al ............................56

Table 5-1 Prescreening results for different GACs.................................................................65

Table 5-2 Particle size distribution of Norit C GRAN..............................................................66

Table 5-3 Characteristic of Norit C GRAN activated carbon.................................................66

Table 5-4: Freundlich adsorption coefficients (K’f) and constants (n) in CD solutions...........75

Table 5-5: Results of SPSS linear regression analyses of adsorption isotherms....................75

Table 6-1: Results of temporal moment analysis of conservative tracer and contaminant......92

Table 6-2: Dispersion coefficients under different flow rates and CD concentration.............92

Table 6-3: Solubility in water and CD solution of tested compounds....................................99
LIST OF FIGURES

Figure 2-1: Principle of Static Headspace Phase Ratio (SHPR) Method*.......................... 14
Figure 3-1: Static headspace distribution of HOPs..................................................30
Figure 3-2a: CD solutions effect on equilibrium time.........................................31
Figure 3-2b: Temperature effect on equilibrium time.........................................31
Figure 3-3: Plots of apparent (K_A12) Henry’s law constants dependence on CD concentration for ethylbenzene...............................................................36
Figure 3-4: Van’t Hoff plots of traditional (K_A12) and apparent (K_A12) Henry’s law constants for tested chemicals .................................................................41
Figure 4-1: CD-water partition coefficients (K_AC2) as a function of temperature (TCE):...52
Figure 4-2: Comparison of CD-water partition coefficients (K_AC2) as a function of temperature for TCE.................................................................53
Figure 4-3: Effect of temperature on solubility enhancement factor.......................55
Figure 4-4: Comparison of the solubility enhancement factors for PCE*.................57
Figure 4-5: Ternary diagrams of HOP mass distribution in air-water-CD systems with equal volumes of air and water...............................................................59
Figure 5-1: Description of chemical adsorption with the absent of CD (left) and with the presence of CD (right).................................................................68
Figure 5-2: Mass distribution of TCE in CD/GAC/Water system............................73
Figure 5-3a: Apparent adsorption isotherm cuves of TCE in CD solutions..............76
Figure 5-3b: Rescaled and traditional adsorption isotherm cuves of TCE in CD solutions...77
Figure 5-4 Correlation of Freundlich adsorption coefficient (K_f) with CD concentration...78
Figure 5-5. Correlation of Freundlich adsorption coefficient (K_f) with solubility enhancement factor (E).................................................................79
Figure 6-1. Experimental set up of column study..................................................85
Figure 6-2a. Breakthrough curve of Br under different flow rates..............................91
Figure 6-2b. Breakthrough curve of Br under different CD concentrations.....................91
Figure 6-3a. Breakthrough curve of TCE under different CD concentrations....................94
Figure 6-3b. Rescaled breakthrough curve of TCE under different CD concentrations........94
Figure 6-4. Breakthrough behavior of TCE under different flow rates............................95
Figure 6-5. Relationship between pore velocity and chemical nonequilibrium parameters.....97
Figure 6-6. Breakthrough behavior of mixture in the presence of CD.............................99
ABSTRACT

Henry’s Law constants of several common, subsurface hydrophobic organic pollutants (HOPs) including trichloroethylene (TCE), perchloroethylene (PCE) and benzene, toluene, ethylbenzene and o-xylene (BTEX), were measured over a range of temperatures (35, 45, 55 and 65°C) and cyclodextrin (CD) concentrations (0, 10, 20, 50 and 100 g L\(^{-1}\)). In aqueous CD solutions, Henry’s constant values decrease by a power law relationship with increasing CD concentration due to an apparent solubility enhancement caused by HOP partitioning to the hydrophobic cavity of CD molecules. The temperature dependence of air-water partitioning under the influence of CD was well described by the van’t Hoff equation for all HOPs tested. A three-phase equilibrium model was used to interpret air-water-CD partitioning data. Our results show that HOP CD-water partition coefficients decrease linearly with increasing temperature.

Adsorption isotherms of TCE to the granular activated carbon (GAC), Norit C GRAN, were determined for aqueous solutions containing a range of CD concentrations (0, 20, 50, 100 g L\(^{-1}\)). The adsorption coefficient \( K'_{j} \) and constant \( n \) of apparent and rescaled Freundlich isotherms was determined by the nonlinear regression of \( C'_{AS} \) versus total aqueous concentration \( (C_{A2} + C'_{A2}) \) and free water phase concentration, \( C_{A2} \) respectively. Our results showed that in aqueous CD solutions, the adsorption to GAC decreased with increasing CD concentration due to the interaction of TCE with CD in the aqueous phase. A linear relationship

\[
(\ln(K'_{j})) = -0.523\ln(E) + 2.058
\]

was derived with the linear coefficient of 0.999.

Breakthrough curves of single solute, TCE were obtained over a range of flow velocities (1-10 ml·min\(^{-1}\)) and HPCD concentrations (0, 20, and 50 g·L\(^{-1}\)). Relationships between the pore
velocities and two-site non-equilibrium parameters obtained from CXTFIT program were illustrated for this specific adsorption. Comparison of original breakthrough curve under different CD concentrations to the solubility-enhancement-rescaled ones showed (1) all 3 curves exhibited similar scaled times at which they reach 50% of the input concentration and (2) cyclodextrin increased the time needed for TCE to reach equilibration between GAC and liquid phases. TCE at higher flow rate had insufficient time to interact with GAC such that non-equilibrium processes were more significant at higher flow rate.
CHAPTER 1 INTRODUCTION

1.1 Background

Hydrophobic organic pollutants (HOPs) are common groundwater contaminants, and the remediation of HOP contaminant sites has become more important as concerns regarding protection of environmental quality have grown. Due to their relative low aqueous-phase solubility, the effectiveness of traditional pump-and-treat techniques for removing these compounds from aquifer sediments is limited. Consequently, alternative methods for removing HOPs from the subsurface are of great interest.

In recent years, a growing body of evidence suggests that various types of cyclodextrins (CD) can be an effective solubility-enhancement agent for in situ flushing and can be used to effectively remediate sites contaminated by HOPs. Application of CD to typical pump-and-treat remediation of groundwater in an economically feasible manner requires that the extracted pollutants be removed from aqueous CD solution following pump-out so that the water can be returned to the subsurface and the CD can be recycled and reused. Pollutant removal may be accomplished by a combination of air stripping and adsorption to granular activated carbon (GAC). In spite of the growing evidence for the utility of CD in groundwater remediation, relatively little is known about the partitioning behavior of HOPs in multi-phase systems (air-water-CD and GAC-water-CD), limiting our ability to accurately design and forecast the performance of different treatment systems.

1.2 Objectives

The broad goal of research described in this dissertation was to obtain a better understanding of the phase partitioning behavior of HOPs in air-water-CD and GAC-water-CD systems and to explore how knowledge of partitioning behavior can be applied for the purpose of developing
post-flushing treatment protocols. To meet this broad goal, the following specific objectives were identified:

(1) Produce an extensive data set using a static headspace phase ratio (SHPR) method of the equilibrium phase partitioning behavior of HOPs between air, water, and CD at different CD concentrations and temperatures for common contaminants.

(2) Develop mathematical models to describe and forecast HOPs distribution between air, water, and CD from thermodynamic parameters describing multiphase equilibrium.

(3) Determine HOP equilibrium distribution between water-CD-GAC phases as a function of CD concentration and GAC loading under standard temperature and pressure conditions.

(4) Develop data sets using common contaminant in column tests to evaluate the removal of target HOP from CD solutions under different conditions. Evaluate the performance of common contaminant transport computer models for predicting GAC column study results.

To meet these objectives, in the research reported here, initial experiments were conducted to determine Henry’s law constants of various types of HOPs using a SHPR method. Using this data, mathematical models capable of prediction of HOP distribution between air and aqueous-phases as a function of temperature, CD concentration, and GAC loading were developed. In addition, thermodynamic parameters were obtained through use of the van’t Hoff equation. Batch studies were employed to determine adsorption isotherms and HOP distribution as a function of CD concentration at standard temperature. To better approximate a GAC treatment system for HOP contaminated CD solution, column studies were conducted, and breakthrough curves were determined so that best fit parameters could be obtained by simulation. Fate and transport parameters for standard advection-dispersion equations were developed from the results of these bench studies which enable design of field scale systems.
1.3 Dissertation Organization

This dissertation is organized into seven chapters. Chapter 2 presents a literature review summarizing the history of CD use as a solubility enhancing agent and models used previously to determine HOP distribution in multi-phase systems. Adsorption isotherms and fate and transport models are also reviewed in this section. Chapter 3 describes experimental methods and results related to the determination of Henry’s law constants for six common HOPs including trichloroethylene (TCE), perchloroethylene (PCE) and benzene, toluene, ethylbenzene and o-xylene (BTEX) over a range of temperatures (35, 45, 55 and 65°C) and CD concentrations (0, 10, 20, 50 and 100 g L⁻¹). In Chapter 4, a mathematical model developed to describe the partition coefficients between aqueous and CD phase using a pseudophase approach is presented. A Henry’s law constant-based-enhancement factor calculation model is also discussed in this chapter for describing mass distribution of HOPs in air-water-CD systems. Chapter 5 presents the results of batch studies of TCE adsorption on GAC from aqueous solutions containing CD, and the relationship between GAC adsorption coefficient and CD solubility enhancement factor is developed. Chapter 6 presents results from column studies conducted using single contaminant loading and and HOP mixtures. It also describes a model for the fate and transport of HOPs in porous media in the presence of CD solutions. Chapter 7 contains a summary of findings from this research as well as recommendations for future research.
CHAPTER 2 LITERATURE REVIEW AND EXPERIMENTAL BACKGROUND

2.1 Aquifer Remediation

2.1.1 Aquifer Contamination and Remediation Techniques

Hydrophobic organic pollutants (HOPs) such as chlorinated solvents, polychlorinated biphenyls and certain pesticides, are common groundwater pollutants. Due to their relatively low solubility in water and the low groundwater flow velocities under natural gradient conditions, these compounds have generally proven to be very difficult to remove from aquifers (MacKay and Cherry, 1989). The historically common method of subsurface aquifer remediation is “pump-and-treat”, an approach in which groundwater within a contaminated aquifer zone is extracted from the ground and contaminants are removed via an ex-situ treatment process. Due to the low solubility of HOPs, strong adsorption of aquifer media and the large interfacial tension between HOPs and water, however, the effectiveness of conventional pump-and-treat techniques is limited. The operation periods required to restore aquifer water quality to an acceptable condition has been estimated as decades or longer in numerous cases (MacKay and Cherry 1989, West and Harwell 1992, Pankow and Cherry 1996). The generally poor performance of such groundwater pump-and-treat schemes has led to research and application of innovative in-situ chemically enhanced flushing remediation methods which are further reviewed in the following sub-sections.

2.1.2 Chemically-Enhanced Flushing (CEF) Techniques

Chemically enhanced-flushing technologies are based on flushing contaminated porous media with chemical agents in order to increase contaminant solubility and, concomitantly, the mass removal rate. This has the potential to reduce the time and cost of remediation. Unfortunately, however, the commonly used additives such as cosolvents and surfactants have been reported to
have many disadvantages for this application. The enhancement effect of alcohol is usually not significant until their volume-fraction is above 10% in aqueous solution. Additionally, the short-chain alcohols typically used also have the disadvantage of having lower densities than groundwater, making it difficult to distribute them uniformly through aquifer sediments (Wang and Brusseau, 1993). Surfactants have good removal properties in the early stages of CEF, but surfactants can absorb to and alter the chemical sorption/desorption properties of soil and aquifer sediments (Brusseau, 1993). Surfactants may also form high-viscosity emulsions that are difficult to remove, and in some cases, precipitation may occur, adversely affecting the CEF performance (Palmer and Fish, 1992; Fountain et al., 1991; Jafvert and Hath, 1991).

2.2 Cyclodextrin-enhanced In-situ Flushing

2.2.1 Cyclodextrin

Cyclodextrin (CD) molecules are polycyclic glucose oligomers derived from starch that have a toroidal shape (Bender and Komiyama, 1978). These glucose-based molecules have a hydrophobic, relatively non-polar interior and a hydrophilic polar exterior, forming a hydrophobic cavity into which HOP of appropriate size and shape can partition. Several factors that contribute to the stabilization of CD-HOP complex were reported, (1) hydrophobic interactions (Rekharsky and Inoue, 1998); (2) hydrogen-bonding (Bastos et al., 1990; Rekharsky et al, 1995; Rekharsky and Inoue, 1998); (3) release of water molecules originally included in CD cavity (Hallen et al., 1992; Barone et al., 1986), and (4) conformation changes or strain release of CD molecular (Bender and Komiyama, 1978; Saenger, 1980). Typically, cyclodextrin molecules are described as α, β, and γ-CD where the Greek letter denotes the number of glucose units in the CD molecule (α = 6, β =7, and γ = 8 respectively)(McCray et al, 2000). Because the solubility of CD with no functional group substitution is relatively low (18g L⁻¹ at 25°C,
Chatjigakis, 1992) compared with that of CD derivatives (2233 g L\(^{-1}\) for hydroxypropyl-\(\beta\)-cyclodextrin, Wacker), derivatized CD is often preferred for the purpose of remediation. Three specific derivatives of \(\beta\)-CD, hydroxypropyl-\(\beta\)-cyclodextrin (HP\(\beta\)CD), methyl-\(\beta\)-cyclodextrin (M\(\beta\)CD), and carboxymethyl-\(\beta\)-cyclodextrin (CM\(\beta\)CD) have been investigated as CEF agents, and among them HP\(\beta\)CD has been determined to have the most potential remediation agent due to its favorable characteristics, as described in the next section.

2.2.2 Environmental Application of HP\(\beta\)CD

- Flow properties

For in-situ remediation application, a vital characteristic of any remediation agent is the conservative flow property, such that the flushing solutions can easily permeate through the entire hydrological compartment without adsorbing or precipitating to aquifer materials. Physical properties of 10 wt. % HPCD solutions, such as density, viscosity, and NAPL-aqueous interfacial tension were measured by McCray et al. (2000). Their results showed that there were no obstacles related to fluid properties of such a solution that would prevent the use of HPCD solutions for subsurface HOP remediation. The density of a 10 wt. % HPCD solution is nearly equal to that of water and the solution is completely miscible with water, precluding the major density-driven problems of many cosolvents (Roeder and Falta, 1998; McCray et al., 2000). The viscosity of a 10 wt. % HPCD solution determined by McCray et al. (2000) is 19% greater than water, which does not pose a major problem for remediation (despite potentially higher pumping costs) because the larger viscosity of a water-miscible fluid has the benefit of creating a more stable front and providing a more efficient sweep of the HOP-contaminated zone (Lake 1989, McCray et al. 2000). Reduction of NAPL-water interfacial tension was reported in several studies (Wang and Brusseau, 1993; McCray et al., 2000; Bizzigotti et al. 1997), resulting in the
mobilization of NAPL globules and effective removal of non aqueous phase organic liquids from the subsurface.

Interaction between CD and soil particles was investigated by Brusseau et al. (1994) using two different soils (Borden sand with a $f_{oc}$ value of 0.3% and Mt. Lemmon soil with a $f_{oc}$ value of 13%) in the presence of dissolved HPCD. No measurable sorption, retardation, or pore exclusion of HPCD was found on either type of soil in their research, indicating that the interaction between CD and soil can be neglected. Brusseau et al. (1994) reported that HPCD-HOP complexes flow conservatively through soil and HPCD flushing solution can enhance the desorption rate of HOPs from contaminated soil due to the high affinity between CD and HOPs, therefore increasing the remediation rate relative to water flushing. In addition, excellent performance of HPCD solutions under typical aquifer conditions has been reported by Boving et al. (2003). Specifically, they reported that HPCD solutions do not alter environmental pH and their flushing performance is observed over a range of pH and ionic strengths.

- **Solubility enhancement**

  The combination of hydrophilic exterior with hydrophobic cavity gives CD molecules surfactant-like properties without the limitation of a critical micelle concentration (CMC). By associating with CD cavities, HOP molecules can significantly increase their apparent aqueous solubility. Boving and Brusseau (1999) investigated the NAPL mass removal effectiveness of several remediation agents (surfactants, alcohol, organic matter, and cyclodextrin) and similar efficiencies was found for all tested agents. They further found rate of NAPL removal by CD solutions in column studies packed with a uniform quartz sand were essentially to those of water divided by the solubility enhancement factor of the CD solution. McCray et al., (2000) measured the solubility enhancement for typical HOPs in 10% w/w HPCD solutions. Their
results showed that the degree to which the apparent solubility of compounds was enhanced by HPCD was inversely related to the polarity of the compound, indicating that the impetuous for organic compounds to enter CD cavies is driven by their hydrophobic properties. The solubility enhancement of decane (DEC) was found more than 1200 times greater than the one for trichloroethene (TCE), a relative soluble HOP (McCray, 2000). It is noteworthy that solubility enhancement occurs at all concentrations which may make it an attractive agent compared to surfactant which need a minimum effective concentration.

- **Self-biodegradation and biodegradation enhancement**

  In addition to having unique physicochemical properties, HPCD also has the advantage of being readily biodegradable. The in-situ biodegradation potential of HPCD was examined by Blanford (2006) in a study of a shallow aquifer at Little Creek Naval Amphibious Base in Virginia, a site contaminated by chlorinated solvents. Experimental results showed that HPCD remaining in the aquifer after cessation of field activities were degraded by indigenous microorganisms during a 425 day period of post-flushing monitoring. This research illustrated another important property of HPCD as a remediation agent, a short term resistance to biodegradation during field application and an ultimate biodegradability such that it will not be present long term.

  An indirect benefit of HPCD as a remediation agent is that it can also reportedly enhance HOP bioremediation (Wang et al. 1998). Biodegradation of phenanthrene in the presence of HPCD was evaluated to determine its effect on the process. Results showed that samples containing higher concentrations of HPCD exhibited more rapid phenanthrene biodegradation, indicating that HPCD can significantly enhance the process. Compared with other surfactants and alcohol, bioremediation enhancement makes HPCD more potential in remediation.
2.2.3 Pilot-scale Field Studies on Cyclodextrin-enhanced In-situ Flushing

CD treatment technologies have been studied at the pilot-scale under field conditions. The mass removal effectiveness of a 10.4% w/w HPCD solution for flushing fuel-based NAPL chemicals (aliphatic, aromatic, and chlorinated hydrocarbons) was examined in a test conducted at Hill Air Force Base (AFB) in Utah (McCray and Brusseau, 1998, McCray et al., 1999). The effectiveness of HPCD flushing was evaluated by comparison of the aqueous concentration of twelve target compounds (including TCE, TCA, BTEX, trimethylbenzene, 1,2-dichlorobenzene, and several alkanes) in extraction wells during both HPCD flushing and water flushing. The study found that the degree to which the extraction rate of the twelve compounds was improved by HPCD over water ranged from a 100 fold increase to 20,000 times.

Whether the HPCD flushing solutions could be delivered and recovered from low permeable zones was evaluated in a field study conducted by Blanford et al. (2000) at the Air Force Plant in Tucson, Arizona. Vertical HPCD flushing was attempted to overcome challenges associated with subsurface heterogeneities. The authors found that only 34% of the tracer was recovered while 54% of the HPCD was recovered indicating a larger quantity of the HOPS would be treated by HPCD flushing. The differences in HPCD solution recovery versus the water tracer were explained by the greater viscosity and density of the HPCD solution, which resulted in a 30% reduction of the effective hydraulic conductivity.

The performance of methods for treating post-flushing solutions to facilitate reuse of HPCD has also been evaluated at the pilot-scale under field conditions. Blanford et al. (2000) investigated air stripping of TCE from HPCD solution under field conditions as part of a vertical circulation study conducted in Arizona. Using a commercially available air stripper, it has shown that the post-flush TCE concentration could be decreased from 900µg L⁻¹ in a 7% wt/vol. HPCD
solution to below detection levels (0.3 µg L⁻¹). In a subsequent field trial, Boving et al. (2006) also reported a HPCD field trial in Naval Amphibious Base Little Creek in Virginia Beach, VA to test the performance of air stripping methods to facilitate the reuse of HPCD. The HPCD post-flushing solution was treated by passing the liquid through drums of granulated activated carbon (GAC) following air stripping. This was the first time GAC had been used to treat liquid HPCD solutions, and it proved highly successful.

2.2.4 Key Knowledge Gaps

The EPA requires that all post-aquifer flushing CD solutions be treated to drinking water standards before reinjection into the aquifer or disposal in storm or wastewater systems. This can be accomplished by passing the CD solutions through an air stripper followed by GAC adsorption beds as described above for previous field studies (section 2.2.3). While these previous studies proved that this treatment approach can effectively separate HOPs from CD solutions, the previous studies did not collect data on the equilibrium and kinetics of HOP phase distribution between the phases present in an air-stripping system (air, water, and CD-complexed) and those present in a GAC treatment bed reactor (water, CD-complexed, and GAC adsorbed). Such information is necessary to go beyond the trial and error testing of treatment and to develop models that can accurately forecast the performance of different treatment system designs. In short, the phase partitioning of HOPs in relevant multiphase systems must studied in greater depth in order for development of more cost-effective alternatives for aquifer remediation with HPCD flushing.

2.3 Measurement of Henry’s Law Constant

Henry’s law, formulated by William Henry in 1803, states the direct proportional relationship between the amount of gas dissolved in a liquid and the partial pressure of that gas in equilibrium
with that liquid at particular temperature. The Henry’s constant is applied to describe the ratio of the pressure/concentration in gas phase to the concentration in liquid phase (Mills et al., 1993). Due to various formats of pressure and concentration, Henry’s constant has different units which are summarized in Table 2-1. It should be noted that Henry’s law is a limiting law that only applies for sufficiently dilute solutions and solutions where the solvent does not react chemically with the gas being dissolved.

<table>
<thead>
<tr>
<th>Henry’s constant definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{h,pc} = \frac{P}{c}$</td>
<td>$\frac{L \cdot atm}{mol}$</td>
</tr>
<tr>
<td>$K_{h,px} = \frac{P}{x}$</td>
<td>atm</td>
</tr>
<tr>
<td>$K_{h,cc} = \frac{C_{gas}}{C_{aq}}$</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>

To properly design an air stripper to extract volatile and semi-volatile HOPs from aqueous solutions, it is essential to have reliable data on the compounds’ air-water partitioning behavior, the tradition form being Henry’s Law constants. Various techniques for determining Henry’s law constants have been developed as further discussed in the following sub-sections.

### 2.3.1 Ratio of Vapor Pressure and Solubility

In 1981, three different methods for determining Henry’s law constants of HOPs were investigated (Mackay and Shiu, 1981). The first method is simply to measure the above pure HOP liquids vapor pressure and solubility of target compounds independently and then calculate Henry’s constant as the ratio of vapor pressure to solubility. This method is satisfactory for compounds with low solubility; however it is subject to significant error when a solute has relatively large aqueous solubility. This condition will often be exceeded in the presence of
solubility enhancement agents. The second method depends on direct measurements of the vapor pressure and solubility in a system at equilibrium. This method is applicable to compounds present in both air and water at high concentrations (such as SO₂ and CO₂) but will lead to excessive errors for those substances with lower solubility or vapor pressure due to difficulty of sampling and accurately measuring the absolute values of both parameters. Therefore the second method is not suitable for the Henry’s law constant measurement of HOP of concern in this study (Robbin, 1993). The third method (Mackay et al., 1979) involves measuring of the vapor pressure and concentration during an equilibrium air-water exchange process. This method requires the measurement of relative (not absolute) concentration changes in one phase and therefore is simpler and potentially more accurate than the other methods (Lincoff and Gossett, 1984). It is not, however, suitable for use on mixtures of compounds (Robbins, 1993).

2.3.2 Equilibrium Partitioning in Closing System Methodology

Lincoff and Gossett (1984) reported a novel methodology for determining Henry’s law constants based on the ratio of concentrations in the gas phases of two identical headspace sampling vials with different air and water volumes, but the same mass of test chemical. They called this approach the Equilibrium Partitioning in Closing System Methodology (EPICs). The Henry’s law constant is obtained using equation 2-1

\[ K_h = \frac{V_{W2} - RV_{W1}}{RV_{G1} - V_{G2}} \]  

(2-1)

Where;

\( K_h \) = Henry’s constant, dimensionless

\( V_{W1\&2} \) = the volumes of water in vials 1 and 2, L

\( V_{G1\&2} \) = the volumes of headspace in vials 1 and 2, L

\( R \) = the ratio of headspace concentration of test chemical in vial 1/vial 2, dimensionless
The precision of the Henry’s law constant determined by this method was reported as 4-5%, expressed as relative standard deviation (Robbin, 1993). However, the disadvantage of the original EPICS method is the difficulty in adding exact masses to the two vials.

2.3.3 Modified EPICS Methodology

In 1987, Gossett et al report a modification of original EPICS method in an attempt to improve precision. This modified approach does not require that the exact same mass of chemical be added to each vial, and uses mass instead of volume ratios. Equations 2-2 describe the calculation of Henry’s law constant by this approach;

\[ K_h = \frac{V_{w2} - rV_{w1}}{rV_{G1} - V_{G2}} \]  

(2-2)

\[ r = \frac{C_{G1}}{M_1} / \frac{C_{G2}}{M_2} \]  

(2-3)

Where,

\[ M_{1&2} = \text{the mass added to vial 1 and 2, g} \]

The original EPICS formulation is a special simplification with the \( M_1 = M_2 \) and then \( r = R \). The modified EPICS eliminates the problems encountered with the original EPICS method and leads to improved precision in the measurement Henry’s law constants, however it still requires the exact mass ratio of target chemicals be added to each bottle. It is also of limited use when the target chemical is present in condition of unknown matrix (Robbins, 1993)

2.3.4 Static Headspace Phase Ratio (SHPR)

In 1993, Robbins reported a new, accurate and experimentally simple method to determine the dimensionless form Henry’s law constant, involving measurement of peak area of target chemicals from aliquots of the same stock solution in three separate enclosed headspace vials
having different gas-to-liquid volume at equilibrium. The Henry’s law constant is calculated from the ratio of the slope to the y-intercept.

Figure 2-1 Principle of Static Headspace Phase Ratio (SHPR) Method*

*Note: Figure re-draw from Robbins, 1993

A significant advantage of this method is that it does not require knowledge of the exact initial concentration of the chemical in the water and therefore is well suited to use in environmentally relevant matrices (Robbins, 1993).

2.4 Distribution Model Development

Several studies of partition coefficients of common HOPs between air, aqueous (dissolved) and CD-complexed phases have been conducted using SHPR methods (Kashiyama and Boving, 2004; Lantz et al, 2005). Among these studies, there are two approaches used to describe the phase interactions of HOPs. Kashiyama and Boving (2004) developed their approach on a system where there are two exchange processes; HOPs can move between the gas and aqueous phases and between the aqueous and CD-complexed phases. Lantz et al. (2005) incorporate a third exchange process between air and CD. In each of these studies, the models of phase relationships are empirically calibrated with HOP data gathered under equilibrium conditions, therefore there are no net HOP mass fluxes. In both approaches, the applied mathematical
models of interphase chemical exchange are based on the assumption that the dissolved concentration is linearly related to the concentration in the air and the amount of chemical complexed with CD. While the models incorporate different exchange processes, they have similar origins in that partition coefficients are determined from mass balances on the chemical and CD.

Kashiyama and Boving (2004) and Lantz et al. (2005) rely on the Gossett (1987) or modified equilibrium partitioning in closed systems (EPICs) method to determine air-water and air-CD solution partition coefficients. From measurements performed with and without CD, the concentration of HOP complexed with CD can be determined and from there CD-water partition coefficients or solubility enhancement factors (McCray et al., 2000) can be estimated. The mass balance approach of Lantz et al. (2005) requires calibration of the gas phase concentration with standards to determine CD-water partition coefficients. Alternatively, Kashiyama and Boving (2004) estimate CD-water partition coefficients that rely on the simplifying assumption that total CD concentration is essentially equal to the concentration of CD that is not complexed with a HOP molecule. This assumption will be invalid in situations where CD is present in low concentrations or when the HOP has a high solubility or a large enhancement factor.

2.5 Activated Carbon

Activated carbon is one type of adsorbent which is created by firstly insufficient combustion of a carbonaceous material (almond, coconut, walnut hulls, woods, bone, and coal) followed by activated process, which produce high energy areas that serve as adsorption sites. (Mattson et al. 1969) During the activated process, two common oxidizing gases, steam (H₂O) and CO₂ are used to develop a porous structure in the char and thus create a large internal surface area (Tchobanoglous et al., 2003).
Three major factors that might affect the adsorption process are (1) surface area, (2) pore size distribution, and (3) the pH of the carbon surface and internal pores. The activated carbon adsorption ability increases as the surface area increases when other factors are constants. Pore widths that fall under 1 nm are considered to be micropores, from 1 nm to 25 nm are mesopores, and above 25 nm are macropores.

Activated carbon is commonly used in separation processes involving removal of organic, inorganic contaminants (nitrogen, sulfides, and heavy metals), taste and odor compounds (Froelich, 1978; Dobbs and Cohen, 1980; Huang and Ostovic, 1978; Perez-Candela et al. 1995; Cousins et al. 1999; Rubio and Izquierdo, 1998; Adib et al. 2000). Despite the extensive amount of research, the adsorption mechanisms still remain unknown (Mcelroy, 2005). Currently, the literature has concentrated on two mechanistic theories, (1) π-π bonding theory, proposed by Coughlin and Ezra (1968), stating that electrons in the 2p orbitals travel above and below the benzene basal plane which create an electron delocalization zone and adsorption occurs at the basal plane and its edge; and (2) the electron donor theory proposed by Mattson et al. (1969) suggests that an exchange of electrons takes place during the adsorption process.

2.6 Sorption Isotherms from Batch Studies

Adsorption of HOPs to activated carbon or other adsorbates such as natural organic matter or mineral surfaces is an important polishing step in most advanced water and wastewater purification systems. Adsorption Isotherms are commonly determined to describe the retention of a substance on a solid at various concentrations and to understand sorption phenomena governing the mobility of substance in aqueous porous media and aquatic systems. A great deal of research has been conducted to describe sorption behavior. In this section, the most common sorption isotherms are summarized based on shape classification and curve modeling description.
Table 2-2 Summarization of the four main shapes of isotherms reported by Giles et al. (1974)

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Zero-origin straight line; often used for a narrow concentration range or very low concentration;</td>
</tr>
<tr>
<td>L</td>
<td>Concave curve; progressive saturation of the solid; two group: a strict asymptotic plateau or no plateau</td>
</tr>
<tr>
<td>H</td>
<td>A particular case of “L” isotherm with high initial slope</td>
</tr>
<tr>
<td>S</td>
<td>Sigmoidal with inflection point; 2 or more opposite sorption mechanism</td>
</tr>
</tbody>
</table>

Four main isotherms (the “C” isotherm, the “L” isotherm, the “H” isotherm, and the “S” isotherm) were first reported by Giles et al. (1974) with emphasis on the shape of the isotherm curves, summarized in table 2-2. A recent review provides information with detailed descriptions of the shape of isotherm curves (Limousin et al., 2007). Concave isotherms are commonly modeled by Freundlich or Langmuir isotherms to estimate the adsorption capacity of an adsorbent for environmental applications.

Van Bemmelen (1888) and Freundlich (1909) reported the empirical Freundlich isotherm which describes the relationship between the adsorbed quantity $Q$, mg HOP · g GAC$^{-1}$ and the remaining solute concentration $C$, mg L$^{-1}$ in solution (eqn 2-4a) for a single solute. Even though the original Freundlich isotherm has been used widely to describe experiment data, it was developed for single-adsorbate systems, while multi-components systems are most common in wastewater purification process. In order to understand the possible competitive adsorption phenomena, Sheindoref et al. (1981) derived modified Freundlich models (eqn 2-4b) for multi-component systems, where the isotherm coefficients are determined from single component isotherms and the adsorption competition coefficient is assessed in multi-component adsorption
experiments. The modified Freundlich isotherm has been successfully applied to systems with 2-3 components (Sheindorf et al. 1982).

\[
Q = F \cdot C^n \quad (2-4a)
\]

\[
Q_i = F_i \cdot C_i \cdot \left( \sum_{j=1}^{m} a_{i,j} \cdot C_j \right)^{n_i-1} \quad (2-4b)
\]

Where;

\( Q \) and \( Q_i \) = the adsorption quality in single and multi-component systems respectively, mg·g⁻¹

\( F \) and \( F_i \) = Freundlich constant in single and multi-component systems respectively

\( n \) and \( n_i \) = Freundlich constant in single and multi-component systems respectively, dimensionless

\( C \) and \( C_i \) = remaining concentration of the single solute or the \( i \)th component, mg L⁻¹

\( m \) = the number of competitive species in multi-component system, dimensionless

\( a_{ij} \) = the dimensionless competition coefficient of species \( i \) in the presence of species \( j \), dimensionless

In 1918, Langmuir reported a reaction-hypothesis-based isotherm, called Langmuir adsorption (2-5a) with the assumption that (1) adsorbents have limited adsorption capacity; (2) all active sites are identical, (3) each site can combine one adsorbate molecule, and (4) all active sites are independent. The original Langmuir isotherm was also modified (2-5b) for multi-species by Murali and Aylmore, (1983).

\[
Q = Q_{\text{max}} \frac{\alpha C}{1 + \alpha C} \quad (2-5a)
\]
\[
Q_i = Q_{\text{max},i} \frac{\alpha_i C_i}{1 + \sum_{j=1}^{m} \alpha_j C_j}
\]

(2-5b)

Where;

\(Q_{\text{max}}\) and \(Q_{\text{max},i}\) = the maximum amount of single solute/ \(i^{\text{th}}\) solute that can be adsorbed; mg g\(^{-1}\)

\(\alpha\) and \(\alpha_i\) = adsorption constant related to the binding energy in single and multi-component systems respectively, dimensionless

\(C\) and \(C_i\) = remaining concentration of the single solute or the \(i^{\text{th}}\) component, mg L\(^{-1}\)

2.7 Column Studies and Transport Models

Activated carbon column studies have been widely used to aid in the design of adsorption equipment for the removal of organic and inorganic contaminants as well as taste and odor compounds. In order to fully understand the transport mechanism in porous media, the fate and transport of contaminants including heavy metals, organic chemicals, and pathogenic microorganisms in groundwater systems have been studied extensively. Fate and transport models in porous media are commonly described by the combination of the advection-dispersion equation with a sorption model. Two factors are considered to affect the contaminant transport; (1) physical non-equilibrium processes caused by aquifer heterogeneity and preferential flow; and (2) chemical non-equilibrium due to the kinetically-limited sorption. Physical nonequilibrium is described as a two-regime process (dual-porosity) with two distinct mobile and immobile phases (Coats and Smith, 1964; van Genuchten and Wierenga, 1976). Chemical non-equilibrium models represent the kinetic distribution of contaminants between the solid and aqueous phases which can be simulated using a two-site contaminant transport model (Bales et al. 1991; McCaulou et al. 1994). In the two-site model, one common assumption is that at the sorption
sites, chemical partitioning can occur either instantaneously (rapid exchange sites) or is rate-limited (slow exchange sites) (van Genuchten, 1981). Many studies have been conducted to investigate the effect of pore velocity on sorption/desorption in the transport of organic contaminants (Lee et al, 1988; Brusseau et al. 1991; and Maroqa et al. 1999) and heavy metals (Akratanakul et al. 1983; Pang et al. 2002); however there are few, if any, detailed activated carbon column studies on the kinetic adsorption of HOP from CD solutions and the transport process of pollutant-CD complexes interacting with GAC.

2.8 References


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CHAPTER 3. EFFECT OF CYCLODEXTRIN CONCENTRATION AND TEMPERATURE ON HENRY’S LAW CONSTANT OF ORGANIC POLLUTANTS

3.1 Introduction

To gain an appreciation of how cyclodextrin affects volatility of common organic pollutants and develop a data base for future mathematical models, a series of tests were performed using a Static Headspace Phase Ratio (SHPR) method (Robbins, 1993; Kolb and Ettre, 1997), Henry’s law constants have been determined for six environmentally relevant Hydrophobic Organic Pollutants (HOPs), including the chlorinated solvents trichloroethylene (TCE) and perchloroethylene (PCE) and the monoaromatic hydrocarbons benzene, toluene, ethylbenzene and o-xylene (BTEX), over a range of hydroxypropyl-β-cyclodextrin (HPβCD) concentrations and temperatures. The objectives of the research presented in this chapter were to (1) obtain quantitative Henry’s Law constants descriptions of HOP air-water partitioning, (2) determine the effect of dissolved CD concentration on air-water partitioning and, (3) determine the effect of temperature on Henry’s Law constants for CD-water-air system.

3.2 Materials and Experimental Methods

3.2.1 Chemicals and Supplies

Methanol, TCE, PCE, benzene, ethylbenzene and o-xylene were purchased from Sigma-Aldrich (>99.5% purity). Toluene was purchased from EMD Chemicals (99.5% purity). Technical grade HPβCD (degree of substitution = 4.98, average MW=1424 g mol⁻¹) was donated by Cargill and used as received (purity wt/wt: moisture content 5.0%; unmodified βCD <0.1%; propylene glycol 0.4%; ash 2.0%; HPβCD 92.6%). High purity deionized water was generated by a US Filter water purification system (Siemens, Warrendale, PA) to 18.2 MΩ and was disinfected by ultraviolet irradiation. Headspace vials and magnetic screw caps with silicone/PTFE-faced septa were purchased from Microliter Analytical Supplies (Suwannee, GA).
Vial volumes were determined by mass using an analytical balance with high purity water at 20°C and found to have an average volume of 20.16 mL with a standard deviation of 0.11 mL (n = 40). This small variation in vial volume was found to result in less than 0.01% variation in computed Henry's law constants. This was deemed negligible and therefore the average vial volume was used in all calculations.

### 3.2.2 Sample Preparation

Aqueous HPβCD solutions with concentrations of 10, 20, 50 and 100 g L\(^{-1}\) were prepared by addition of HPβCD powder to high purity water. These solutions were allowed to equilibrate overnight prior to use. Concentrated solutions of HOPs (2.872 g L\(^{-1}\)) were prepared in methanol. Samples were prepared by adding methanol containing a single HOP to the HPβCD solutions. Methanol volume fractions (v/v) were kept below 0.005 in all HPβCD solutions and it has been shown in a previous study (Ladaa et al., 2001) that small quantities of methanol (< 0.05 v/v) have no discernable effect on HOP air-water partitioning. Concentrations of TCE, PCE and BTEX in all HPβCD solutions were 47.03, 10.72 and 9.39 mg L\(^{-1}\), respectively; these concentrations are all less than 5% of the HOP aqueous solubility at 25°C. To improve accuracy, all volumetric measurements were verified gravimetrically (e.g. syringes and containers were weighed when materials were added).

Samples were prepared by adding methanol HOP stock solution to amber headspace vials containing aqueous HPβCD solution. Liquid volumes were 2, 5 and 10 mL for TCE and BTEX and 3, 5 and 10 mL for PCE. For each of the different air-to-solution volume ratios, samples were prepared in triplicate, so each Henry’s constant measurement for a particular HOP, temperature and HPβCD concentration is calculated from nine data points. Vials were sealed immediately after filling and allowed to equilibrate at room temperature for between 1.5 and 13
hours (waiting in the autosampler rack) prior to incubation at the desired temperature and headspace sample analysis by gas chromatography (GC) with mass selective detection (MSD).

3.2.3 Static Headspace Parameters

A static headspace autosampler equipped with a temperature-stabilized shaking incubator (Combi PAL, Leap Technologies, Carrboro, NC) was used to equilibrate sample vials and obtain headspace samples for GC injection using a gas syringe. Vials were incubated at the temperature of interest and shaken at 250 RPM for 30 minutes. To prevent condensation prior to injection, the syringe was heated to 2°C above the incubation temperature. Carryover was prevented by a 120 second helium flush between analyses. It is of obvious interest to examine partitioning phenomena at environmentally relevant temperatures. Unfortunately, we were unable to obtain stable incubation temperatures below 35°C using our particular apparatus. However, we contend that the data generated in the temperature range examined in this study are useful for understanding the air-water partitioning behavior of HOPs in the presence of CD.

3.2.4 Gas Chromatograph

Analyses were performed using an Agilent 6890 gas chromatograph fitted with a HP-5MS column with a length of 30.0 m and a diameter of 250 µm. The carrier gas was helium at a constant flow rate of 1 ml min⁻¹. The injection port was set to the split-less mode and was equipped with a 900 µl deactivated inlet liner (Hewlett Packard, Part No.5181-3316). The following GC oven temperature was used to elute HOPs, initial temperature of 35 °C holding for 2 minutes and increased to 55 °C at a rate of 5 °C min⁻¹. Then the temperature was increased to 100 °C at a rate of 5 °C min⁻¹. After elution, PCE was quantified by an Agilent 5973 mass selective (MS) detector with the following conditions. MS was operated in the electron impact
ionization (EI) mode at 70ev with the ion source temperature of 250 °C. Total Ion Chromatograph (TIC) scan mode was applied with a mass range from m/z of 59 to 171 m/z.

3.2.5 Conductivity and pH Measurement

According to the manufacturer, the HPβCD used in this study contains some salts in the form of ash. It is known that high ionic strength in aqueous solutions can increase Henry’s law constants for HOPs (Peng and Wan, 1998; Dewulf et al, 1995). To determine if ionic strength had an effect on our experiments, conductivity was measured for each HPβCD concentration (0, 10, 20, 50, 100 g L⁻¹) using an Ultrameter II 6P (Myron L Company, Carlsbad, CA). The conductivity and pH determination of HPβCD solutions was carried out in triplicate and the results were averaged.

3.2.6 Incubation Time Determination

Incubation time to achieve equilibrium between the gas and aqueous phases is important for accurate and reliable measurement. In order to determine the time needed to achieve equilibrium, the incubation time was examined for the temperature (35°C, 45°C and 65°C) and CD concentration ranges (0, 10, 50, 100 g L⁻¹) employed in this study by sampling the headspace after contact times of 1 to 30 minutes. The volume of liquid used in these tests is 10 ml. The equilibrium time is defined as the time after which the GC area ceased changing with increasing time.

3.2.7 Henry’s Law Constant Determination

Henry’s law constant is defined as the linear distribution of a volatile contaminant between aqueous and gas phase;

\[ K_{A12} = \frac{C_{A1}}{C_{A2}} \]  

(3-1)
where;

\[ C_{A1} = \text{the concentration of a compound (designated by the letter A) in air phase designated by the number 1), mg L}^{-1} \]

\[ C_{A2} = \text{the concentration of a compound in aqueous phase (designated by the number 2), mg L}^{-1} \]

The total mass of the solute in an enclosed vial is given by a mass balance on the air-water phase (Figure 3-1)

\[ C_{A20} \cdot V_2 = C_{A2} \cdot V_2 + C_{A1} \cdot V_1 \] (3-2)

where;

\[ C_{A20} = \text{the initial concentration of the compound in liquid, mg L}^{-1} \]

\[ V_0 = \text{the initial volume which is approximately the volume of the aqueous phase, V}_L, L \]

Substituting equation 3-1 into 3-2 and rearranging gives

\[ \frac{1}{C_{A1}} = \frac{1}{C_0} \left( \frac{1}{K_{A12}} + \alpha \right) \] (3-3)

where;

\[ \alpha = \text{the phase volume ratio of headspace to aqueous in the enclosed vial.} \]

Since the GC area is proportional to the concentration, equation 3-3 can be simplified to a linear relationship between the inverse of the GC area (A) and air-water phase ratio (\( \beta \)) as following;

\[ \frac{1}{A} = \frac{1}{K_{A12}} \alpha + b \] (3-4)

Briefly, this approach allows for the determination of Henry’s law constants by comparing the GC area response from the headspace of a set of samples with the same total volume and
solution composition that are prepared with different air-to-solution volume ratios. Plotting the reciprocal of the GC area response (ordinate) against the air-solution ratio (abscissa) generates a line by which Henry’s constant can be calculated from the ratio of the slope to the y-intercept.

![Figure 3-1 Static headspace distribution of HOPs](image)

### 3.3 Results and Discussion

#### 3.3.1 Conductivity and pH

<table>
<thead>
<tr>
<th>CD Concentration (g L(^{-1}))</th>
<th>Avg. Conductivity ± standard deviation ((\mu)S cm(^{-1}))</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.76 ± 0.01</td>
<td>5.3*</td>
</tr>
<tr>
<td>10</td>
<td>394.1 ± 2.8</td>
<td>5.3*</td>
</tr>
<tr>
<td>20</td>
<td>755 ± 1.4</td>
<td>5.2*</td>
</tr>
<tr>
<td>50</td>
<td>1717 ± 13</td>
<td>5.2*</td>
</tr>
<tr>
<td>100</td>
<td>2996 ± 32</td>
<td>5.1*</td>
</tr>
</tbody>
</table>

*consistent with the pH of deionized water

Average conductivities (n = 4) for the tested CD solutions (0, 10, 20, 50, 100 g L\(^{-1}\)) are listed in Table 3-1. The results show that all HPβCD solutions used for the Henry’s law constant determination had conductivities less than 3000 \(\mu\)S cm\(^{-1}\) which is well below the ionic strength needed to cause increases in Henry’s law constant values for air-water systems. Therefore the
salts present in the HP\(\beta\)CD powder were determined to have a negligible effect in all experiments.

### 3.3.2 Incubation Time Determination

**Figure 3-2a.** CD solutions effect on equilibrium time. Note: filled square, open square, filled triangle, and open triangle represent CD concentrations of 0, 20, 50, 100 g L\(^{-1}\) respectively.

**Figure 3-2b.** Temperature effect on equilibrium time. Note: filled circle, open circle, and cross represent the temperature of 35\(^\circ\)C, 45\(^\circ\)C, and 65\(^\circ\)C respectively.
Achieving equilibrium between the liquid and headspace phases is one of the most important factors required to determine the Henry’s law constant. This time varies for different volatiles, mixing type (shaking or stirring), and temperatures. In this study, a temperature-stabilized shaking element was used as an incubator in order to reduce the required time. Figure 3.2 shows the results of equilibrium tests for different CD concentrations and temperatures. As shown in Figure 3.2a, the time to reach equilibrium in systems with lower CD concentrations is considerably longer than those with larger CD concentrations. The reason is as following. With increasing of CD concentration, the amount of contaminant that is distributed among the air water phases is inherently less. Hence, lower concentration CD samples require longer time to equilibrate. Figure 3.2b shows the temperature effects on equilibration. As the incubation temperature is increased the amount of contaminant that must be transferring to the gas phase increases. This is reflected in the data where equilibrium distribution for 65°C had a greater GC area than the lower temperatures. In general, it was found for all variations that equilibration was achieved within 20 minutes, which is consistent with equilibration times used in other headspace studies of volatile organic compounds (Chai et al., 2005; Gupta et al, 2000; Vane and Giroux, 2000; Shimotori and Arnold, 2003). We used a contact time of 30 minutes to ensure equilibrium was achieved. Longer contact times were not used due to concerns regarding vial leakage (Vane and Giroux, 2000).

3.3.3 Accuracy and Reliable Analysis on the Henry’s Law Constant Determination

Static Headspace Phase Ratio (SHPR) was applied for the determination of Henry’s constant in this study with the advantage of not requiring knowledge of the exact HOP initial concentration in the aqueous phase. This method is especially suitable for systems that include an agent which is expected to affect the Henry’s law constant. Another benefit of SHPR is that it
does not require external or internal calibration, which has many drawbacks (Peng and Wan, 1997) in partitioning studies. The sensitivity response (SR) was evaluated by calculating the parameter of relative change in GC response to the relative change in the phase ratio (Peng and Wan, 1997). The results showed that the method is sensitive when the Henry’s constant are greater than 0.1 and will lose sensitivity if Henry’s constant less than 0.05. In this study, Henry’s constants decreased with the increase of CD concentration; however most fall within the sensitive range. In addition, the autosampler provides very reproducible performance during equilibrium and headspace sampling, which is beneficial to avoid system error. Therefore it is reasonable to believe the method gives accurate results.

The plots of phase ratio versus the inverse GC area for the systems with and without CD were highly linear with correlation coefficients near 1.0. The Henry’s law constants determined by SHPR are summarized in Table 3-1. Little comparable data (except Kashiyama and Boving, 2004) exists in the literature for this type of CD, these HOPs and this range of temperature. Dimensionless $K_{A1/2}$ values for TCE, PCE and BTEX compounds presented here are consistent with those reported in a wide range of published studies (Vane and Giroux, 2000; Shimotori and Arnold, 2003; Gossett, 1987; Robbins, 1993; Dewulf et al, 1995; Lantz et al., 2005; Shiu and Ma, 2000; Görgényi and Dewulf, 2002; Anderson, 1992) and were in good agreement with Henry’s constants calculated using vapor pressure and aqueous solubility data (Mackay and Shiu, 1981; Altschuh et al., 1999). Examination of replicate samples showed that the average standard deviation for $K_{A1/2}$ and $K'_{A1/2}$ values determined in this study by the phase ratio method was 5.1% (n = 120; six HOPs, 4 temperatures, 5 CD concentrations). Only 10% of the Henry’s constants had standard deviations higher than 10% and nearly half of those were in the ethylbenzene data set (n = 6).
Table 3-2. Dimensionless Henry’s law constants for TCE, PCE and BTEX ($K_{A_{12}}$, $K'_{A_{12}}$) determined at different temperatures and CD concentrations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp (°C)</th>
<th>No CD</th>
<th>10 g L$^{-1}$ CD</th>
<th>20 g L$^{-1}$ CD</th>
<th>50 g L$^{-1}$ CD</th>
<th>100 g L$^{-1}$ CD</th>
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<td>0.4401</td>
<td>0.2981</td>
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<td>55</td>
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<td>0.2512</td>
<td>0.1364</td>
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<tr>
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<td>0.1735</td>
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<td>0.0602</td>
<td>0.0337</td>
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<td>0.1786</td>
<td>0.0874</td>
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<td>45</td>
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<tr>
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<td>0.0323</td>
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<td>0.1660</td>
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<td>0.2426</td>
<td>0.1173</td>
<td>0.0641</td>
</tr>
</tbody>
</table>
3.3.4 Dependence of $K'_{A12}$ on CD Concentration

Henry’s law constant decreased with increasing of CD concentration. This result is explained by the specific structural properties of the hydrophobic CD interior. PCE, a relatively low-polarity compound, partitions to the CD cavity to form a CD-PCE complex. The more CD present, the more hydrophobic cavities are available to complex with PCE and the less PCE is available to partition into the headspace. Henry’s Law constants for HOPs in CD solutions were plotted against CD concentration to determine how the two were correlated. The data collected on ethylbenzene is shown in Figure 3-3. A power law function was found to provide the best fit, as indicated by the high coefficients of determination obtained ($R^2 > 0.98$). Table 3-2 contains regression coefficients for data fit to the following equation

$$K'_{A12} = a \cdot C_{C2}^b$$

(3-5)

where;

$C_{C2} =$ the concentration of CD, g L$^{-1}$

$K'_{A12} =$ the apparent Henry’s Law constant for a solution with CD concentration $C_{C2}$ (g L$^{-1}$)

$a$ and $b =$ the power law constants.

In general, the pre-power constant ($a$) increased with CD concentration. Values of the power law exponent ($b$) were higher for HOPs with higher CD-water partition coefficients. The effects of CD concentration on HLCs were similar among all six HOPs. Measured $K'_{A12}$ values were between 30-70% lower than $K_{A12}$ at the same temperature in 10 g L$^{-1}$ HPβCD solutions and between 1 and 2 orders of magnitude lower in 100 g L$^{-1}$ solutions. These significant decreases in Henry’s law constant values are consistent with those reported elsewhere (Kashiyama and Boving, 2004) for TCE in HPβCD solutions over comparable temperature and CD concentration ranges.
Figure 3-3. Plots of apparent ($K'_{A12}$) Henry’s law constants dependence on CD concentration for ethylbenzene: Note: filled circle for 35°C; inverse open triangle for 45°C; filled square for 55°C and open diamond for 65°C
Table 3-3. Power law constants describing CD concentration dependence of $K'_{A12}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>35°C</th>
<th>45°C</th>
<th>55°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>a</td>
<td>2.3564</td>
<td>3.5674</td>
<td>3.8445</td>
<td>4.5906</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>-0.7183</td>
<td>-0.7075</td>
<td>-0.6357</td>
<td>-0.5870</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9828</td>
<td>0.9958</td>
<td>0.9937</td>
<td>0.9803</td>
</tr>
<tr>
<td>PCE</td>
<td>a</td>
<td>1.9917</td>
<td>3.0941</td>
<td>2.9341</td>
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</tr>
<tr>
<td></td>
<td>b</td>
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<td>-0.7955</td>
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<td>-0.7373</td>
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<tr>
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<td>$R^2$</td>
<td>0.9946</td>
<td>0.9969</td>
<td>0.9823</td>
<td>0.9945</td>
</tr>
<tr>
<td>Benzene</td>
<td>a</td>
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<td>1.1721</td>
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<tr>
<td></td>
<td>b</td>
<td>-0.6444</td>
<td>-0.6593</td>
<td>-0.6222</td>
<td>-0.6013</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9815</td>
<td>0.9904</td>
<td>0.9832</td>
<td>0.9913</td>
</tr>
<tr>
<td>Toluene</td>
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<tr>
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<td>b</td>
<td>-0.6938</td>
<td>-0.7123</td>
<td>-0.7100</td>
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<tr>
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<td>Ethylbenzene</td>
<td>a</td>
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<td>1.3596</td>
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<td>2.6747</td>
</tr>
<tr>
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<td>-0.8360</td>
<td>-0.8604</td>
<td>-0.8116</td>
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<tr>
<td></td>
<td>$R^2$</td>
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<td>0.9928</td>
<td>0.9985</td>
<td>0.9999</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>a</td>
<td>0.6176</td>
<td>0.9506</td>
<td>1.4301</td>
<td>1.8254</td>
</tr>
<tr>
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<td>b</td>
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<td>-0.7224</td>
<td>-0.7338</td>
<td>-0.6950</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9994</td>
<td>0.9985</td>
<td>0.9961</td>
<td>0.9929</td>
</tr>
</tbody>
</table>

3.3.5 Dependence of $K_{A12}$ and $K'_{A12}$ on Temperature

Values of $K_{A12}$ and $K'_{A12}$ increased exponentially with increasing temperature. Even though the values of $K'_{A12}$ were less than those of $K_{A12}$ at the same temperature, the relative effect of increasing temperature on $K'_{A12}$ values were greater than the effect for $K_{A12}$, indicating that the HOP-CD complex is less stable at higher temperature, as would be expected. This lead to larger relative increases in the apparent Henry’s constant for the CD-solutions as some of the CD-
complexed chemical that was unavailable for partitioning to the vapor phase at lower temperatures can participate in air-water partitioning at higher temperatures. The destabilization of CD-complexes is further influenced by increasing HOP aqueous solubility and vapor pressure with increasing temperature.

It is well known that Henry’s Law constants vary with temperature and pressure. For systems where pressure differences are small, the temperature dependence of Henry’s Law constant can be described using the van’t Hoff equation (Chai and Falabella, 2005; Gupta et al., 2000; Ashworth et al., 1988; Saudinger and Robert, 2001; Warneck, 2007)

\[
\ln K_{Aij} = - \frac{A_{ij}}{T} + B_{ij} \tag{3-6}
\]

where;

\( K_{Aij} \) = the partition coefficient describing the concentration ratio for \( A \) in phases \( i \) and \( j \) at equilibrium (dimensionless),

\( T \) = temperature (K)

\( A_{ij} \) and \( B_{ij} \) = constants for a particular HOP

Because these parameters are approximately constant over narrow temperature ranges, the van’t Hoff equation allows for interpolation of Henry’s Law constants within and limited extrapolation to values outside of the evaluated temperature range.

The temperature dependence of the measured Henry’s Law constants for air-water and air-CD solutions is well described by the van’t Hoff equation (eq 3-6), as indicated by high values of the correlation coefficient (\( R^2 \geq 0.95 \)) for all HOPs and CD concentrations. Parameter values and regression statistics are listed in Table 3-3 and van’t Hoff plots for tested chemicals are shown in Figure 3-4. Values of the van’t Hoff parameters for the air-water systems (\( K_{A12} \)) of all six HOPs
were similar to values calculated using Henry’s constants reported by Robbins et al. (1993) over a similar temperature range. However, values reported in other studies vary widely (see Table 3-3). For the BTEX compounds, such ranges are common as indicated by the large number of different van’t Hoff parameters reported in a review of the air-water partitioning behavior of mono- and polyaromatic compounds (Shiu and Ma, 2000). While the specific values of the van’t Hoff parameters may not represent true thermodynamic quantities, trends between parameters for air-water and air-CD solutions are still useful for interpolating and extrapolating to $K_{A12}$ and $K'_{A12}$ values from the measured data. In addition, trends in $A_{12}$ and $B_{12}$ with CD concentration are useful for understanding air-CD solution partitioning phenomena.

The slopes ($A_{12}$) of the van’t Hoff plots for the air-CD solution systems were higher than those of the air-water systems for all of the HOPs and at all CD concentrations in this study. It has been shown that the heat capacity of HPβCD solutions change little (< 5%) over the range of CD concentrations employed here (Cardoso-Mohedano and Pérez-Casas, 2004), therefore changes in van’t Hoff parameters with CD concentration are unlikely to be attributable to changes in heat capacity. van’t Hoff plots for toluene showed only a very slight increase in slope with CD concentration. Four of the other HOPs showed a trend of increasing $A_{12}$ values with increasing CD concentration. The sixth HOP, o-xylene, showed an increase in $A_{12}$ up to a CD concentration of 20 g L$^{-1}$, then decreasing values at higher CD concentrations. Increases in slope of van’t Hoff plots have also been observed for TCE in sodium dodecyl sulfate (SDS) solutions above the CMC. This change in slope indicates that more energy is required for HOP transfer from the solution to the air phase, which is consistent with the need to break up HOP-CD complexes prior to HOP volatilization.
### Table 3-4. Van’t Hoff Parameters for TCE, PCE and BTEX for dimensionless Henry’s constants in water and CD solutions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>No CD</th>
<th>10 g L(^{-1}) CD</th>
<th>20 g L(^{-1}) CD</th>
<th>50 g L(^{-1}) CD</th>
<th>100 g L(^{-1}) CD</th>
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</thead>
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<tr>
<td>TCE</td>
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<td>3619</td>
<td>4056</td>
<td>4888</td>
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<tr>
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<td>9.8</td>
<td>10.5</td>
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</tr>
<tr>
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<td>R(^2)</td>
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<td>0.9827</td>
</tr>
<tr>
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<td></td>
<td>1989-3702(^{1,2})</td>
<td>5271(^*)</td>
<td>4769(^*)</td>
<td>2742(^*)</td>
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<td>5.2-9.9(^{1,2})</td>
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<td>13.3(^*)</td>
<td>6.2(^*)</td>
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<td>3252</td>
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<td>5.1-10.1(^{1})</td>
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<td>10.1</td>
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</tr>
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</tr>
<tr>
<td></td>
<td>B(_{12}) Lit. range</td>
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<td>5.1-9.0(^{1})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>4384</td>
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</tr>
<tr>
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<td>B(_{12})</td>
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<td>11.2</td>
<td>11.6</td>
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</tr>
<tr>
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</tr>
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<td></td>
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</tr>
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<td>5.0-8.8(^{1})</td>
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</tr>
</tbody>
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\(^{1}\) Ranges determined from values reported in refs. Boving and Brusseau, 2000 and Shirin et al., 2003, and values calculated from data presented in ref. Lantz et al., 2005.

\(^{2}\) Calculated from values reported in ref. Kashiyama and Boving, 2004.
Figure 3-4. Van’t Hoff plots of traditional ($K_{A12}$) and apparent ($K'_{A12}$) Henry’s law constants for tested chemicals. (Note: Circle, inverse triangle, square, diamond, and triangle represent CD concentration of 0, 10, 20, 50 and 100 g L$^{-1}$ respectively).
3.4 References


CHAPTER 4 THE PSEUDOPHASE APPROACH TO ASSESSING CHEMICAL PARTITIONING IN AIR-WATER-CYCLODEXTRIN SYSTEMS

4.1 Introduction

The cyclodextrin (CD) cavity provides a more favorable environmental for HOP than being dissolved in water. This leads to HOP partitioning to CD and therefore the apparent solubility enhancement, removal of HOP from the dissolved phase and a reduction in Henry’s constant. The measurements made using the SHPV method (Chapter 3) describe the distribution of chemical between the air and CD solution, but do not provide direct information regarding the partitioning behavior between the CD cavity and aqueous phases. Air stripping removes chemical from the dissolved phase, therefore the reduction in the dissolved concentration due to CD-complexation is expected to make air stripping more difficult. Higher temperatures, taller columns, lower air flow rates, and other operating parameters will likely have to be adjusted, potentially making the treat part of pump-and-treat more expensive and time consuming.

In order to fully describe the distribution of solute in a three-phase (aqueous, air phase, and the CD pseudophase), partition coefficients are required. However, some of the parameters describing the partition coefficients cannot be readily measured. A common mass balance approach can be used to quantify partition coefficients for the cyclodextrin or micellar cavity, which is treated as a pseudophase, for three-phase chromatography using micelles and cyclodextrin (Armstrong and Nome, 1981; Armstrong and Stine, 1983; Pino et al., 2006), for octanol/aqueous micellar solutions with polar analytes (Janini and Attari, 1983), and for highly volatile analytes in aqueous solutions of various CDs (Lantz et al., 2005). In these methods, more variables are involved in the calculation leading to greater errors in the results. In this chapter, mathematical models were developed to calculate the partition coefficient between CD
pseudophase and aqueous phase by inference using Henry’s constant measured in water and CD solutions. The solubility enhancement factors for 6 tested HOPs (TCE, PCE, benzene, ethylbenzene, o-xylene and toluene) were determined; also the mass distribution of contaminant among aqueous phase, air phase, and CD pseudophase are calculated using partition coefficients and overall HOP mass balance.

4.2 Materials and Experimental Methods

Methanol, contaminants (TCE, PCE, benzene, ethylbenzene, o-xylene and toluene), and solubility enhancement agent (HPβCD) described in this chapter are the same as those described in chapter 3. The apparent Henry’s law constant ($K_{A12}^\prime$) for air and CD solution and the air water Henry’s law constant ($K_{A12}$) of above contaminants were determined by Static Headspace Phase Ratio method (SHPR) described in chapter 3 using gas chromatography (GC) and mass selective detection (MSD) coupled with a static headspace autosampler with the same operation parameters.

4.3 Data Analysis

4.3.1 Mathematics Model of CD Pseudophase-water Partitioning Behavior

Using Henry’s Law constants determined from solutions with and without HPβCD, a CD-water partition coefficient can be determined for a particular HOP and temperature. The following treatment was developed based on differentiation of the dissolved and CD-complexed chemical present in the aqueous phase. Though it was developed independently for this study, a similar method was applied to describe micelle-water partition coefficients for surfactants by Shimotori and Arnold (2003). The traditional Henry’s Law constant for air and water only is expressed,
\[ K_{A12} = \frac{C_{A1}}{C_{A2}} \]  
\( \text{(4-1)} \)

where;

\[ K_{A12} = \text{the traditional Henry’s constant (dimensionless)}, \]
\[ C_{A1} = \text{the concentration of chemical } A \text{ in air (mg L}^{-1} \text{)}, \]
\[ C_{A2} = \text{the concentration of } A \text{ dissolved in water (mg L}^{-1} \text{)}. \]

For air in contact with CD solutions, the apparent Henry’s constant is defined as

\[ K'_{A12} = \frac{C_{A1}}{C_{A2} + C'_{A2}} \]  
\( \text{(4-2)} \)

where;

\[ K'_{A12} = \text{the apparent Henry’s constant (dimensionless)} \]
\[ C'_{A2} = \text{the concentration of } A \text{ in water complexed with CD (mg L}^{-1} \text{)}. \]

\( K_{A12} \) and \( K'_{A12} \) are determined experimentally as described above and can be used to determine the concentrations of \( A \) in the air, dissolved and CD-complexed phases using a mass balance approach

\[ V_2 C_{A20} = V_1 C_{A1} + V_2 C_{A2} + V_2 C'_{A2} \]  
\( \text{(4-3)} \)

Where;

\[ V_2 = \text{the volume of water or CD-solution (L)}, \]
\[ C_{A20} = \text{the initial concentration of } A \text{ in solution with air and CD (mg L}^{-1} \text{)}, \]
\[ V_1 = \text{the volume of air in a particular sample (L)}. \]

Combining eq 2 and 3 and rearranging allows for calculation of the air phase concentration.
\[ C_{A1} = \frac{C_{A20}}{\frac{V_1}{V_2} + \frac{1}{K'A_{12}}} \]  

which can then be used with eqn 4-1 to calculate the dissolved concentration \( C_{A2} \) and finally eqn 4-3 can be rearranged and solved for \( C'A_{2} \) using the results from eqs 4-4 and 4-1. It should be noted that this treatment depends on the assumption that the distribution of \( A \) between the air and dissolved phases can be described by the traditional Henry’s law constant and is not affected by the presence of CD. In other words, the only effect the presence of CD has on the distribution of chemical \( A \) between air and water is to remove a fraction of \( A \) from being available for air-water partitioning. The ratio of the CD-complexed and dissolved concentrations of \( A \) in CD solutions can be used to define a CD-water partition coefficient

\[ K'_{AC2} = \frac{C'_{A2}}{C_{A2}} = K_{AC2}C_{C2} \]  

where;

\( K'_{AC2} = \) the dimensionless CD-water partition coefficient for chemical \( A \) (subscript \( C \) denotes the CD pseudophase),

\( K_{AC2} = \) the CD-normalized partition coefficient (L kg\(^{-1}\)) and \( C_{C2} \) is the concentration of CD in solution (kg L\(^{-1}\)).

The CD-normalized partition coefficient can be determined directly from \( K_{A12} \) and \( K'_{A12} \) using a relationship derived from eqs 4-1, 4-2 and 4-5

\[ K_{AC2} = \left( \frac{K_{A12}}{K'_{A12}} - 1 \right) \frac{1}{C_{C2}} \]  

\[ (4-6) \]
where all terms have been defined previously.

**4.3.2 Development of Solubility Enhancement Factor**

Solubility enhancement factor (SEF), ratio of the apparent solubility in presence of SEAs over the water solubility without SAs, is an important parameter to evaluate the performance of various types of SAs. The methods to determine SEF rely on the procedure of solubility measurement, which commonly involves adding excess amount of solute to aqueous, centrifuging after equilibrium, and measuring the supernatant concentration. These methods involved using excess organic chemicals, which is not an environmental-friendly step or hard to carry out experimentally. In addition these methods are not suitable for a compound in an unknown matrix, as would exist for an environmental sample in the presence of SAs. In the present study, a novel and experimentally simple method is developed to determine SEF, in which neither excess amount of chemicals nor its matrix is needed.

Several previous researchers have reported that the apparent solubility of organic compounds ($S_A$) in aqueous solution containing CD increase linearly with the concentration of CD (Wang and Brusseau 1993; Bizzigotti et al. 1997). In order to fully understand solubility enhancement behavior, a linear partition model for the solubility enhancement of surfactants presented by Chiou and colleagues (Kile et al. 1999; Chiou et al.1986) can be used to represent the interaction between the solutes and the CD cavity. The intensity of this partition-like interaction for an organic solute with respect to the CD cavity can be expressed as

$$S_A = S_w + C_{c2} \cdot C_{rop}$$  \hspace{1cm} (4-7)

Where;

$S_A =$ the apparent solute solubility in water containing CD, mg L$^{-1}$
\( S_w \) = the solubility in pure water, mg \( L^{-1} \)

\( C_{c2} \) = the concentration of CD in water phase, kg \( L^{-1} \)

\( C_{HOP} \) = the mass of solute partitioned into a unit mass of CD, g kg\(^{-1} \)

An expression of the relationship between the solubility in pure water (\( S_w \)) and the amount of solute partitioned into CD cavity (\( C_{HOP} \)) is

\[
K_{AC2} = \frac{C_{HOP}}{S_w} \quad (4-8)
\]

A function describing the apparent solubility (\( S_A \)) can be shown by rearranging and combining eqn 4-7 and 4-8 and gives

\[
S_A = S_w + C_{c2} \cdot K_{AC2} \cdot S_w = S_w (1 + C_{c2} \cdot K_{AC2}) = S_w \cdot E \quad (4-9)
\]

Therefore the solubility enhancement factor (\( E \)) is defined as

\[
E = 1 + K_{AC2} \cdot C_{c2} = 1 + \left( \frac{K_{AI2}}{K'_{AI2}} \right) \cdot C_{c2} = \frac{K_{AI2}}{K'_{AI2}} \quad (4-10)
\]

4.3.3 Mass Distribution of HOPs in Air-water-CD Systems

The mass distribution of solute between compartments of a multiphase system can be determined using a mass balance as described by eqn 4-3. The amount of HOP present in the air phase can be obtained from eqn 4-4 or direct measurement and a response factor determined using calibration standard. The total mass of HOP present in aqueous phase is calculated by combining eqn 4-3 and 4-5,
\[ M_T = V_1 C_{A1} + V_2 C_{A2} + V_2 K'_{AC2} C_{A2} \]
\[ = V_1 C_{A1} + C_{A2} V_2 \cdot (1 + K'_{AC2}) \] (4-11a)

Therefore
\[ M_2 = C_{A2} V_2 = \frac{M_T - V_1 C_{A1}}{(1 + K'_{AC2})} \] (4-11b)

\[ M_{CD} = M_T - M_2 - M_1 \] (4-11c)

where;

\[ M_T \] = the total mass of HOP added to the system, mg
\[ M_2 \] = the total mass of HOP dissolved in the water phase, mg
\[ M_{CD} \] = the total mass of HOP associated with the CD pseudophase, mg
\[ M_1 \] = the total mass of HOP presented in the air phase, mg

The volume of each phase \((V_1, V_2)\) and the total amount of HOP added to each system \((M_{total})\) are known quantities, therefore the mass present in each phase is only related to the partitioning coefficient between the aqueous phase and CD pseudophase \((K'_{AC2})\). According to equation 4-5 and 4-6, \(K'_{AC2}\) is a function of apparent and traditional Henry’s law constants. Once both Henry’s law constants are determined, \(K'_{AC2}\) can be readily calculated and the fraction of HOP present in each phase can be estimated.

4.4 Results and Discussion

4.4.1 CD Pseudophase-Water Partitioning

Values of the CD-water partition coefficients \((K_{AC2})\) for the four CD concentrations tested were calculated using eq 4-6 and the averages and standard deviations (error bars) are shown in Figure 4-1. The effect of increasing temperature on CD-complexation for each HOP can be
described using the slope of the lines shown in Figure 4-1: TCE, -0.80 L kg\(^{-1}\) °C\(^{-1}\); PCE, -1.36 L kg\(^{-1}\) °C\(^{-1}\); benzene, -1.04 L kg\(^{-1}\) °C\(^{-1}\); toluene, -0.01 L kg\(^{-1}\) °C\(^{-1}\); ethylbenzene, -3.42 L kg\(^{-1}\) °C\(^{-1}\); and \(\alpha\)-xylene, -1.21 L kg\(^{-1}\) °C\(^{-1}\). For all HOPs except toluene, a clear decrease in \(K_{AC2}\) with increasing temperature is observed. This is indicative of decreasing CD-HOP complex stability at higher temperatures. The \(K_{AC2}\) values for toluene appeared to be almost independent of temperature over the range tested, indicating that complexes formed between HP\(\beta\)CD and toluene are particularly stable over the temperature range examined. \(K_{AC2}\) was higher for the more hydrophobic HOPs, and followed the trend: ethylbenzene > PCE > \(\alpha\)-xylene > toluene > benzene > TCE. The chlorinated solvents had lower \(K_{AC2}\) values than comparable BTEX compounds despite having higher octanol-water partition coefficients. This is attributed to the greater effect increasing temperature has on the vapor pressure of chlorinated solvents compared to BTEX compounds with similar solubilities (i.e. TCE and benzene or PCE and ethylbenzene/\(\alpha\)-xylene).

![Figure 4-1. CD-water partition coefficients (\(K_{AC2}\)) as a function of temperature: Note: filled circle for TCE; open circle for PCE; inverse filled triangle for benzene; open triangle for toluene; filled square for ethylbenzene and open square for \(\alpha\)-xylene. Trend lines shown for reference).](image-url)
Wang and Brusseau (1993) have observed a linear increase in HOP saturation with increasing CD concentration in aqueous solutions, indicating that $K_{AC2}$ values are independent of CD concentration. In general, this was true of the results presented here for experiments conducted at HOP concentrations which are several orders of magnitude below saturation. The exceptions were TCE and ethylbenzene, which showed increases in $K_{AC2}$ with increasing CD concentration. In the case of TCE at 55°C and below, $K_{AC2}$ nearly doubles as CD concentration increases from 10 to 100 g L$^{-1}$, while for ethylbenzene this increase is only ~30% between 35 and 45°C. One condition that must be satisfied for $K_{AC2}$ to be independent of CD concentration is that all CD-HOP molecular complexes occur on a 1:1 basis. The discrepancies for TCE and ethylbenzene may be the result of the formation of 2:1 CD-HOP complexes at higher CD concentrations, which could further enhance the solubility of TCE and ethylbenzene. At higher temperatures, these 2:1 complexes would become less stable and therefore would not contribute to increasing $K_{AC2}$. However, it is not clear from their chemical structures why TCE and ethylbenzene would form 2:1 complexes and the other HOPs would not, so it is possible that this phenomenon is an artifact of the data.

![Figure 4-2](image.png)

**Figure 4-2.** Comparison of CD-water partition coefficients ($K_{AC2}$) as a function of temperature for TCE: (Note: filled circle for Kashiyama and Boving’s study and open circle for this study.)
The effects of HPβCD on TCE air-water partitioning were examined by Kashimaya and Boving (2004) over the same CD concentration range and a similar range of temperatures (20 – 60°C). Using their Henry’s constant measurements, $K_{AC2}$ values were calculated for comparison with those presented here. The results are shown in Figure 4-2. The plot illustrates three major differences in the two data sets: (1) the error bars (representing the standard deviation between $K_{AC2}$ values determined at different CD concentrations) are much narrower in our data set; (2) the values of $K_{AC2}$ determined from our Henry’s constant measurements are lower by a factor of 2 or more; and (3) the temperature trend we determined for $K_{AC2}$ is the opposite of that indicated by Kashiyama and Boving. The first discrepancy between the two data sets relates to the dependence of $K_{AC2}$ on CD concentration. Examination of the results of both studies reveals no trends in $K_{AC2}$ with CD concentration at any particular temperature, therefore the large error bars are likely the result of experimental variability. The second discrepancy is attributed to the higher HOP affinity of the HPβCD used in the study by Kashiyama and Boving (CAVASOL W7 MTL, Wacker Inc.) due to its lower degree of substitution (DS = 1.6 – 1.9) by hydroxypropyl groups. It has been shown that complex stability for HPβCD is reduced at higher DS (Mosher and Thompson, 2000). The third discrepancy indicates very different properties for CD-TCE partitioning. An increase in $K_{AC2}$ with temperature would indicate that complexation was in some way enhanced at higher temperatures, despite the concurrent increase in aqueous solubility and vapor pressure which would be expected to drive chemical out of the complexed phase. This may be the case for some HOP-surfactant systems (Shimotori and Arnold, 2003, TCE – Triton X-100) because of changes in micelle structure at higher temperatures. However, CD molecules are essentially fixed structures rather than loose assemblies of molecules and therefore it is unlikely
that increasing temperature would affect CD structure in such a way as to enhance partitioning of HOPs to CD. All of the HOPs studied here showed decreasing values of $K_{AC2}$ with increasing temperature, with the exception of toluene which showed essentially no change in the 35 – 65°C range. This leads us to conclude that the increase in $K_{AC2}$ with temperature observed by Kashiyama and Boving is an experimental artifact, which may be due to the use of manual sampling and GC injection of headspace vapor samples.

4.4.2 Solubility Enhancement

The solubility enhancements factors determined using eqn 4-10 with a normalized CD concentration are reported in Figure 4-3. The error bars represent the standard deviation due to differences in concentrations. As can be seen in figure 4-3, CD moleculars provide greater solubility enhancement for less soluble HOPs with the exception of data obtained with Ethylbenzen at 55°C and PCE at 65°C. The enhancement factors decrease with increasing temperature for most of the HOPs examined in this study, which is consistent with the assertion that the CD-HOP complexes are less stable at higher temperatures.

Figure 4-3. Effect of temperature on solubility enhancement factors: (Note: Labels represent 35°C, 45°C, 55°C, and 65°C from left to right respectively).
The effects of HPβCD on solubility enhancement factors were examined by McCray et al (2000) and the results are shown in table 4-1. The same trend of less enhancements for higher soluble HOPs was found in their study; however the E values for TCE and PCE reported by McCray’s group (2000) are lower by a factor of 2 or more. The discrepancy is considered to be due to the differences in the methods applied in the two studies. For the quantification of TCE and PCE enhancement factors, ultraviolet-visible absorbance spectroscopy was applied in McCray’s study. However the method assumes that absorbance response to the concentration of TCE or PCE in pure water or an aqueous-CD solution will be the same, which is may not be a valid assumption. For Beer’s Law to be applicable (that absorbance is proportional to concentration), a solution with a uniform refractive index is required; this is not possible when a CD pseudophase presents in solution. The cavity environment is different from the aqueous environment because the polarity within the CD cavity is significantly lower than that of water (more similar to ethanol or dioxane), resulting in a different refractive index. Therefore the absorbance response of dissolved TCE or PCE will be different from that of CD-complexed TCE or PCE. The gas chromatography (GC) techniques used for other contaminants do not have this limitation because they do not rely on Beer’s Law assumptions. This is why the enhancement

<table>
<thead>
<tr>
<th></th>
<th>TCE</th>
<th>PCE</th>
<th>Benzene</th>
<th>Ethylbenzene</th>
<th>Toluene</th>
<th>o-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>*$S_p$ (mg/L)</td>
<td>1150</td>
<td>150</td>
<td>1750</td>
<td>153</td>
<td>464</td>
<td>152</td>
</tr>
<tr>
<td>†$E$</td>
<td>0.65</td>
<td>0.89</td>
<td>NA</td>
<td>2.49</td>
<td>0.96</td>
<td>1.61</td>
</tr>
</tbody>
</table>

‡ McCray et al (2000)

* Solubility in water, mg/L
† Solubility enhancement
NA = not available
factors determined from this study for TCE and PCE are very different than those reported by McCready et al. (2000), but the BTEX values are similar.

Many types of solubilizing agents (SA) have been proposed for and applied to the remediation of subsurface contamination by HOPs. For chlorinated solvents and BTEX, there have been several studies conducted using a wide range of SAs (Lataa, 2001, Anderson, 1992 Shimotori and Arnold, 2003). Here, we compare solubility enhancement factors of several SAs, including simple alcohols (ethanol, isopropanol and tert-butanol (Lataa, 2001) and commonly used surfactants (Triton X-100, SDS and cetyltrimethylammonium bromide (CTAB) (Shimotori and Arnold, 2003) to the values of HPβCD determined in this study. Because most experiments in this area of study are conducted at ambient conditions (23-25°C), values for the CD solubility enhancement factor at 25°C were determined using eq 4-10 with values of \( K'_{412} \) and \( K''_{412} \) estimated using eq 3-6 and the parameters in Table 3-4.

![Figure 4-4. Comparison of the solubility enhancement factors for PCE.*. (*Note: Values for alcohols determined from data in Lataa, (2001); Triton X-100, SDS and CTAB values determined from Shimotori and Arnold, 2003)](image)
Figure 4-4 shows PCE SA-solubility enhancement factors. It should be noted that unlike the values for the surfactants (above the CMC) and CD, the solubility enhancement factor calculated for the simple alcohols were not independent of alcohol concentration, therefore the values shown in Fig. 4-4 are those for 15% v/v alcohol-water solutions. It is clear that the alcohols provide small solubility enhancement for PCE at 15% v/v compared to the surfactants and HPβCD. SDS has a higher solubility enhancement factor then HPβCD among the SAs.

4.4.3 Mass Distribution among Phases

In order to illustrate how the HOP mass distribution in air-water-CD systems changes with temperature and CD concentration, ternary phase diagrams (Figure 4-5) showing the total HOP mass present in each phase were constructed based on the mass balance treatment described previously. The plots represent systems with equal volumes of air and water.

For all compounds, the HOP fraction in the gas phase decreases with increasing of temperature. As CD concentration increases, the fraction of HOP mass present in CD-complexes proportionally rises. As temperature increases, the HOP mass fraction present in CD-complexes decreases, with most of the displaced mass moving to the air phase. CD provides a large solubility enhancement for ethylbenzene when the CD concentration is low. For example at the lowest CD concentration over 60% ethylbenzene is present in the CD phase. At the highest CD concentration, 65% or more of the total mass of each HOP was present in CD-complexes across the entire temperature range. The CD concentration required for ≥ 50% of the total HOP mass to be present in CD-complexes at 35°C followed the trend: TCE > benzene > toluene > o-xylene ≈ PCE > ethylbenzene. A slightly different trend was observed for 65°C: TCE > benzene > toluene ≈ PCE > o-xylene > ethylbenzene. This difference results from the stronger temperature dependence of PCE vapor pressure relative to that of o-xylene or ethylbenzene.
Figure 4-5. Ternary diagrams of HOP mass distribution in air-water-CD systems with equal volumes of air and water (10 mL): (Note: filled circle, inverse open triangle, filled square, open diamond, filled triangle for no CD 10 20 50 and 100 g L⁻¹ CD respectively. The toluene plot provides guidance for reading the mass fractions (dashed lines for CD conc. 10 g L⁻¹ at 65°C: air = 0.34, dissolved = 0.29, CD-complexed = 0.37) and indicates isotherms for 35 – 65°C (solid lines))
4.5 References


CHAPTER 5 ADSORPTION OF ORGANIC POLLUTANTS TO GRANULAR
ACTIVATED CARBON IN THE PRESENCE OF CYCLODEXTRIN – RESULTS FROM
BATCH STUDIES

5.1 Introduction

Application of CD to typical pump-and-treat remediation of groundwater requires that the extracted pollutants be removed from aqueous CD solution following pump-out so that the water can be returned to the subsurface and the cyclodextrin can be recycled and reused. As described in previous chapters, one approach for pollutant removal is to employ a combination of air stripping and adsorption to granular activated carbon (GAC). To further investigate the quantity of HOPs that can be adsorbed per unit mass of GAC, adsorption isotherms were determined for a common chlorinated solvent, trichloroethylene (TCE), with aqueous solutions containing a range of hydroxypropyl-β-cyclodextrin (HP β CD) concentrations (0, 20, 50, 100 g L⁻¹). Mass distribution of contaminants among phases in TCE-CD system was determined. An empirical correlation of adsorption coefficient with solubility enhancement factor was developed to explain the adsorption behavior.

5.2 Materials and Experimental Methods

5.2.1 Chemicals

Trichloroethylene (TCE) was purchased from Sigma-Aldrich (>99.5% purity). HPβCD (degree of substitution = 4.98, average MW 1424 g mol⁻¹) was donated by Cargill and used as received (purity wt/wt: moisture content 5.0%; unmodified CD <0.1%; propylene glycol 0.4%; ash 2.0%; HPβCD 92.6%). High purity deionized water was generated by water purification system (Siemens, Warrendale, PA) to 18.2 MΩ and was disinfected by ultraviolet irradiation. Headspace vials and magnetic screw caps with silicone/PTFE-faced septa were purchased from Microliter Analytical Supplies (Suwannee, GA).
5.2.2 Preliminary GAC Screening

Eleven commercially available GACs (CC602 12×30, Norit C GRAN, Fisher, GAC 830, GAC 830 PLUS, GAC 1240, HYDRODARCO 3000, KG401 8x30, KG502 12×40, KG503 12×40, RO 0.8) were obtained and prescreened for compatibility to testing methods. The preliminary GAC screening testing involved weighing 0.5± 0.05 g of GAC into a 15ml plastic centrifuge tube. Then either 10ml of water or 10ml of aqueous HPβCD solution (20.015g L⁻¹) solution was added. After the liquid was added, each vial was visually evaluated the degree of bubbling or foaming. For some of the GACs the foam that was created when cyclodextrin was added persisted for several minutes. To quantify this factor, the volume of the foam remaining 5 minutes after inundation was recorded. Subsequently, the vials were agitated for 24 hours on an orbital shaker (Big Bill at 50rpm). After removing the vials and resting for 30 minutes on the lab bench to permit the GAC to settle, the GAC integrity was firstly evaluated through visual inspection for solution clarity and the presence of a black film on the vial. Subsequently, the liquids were decanted into a fresh centrifuge tube where the solution clarity was reexamined. The GAC was then placed on sheet of aluminum where the GAC grains were visually examined for breakdown and their integrity evaluated through crushing with a flat spatula. The results are shown in Table 5-1.

Inundation with aqueous CD solution resulted several of the GACs producing a relatively significant amount of persistent foam. In addition, the presence of cyclodextrin did lead in many GACs to more degradation of the particles during agitation. Of the GACs, KG502 and Gran C were the top two performers (Table 5-1). To increase the consistency of following batch and column studies conditions, the uniformity of the GAC grains was set as a final screening factor. While KG502 is composed of rough grains of varying shapes, the Gran C used in this test is
composed of fairly uniform oblong smooth pellets. Because the objective of this study is to characterize the mass transfer processes for HOPs in water-CD-GAC systems, the more uniform Norit C GRAN was chosen for subsequent testing.

Norit C GRAN particle size distribution was determined and the results were summarized in Tables 5-2. As can be seen from Table 5-2 the median particle size was approximately 1210µm and the particles where fairly uniform in size with two uniformity indexes U(d80/d20) and U(d60/d10) being 1.28 and 1.25 respectively. Other physical and chemical characteristics of this type of GAC were summarized in Table 5-3.

<table>
<thead>
<tr>
<th>GAC Brand Name</th>
<th>Water/ Cyclodextrin</th>
<th>Pre-Agitation Bubble or Foam Formation†</th>
<th>Pre-Agitation Foam Residual Vol. (ml) ‡</th>
<th>Post-Agitation GAC Integrity ‡</th>
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<td>0.5</td>
<td>3</td>
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</tr>
<tr>
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<tr>
<td>GAC 830</td>
<td>Water</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>GAC 830 PLUS</td>
<td>Water</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>GAC 1240</td>
<td>Water</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>HYDRODARCO 3000</td>
<td>Water</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>KG401 8×30</td>
<td>Water</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>KG502 12×40</td>
<td>Water</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>KG503 12×40</td>
<td>Water</td>
<td>2</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>RO 0.8</td>
<td>Water</td>
<td>5</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

† Pre-agitation severity of bubble formation in water or foaming in cyclodextrin (1 = none, 5 = severe)
‡ Pre-agitation volume of residual foam after 5 minutes
‡ Post-agitation GAC integrity (1 = clear solution and no visible GAC breakdown, 5 = obvious breakdown of GAC)
5.2.3 Batch Mode Adsorption Studies

Aqueous CD solutions with concentrations of 0, 20, 50 and 100 g·L⁻¹ were prepared by addition of CD powder to high purity water. TCE solution (54.32 mg L⁻¹) was prepared by dissolving pure TCE into the different CD solutions. For the batch adsorption isotherm experiments, weighed activated carbon aliquots were placed in seven brown bottles (135 ml)
which were subsequently filled with TCE-CD solutions in the solid/liquid ratio of 1:20-1:200 g ml\(^{-1}\). All bottles were capped immediately using PTFE-faced silicon septa to create headspace-free conditions. Continuous mixing was providing during the adsorption experimental period with a constant agitation speed of 250 rpm through a rotary shaker (Model: LE "Big Bill", Sybron Thermolyne). A preliminary experiment demonstrated that after 5 days mixing, the remaining concentration of TCE in aqueous solution changed by less than 0.1%, which is considered to represent adsorption equilibrium. In this study, a mixing time of 7 days was employed to ensure that equilibrium was achieved. Longer contact times were not used due to concerns regarding GAC particle destruction (Sposito, 1980).

At the end of the 7-day equilibration period, mixing was halted and suspended GAC particles were allowed to quiescently settle for one hour. Supernatant (2ml) was then transferred into brown glass headspace vials via a glass, gas-tight syringe. Vials were sealed immediately after filling and placed in a Gas Chromatograph (GC) autosampler rack for equilibration. No filtration of the post adsorption solution was conducted due to concerns regarding TCE leakage or adsorption to filters. Because static headspace analysis is based on sampling and measurement of vapor phase concentrations, the potential trace GAC residue in the liquid phase would not be expected to markedly influence results. The TCE concentration remaining in the aqueous solution after adsorption was measured by an Agilent 6890 GC fitted with a static headspace autosampler (Combi PAL, Leap Technologies, Carrboro, NC). The analysis condition, including the flow rate of carrier gas oven temperature protocol and mass operation condition was as described in Chapter 3. The amounts of TCE adsorbed to GAC were calculated from the mass balance relation. Two replicates per sample were analyzed, and the average results are presented.
Freundlich Isotherm was used to simulate the process of TCE absorption to GAC and the parameters are determined by linear regression.

## 5.3 Data Analysis

### 5.3.1 Adsorption Isotherms and Mass Distribution

For this specific research, the adsorption activities are expected to be complicated by the presence of CD in solution. The apparent adsorption isotherm curves describe the distribution of chemical between the GAC and aqueous phase, but do not provide direct information regarding the adsorption behavior between the chemicals partitioned to CD cavities and activated carbon. In this study, the following treatment was developed based on differentiation of the dissolved and CD-complexed chemical present in the aqueous phase. This allowed the adsorption/partitioning between the different phases to be calculated.

![Figure 5-1. Description of chemical adsorption with the absence of CD (left) and with the presence of CD (right)](image)

For systems containing only water and GAC (Figure 5-1), the traditional Freundlich isotherm is defined as the relationship between the adsorbed concentration $C_A$ (phase S, mg g$^{-1}$) in the
GAC and the solute concentration $C_{A2}$ (phase 2, mg L$^{-1}$) remaining in water (Van Bemmelen, 1888; Freundlich, 1909; Weber and DiGiano 1996).

$$C_{AS} = K_f \cdot C_{A2}^n$$

(5-1)

Where,

- $K_f$ = Freundlich adsorption coefficient which indicates the adsorption ability;
- $n$ = a constant indicative of adsorption affinity;
- $C_{A2}$ = chemical concentration remaining in liquid phase, mg L$^{-1}$;
- $C_{AS}$ = adsorbed concentration in the solid phase, mg g$^{-1}$

In systems that contain CD (Figure 5-2), an apparent Freundlich isotherm between the adsorbed concentration $C'_{AS}$ (phase $S$, mg g$^{-1}$) and remaining concentration in the aqueous CD solution is obtained. A term is added to the water concentration ($C_{A2}$) of equation 5-1 that accounts for the chemical present in the aqueous solution that is associated with CD cavities ($C'_{A2}$, mg L$^{-1}$).

$$C'_{AS} = K_f' \cdot (C_{A2} + C'_{A2})^n'$$

(5-2)

Where,

- $K_f'$ = apparent Freundlich adsorption coefficient with the presence of CD;
- $n'$ = adsorption constant with the presence of CD;
- $C'_{AS}$ = adsorbed quantity with the presence of CD, mg g$^{-1}$
- $C'_{A2}$ = chemicals associated with CD cavities, mg L$^{-1}$

In order to describe the mass distribution of chemical in each phase (GAC, water, and CD pseudophase), partition coefficient $K'_{AC2}$, describing the ratio of the CD-associated and dissolved
concentrations was adopted from previous research which is summarized as following (Gao et al, 2009),

\[ K'_{AC2} = \frac{K_{A12}}{K_{A12}} - 1 \]  

(5-3)

Where;

\[ K'_{A12} \text{ and } K_{A12} = \text{the Henry’s law constants with and without the presence of CD} \]

According to equation 5-3, \( K'_{AC2} \) is easily obtained if \( K'_{A12} \) and \( K_{A12} \) are known. Because both \( K_{A12} \) and \( K'_{A12} \) were determined in a temperature range of 35°C-65°C in previous research (Gao et al, 2009), the parameters under room temperature (23°C) at which the adsorption experiment was conducted could be determined by applying the van’t Hoff equations (Robbins et al., 1993; Vane and Giroux, 2000; Gossett, 1987) coupled with corrected coefficients, \( A_{12} \) and \( B_{12} \) obtained from previous research (Table 3-4, Gao et al, 2009). Once the partition coefficients \( K'_{AC2} \) are obtained, the quantity present in water phase can be determined and the traditional Freundlich adsorption isotherms can be rescaled from apparent ones by nonlinear regression of \( C'_{AS} \) versus water phase concentration, \( C_{A2} \).

5.3.2 Statistical Analyses

A modified linear regression model was built to evaluate the significance of adsorption coefficients under different CD concentrations. A log-transform was imposed on both the concentration and the absorption quantity to convert the power relationship \( (C_{AS} = K_f \cdot C_{A2}^n) \) to a linear model \( (\ln C_{AS} = n \cdot \ln C_{A2} + \ln K_f) \). This model (eqn. 5-4) coupled with dummy variables, \( L_1, L_2, \) and \( L_3 \) (eqn 5-5) and interaction terms, \( I_1, I_2 \) and \( I_3 \) (eqn 5-6) was used to
evaluate whether the intercept, $\ln K_f$ and the slope, $n$ are significantly different among the isotherms. To be specific, significant parameters for the dummy variables and interaction terms indicate significant difference regarding $\ln K_f$ values and $n$ among the isotherms respectively.

The linear regression model and the dummy variables are described below. The model is run via statistical software SPSS and the significance values are used to make a conclusion.

$$\ln C_{AS} = \beta_0 + \beta_1 \cdot \ln C_{A2} + \beta_2 \cdot L_1 + \beta_3 \cdot L_2 + \beta_4 \cdot L_3 + \beta_5 \cdot I_1 + \beta_6 \cdot I_2 + \beta_7 \cdot I_3 \quad (5-4)$$

Where;

$$\ln C_{AS} \text{ and } \ln C_{A2} = \text{values of dependent and independent variables;}$$

$$\beta_{0,1,2,3,4,5,6,7} = \text{regression parameters;}$$

$$L_{1,2,3} = \text{dummy variables served as the indicator of the individual isotherms;}$$

$$I_{1,2,3} = \text{interaction items}$$

$$L_1 = \begin{cases} 1 \rightarrow C_{CD} = 0g \cdot L^{-1} \\ 0 \rightarrow \text{others} \end{cases} ,$$

$$L_2 = \begin{cases} 1 \rightarrow C_{CD} = 20g \cdot L^{-1} \\ 0 \rightarrow \text{others} \end{cases} ,$$

$$L_3 = \begin{cases} 1 \rightarrow C_{CD} = 50g \cdot L^{-1} \\ 0 \rightarrow \text{others} \end{cases} ,$$

$$I_1 = \ln C_{A2} \cdot L_1$$

$$I_2 = \ln C_{A2} \cdot L_2$$
\[ I_3 = \ln C_{A2} \cdot L_3 \]  

(5-6)

5.3.3 Correlation of Freundlich Adsorption Coefficient \((K'_f)\) with Solubility Enhancement Factor \((E)\)

An empirical relationship between the Freundlich adsorption coefficient, \(K'_f\) of activated carbon, and the aqueous solubility, \(S\) was reported by a previous researcher (Mcelroy, 2005).

\[ \ln K'_f = -A \cdot \ln S + B \]  

(5-7)

Where \(A\) and \(B\) are constants. In systems that contain CD, aqueous solubility of chemicals, \(S\) can be estimated by

\[ S = E \cdot S_w \]  

(5-8)

Where \(E\) is solubility enhancement factor. Substitute equation 5-8 to eqn 5-7, an overall correlation of \(K'_f\) with \(S\) is obtained as

\[ \ln K'_f = -A \cdot \ln(E \cdot S_w) + M \]  

(5-9)

For specific chemicals \(S_w\) is a constants, therefore eqn 5-9 could be rearranged and a linear relationship between \(K'_f\) and \(E\) is developed as follow,

\[ \ln K'_f = -A \cdot \ln E + N \]  

(5-10)

Where;

\[ A \text{ and } F = \text{ constants, which could be calculated by plotting } \log K_f \text{ versus } \log E. \]

5.4 Results and Discussion

5.4.1 Mass Distribution among Phases

The chemical concentration in the liquid phase \((C_{A2} + C'_{A2})\) was determined via GC/MS analysis; the individual concentration was calculated by applying the partition coefficient,
$K'_{AC2}$ and the adsorbed quantity was calculated from the mass balance relation. In order to illustrate how the mass distribution in GAC-water-CD systems changes with CD concentration, a 3-D column diagram (Figure 5-2) shows the faction present in each phase. The plots represent systems with the solid: liquid ratio of 1:280. As can be seen in Figure 5-2, the amount of TCE initially in the aqueous phase was adsorbed to the GAC phase with the mass fraction adsorbed to GAC of 93%, 86%, 74% and 60% for 0, 20, 50 and 100 g L$^{-1}$ CD solutions respectively. As CD concentration increased, the mass fraction in both GAC and water phases decreases, which can be explained by the hydrophobic property of CD cavity. As the CD concentration increased, more hydrophobic cavities were available to combine TCE (Kashiyama et al, 2004; Boving, 2001). This apparently resulted in a lower fraction of TCE present in the freely dissolved phase; hence, the trend of decrease in fraction adsorbed in GAC phase.

![Figure 5-2. Mass distribution of TCE in GAC-Water-CD system](image)
5.4.2 Batch Mode Adsorption of TCE

The apparent Freundlich isotherm was obtained by first measuring the total amount of chemical remaining in the aqueous phase \( (C_{a2} + C'_{a2}) \) and then calculating the absorption amount \( C'_{as} \). The apparent adsorption coefficient \( K' \) and constant \( n' \) were then determined by the nonlinear regression of \( C'_{as} \) versus \( (C_{a2} + C'_{a2}) \). The apparent Freundlich isotherms of TCE are illustrated in Figure 5-3a, and tabulated values of the adsorption coefficients are shown in Table 5-4. As shown, the Freundlich isotherm well-described the experimental TCE data, with all correlation coefficients above 0.90 (Figure 5-3a). Further evidence of the good fit of the Freundlich isotherm can be seen from the results of the statistical analyses (Table 5-5). The P-values for the constant and \( \ln C_{a2} \) of both apparent and traditional isotherms are less than the significance level (0.05), indicating strong power relationship between the aqueous concentration, \( C_{a2} \) and adsorption ability \( C'_{as} \). Significant difference among the \( K' \)'s of apparent isotherms is demonstrated by results from SPSS linear regression analyses (\( P \)-value <0.05). As can be seen from Figure 5-3a, the isotherms illustrated a radial spread trend, and the GAC showed larger \( K' \) value in 0 g·L\(^{-1}\) CD, followed by 20, 50, and 100 g L\(^{-1}\) CD. This can be readily attributed to the fact that with an increase of CD concentration, a greater mass of TCE partitioned to CD; therefore, there is a decrease trend of the adsorption ability and hence \( K' \) values (Figure 5-4). The P-values for interaction items (\( I_1 \), \( I_2 \), and \( I_3 \)) of both apparent and rescaled isotherms, however, are far larger than 0.05. Therefore, there was no statistically significant difference among the \( n' \)'s of the isotherms, showing close values in Table 5-4 (0.48, 0.47, 0.46, and 0.49 for 0, 20, 50, 100 gL\(^{-1}\) CD solutions respectively).
The traditional Freundlich isotherms for 20, 50, and 100 g L\(^{-1}\) CD solutions were rescaled from apparent ones using the partitioning coefficient, \(K_{AC2}\), and a comparison was conducted with the isotherm obtained from CD-free (0 g L\(^{-1}\) CD) solutions. The \(K_f\) and \(n\) values of the rescaled isotherms are showed in Table 5-4, and the P-values of the statistical analysis of the comparison are listed in Table 5-5. Because the P-values of \(L_1\), \(L_2\), and \(L_3\) (Table 5-5) are far larger than the critical level (0.05), it can be concluded that there was no significant difference between the derived rescaled Freundlich isotherms in CD solutions and the traditional one obtained from CD-free solution (overlapped traditional isotherms in Figure 5-3b). This is an indication that CD presence did not meaningfully impact the TCE sorption proficiency of the GAC.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Isotherms</th>
<th>No CD</th>
<th>20 g L(^{-1}) CD</th>
<th>50 g L(^{-1}) CD</th>
<th>100 g L(^{-1}) CD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_f)</td>
<td>Apparent isotherms</td>
<td>7.72</td>
<td>4.99</td>
<td>3.46</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>Rescaled isotherms</td>
<td>7.72</td>
<td>7.53</td>
<td>7.25</td>
<td>7.13</td>
</tr>
<tr>
<td>(n)</td>
<td>Apparent isotherms</td>
<td>0.48</td>
<td>0.47</td>
<td>0.46</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>Rescaled isotherms</td>
<td>0.48</td>
<td>0.47</td>
<td>0.46</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 5-5. Results of SPSS linear regression analyses of adsorption isotherms

<table>
<thead>
<tr>
<th>Variables</th>
<th>Apparent isotherms</th>
<th>Rescaled isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Regression Parameters</td>
<td>P values</td>
</tr>
<tr>
<td>Constant</td>
<td>(\beta_0)</td>
<td>0.000</td>
</tr>
<tr>
<td>LnC(_{A2})</td>
<td>(\beta_1)</td>
<td>0.000</td>
</tr>
<tr>
<td>(L_1)</td>
<td>(\beta_2)</td>
<td>0.000</td>
</tr>
<tr>
<td>(L_2)</td>
<td>(\beta_3)</td>
<td>0.000</td>
</tr>
<tr>
<td>(L_3)</td>
<td>(\beta_4)</td>
<td>0.000</td>
</tr>
<tr>
<td>(I_1)</td>
<td>(\beta_5)</td>
<td>0.558</td>
</tr>
<tr>
<td>(I_2)</td>
<td>(\beta_6)</td>
<td>0.903</td>
</tr>
<tr>
<td>(I_3)</td>
<td>(\beta_7)</td>
<td>0.258</td>
</tr>
</tbody>
</table>
Figure 5-3a. Apparent Freundlich isotherm curves of TCE in CD solutions
Figure 5-3b. Recaled and traditional Freundlich isotherm curves of TCE in CD solutions
Figure 5-4. Correlation of Freundlich adsorption coefficient ($K_f$) with CD concentration

The equation of the line is:

$$y = -0.013x + 1.950$$

$$R^2 = 0.979$$
5.4.3 Correlation of $K'_f$, CD Concentration, and $E$

The Freundlich adsorption coefficient, $K'_f$, was obtained through isotherms and the solubility enhancement factor was calculated using eqn 4-10. The plot of Freundlich adsorption coefficient, $K'_f$, versus solubility enhancement factor, $E$, is illustrated in Figure 5-5. For the tested chemical, the $K'_f$ of TCE decreased when $E$ increased with the natural logarithms linear relationship coefficient of 0.999. $K'_f$ is considered to be a representation of the energy necessary for a chemical to displace a solvent in order to be adsorbed on the adsorbent (Chiou, 2002). For similar solutions under constant conditions, more energy is required to adsorb more chemical due to the increased amount of solvent that must be displaced (Mcelroy, 2005). For this specific study, a further understanding is that as the solubility enhancement factor increases, more TCE partitions to CD; therefore, the amount available to adsorb is decreased and fewer water molecules need to be displaced, resulting in less required energy and smaller $K'_f$ values.

![Figure 5-5 Correlation of Freundlich adsorption coefficient ($K'_f$) with solubility enhancement factor ($E$)](image)

Figure 5-5 Correlation of Freundlich adsorption coefficient ($K'_f$) with solubility enhancement factor ($E$)
5.5 Conclusions

In this chapter, adsorption Freundlich isotherms of TCE on Norit C GRAN activated carbon were determined with aqueous solutions containing a range of CD concentrations (0, 20, 50, 100 g L\(^{-1}\)). The adsorption ability of GAC in aqueous CD solutions decreased with increasing CD concentration. This can be attributed to CD’s characteristic hydrophobic cavity resulting in a trend of decreasing fraction TCE adsorbed in GAC phase. A linear relationship between the logarithms of \( K_f \)'s and solubility enhancement factors with coefficient of 0.99 were verified theoretically and experimentally, which is consistent with the finding of \( K_f \)'s versus CD concentration. In addition, \( K_f \) was found to decrease as HPCD concentration increased while n maintained essentially constant value at different CD concentrations.

Statistical analysis showed that there was no significant difference between the traditional Freundlich isotherm derived from CD solutions and the one in CD-free solution, indicating nearly ideal behavior in GAC-water-CD systems. Specifically, the phase distribution of HOPs can be explained with knowledge of the partitioning equations between CD-water and GAC-water. In other words, it is thought that if the mass of HOP present within CD cavities is excluded from consideration, then the distribution of the HOP between water and GAC is the same as if CD were not present.

5.6 References


CHAPTER 6 INTERACTIONS BETWEEN GRANULAR ACTIVATED CARBON, CYCLODEXTRIN, AND ORGANIC POLLUTANTS IN COLUMN STUDIES

6.1 Introduction

In spite of the large number of diverse studies on the removal of organic, inorganic taste, and odor compounds (Froelich, 1978; Dobbs and Cohen, 1980; Huang and Ostovic, 1978; Perez-Candela et al. 1995; Cousins et al. 1999; Rubio and Izquierdo, 1998; Adib et al. 2000), there are few previously published studies investigating dynamic adsorption of hydrophobic organic pollutants (HOPs) from cyclodextrin solutions to activated carbon. Based on the potential use of cyclodextrin in groundwater remediation and the requirement to treat post flushing solutions, further research to investigate the kinetic adsorption of HOP from cyclodextrin solutions is warranted. Therefore, the objectives of research presented in this chapter were to: (1) assess the breakthrough behavior of trichloroethylene (TCE) in cyclodextrin solutions in a granular activated carbon (GAC) column; (2) investigate the effect of pore velocity (1-10 ml·min⁻¹) on HOP transport in cyclodextrin solutions; (3) investigate the effect of cyclodextrin concentration (0, 20, 50 g L⁻¹) on the breakthrough of TCE in GAC columns; and (4) obtain the breakthrough curves and assess the adsorption behavior of HOP mixtures comprised of perchloroethylene (PCE), TCE, ethylbenzene, o-xylene, and naphthalene in cyclodextrin solutions.

6.2 Materials and Experimental Methods

6.2.1 Chemicals and Suppliers

TCE, PCE, ethylbenzene, o-xylene, and naphthalene were purchased from Sigma-Aldrich (>99.5% purity). The biological preservative sodium azide (CAS: 26628-22-8, (>99.5% purity) and calcium bromide hydrate (98% purity) were also purchased from Sigma-Aldrich. Sodium nitrate (98%) was purchased from Fisher Scientific. HPβCD and GAC characteristics and purity were as described in Chapter 5.
6.2.2 Column Setup and Experiments

- Column Setup

Bench-scale column tests were carried out to evaluate the capacity of Norit C Gran for removing contaminants from CD solutions under continuous flow conditions. Figure 6-1 graphically depicts the experimental apparatus configuration. The initial HOP-CD solutions were prepared in 4 L amber glass bottles. Because the tested compounds are volatile, sample might evaporate to air phase with the experiment goes. To minimize loss and provide consistent HOP and bromide tracer concentrations, the CD-HOP solution was then transferred to Teflon bags that are commonly used for sampling gases (Jensen Inert Product, FL) with no headspace. Packed columns, inner diameter of 2.54 cm, were constructed with a packed bed depth of 25.0 cm. (Alltech, IL). A stainless steel distribution plate and a filter (d = 0.22 μm) were attached at each end of the columns in order to provide even fluid supply and avoid clogging. Column, pump, and tracer bag were connected using stainless steel tubing (1/8” OD x 0.085” ID) and associated connectors (Swagelok). Samples for HOP and Br- analysis were taken with 10ml gas tight syringes with luer lock connectors (Swagelok). A gate valve (Swagelok, LA) was incorporated in the effluent line of the column in order to decrease the influence of back pressure caused by the gas-tight sampling syringe. The columns were oriented vertically and flow was introduced into the basal end to minimize the possibility of preferential flow using a piston pump with stainless steel fittings (LabAlliance Series I Pump, Fisher Scientific).

Columns were saturated by firstly extracting air through vacuum followed by 200-ml flushing tracer free solutions into the opposite end at 1ml min⁻¹, and then re-circulating through the column at the study flow rate for 24 hours. After saturation, the columns were ready for the following operation.
Two primary variables, flux rates and CD concentrations, which can influence the application of GAC for treatment of post-flushing solution, were evaluated in this study. Column tests were performed at flow rate of 1.0, 4.0, and 10.2 ml min$^{-1}$ with a series of solutions of TCE dissolved in 50 g L$^{-1}$ CD. The effect of CD concentrations (0, 20, and 50 g·L$^{-1}$) was investigated in columns supplied with a flow rate of 4.0 ml min$^{-1}$. In addition, a column study using a HOP mixture containing TCE, PCE, ethylbenzene, o-xylene and naphthalene dissolved in a CD solution (50 g·L$^{-1}$) was conducted to assess mixture effects. Due to the solubility enhancement of CD, naphthalene can be dissolved with higher concentration than its aqueous solubility. The conservative tracer, bromide was used to assess the effects of sorption and dispersion on TCE fate and transport in the column studies. Effluent flow rates were measured regularly, and
cumulative flow volumes exiting the columns were recorded to verify that flow was steady. All adsorption experiments were carried out at ambient room temperature (23±1 °C). The residual concentration of HOPs in liquid samples entering and exiting the columns was indirectly determined via the gas chromatography as described in chapter 3. A bromide ion electrode (Cole-Parmer) coupled with an Orion Star pH/mV meter (Thermo Scientific) was used to measure the conservative tracer concentrations in influent and effluent samples.

6.3 Temporal Moment Analysis

The method of temporal moments (MOM) was applied in this study for analysis of breakthrough curves. The nth absolute and normalized temporal moments of a concentration distribution at a location, x are defined as shown in eqn 6-1 and 6-2.

\[
\begin{align*}
    u_n &= \int_0^\infty t^n c(x,t) dt \\
    \overline{u}_n &= \frac{u_n}{u_0} = \frac{\int_0^\infty t^n c(x,t) dt}{\int_0^\infty c(x,t) dt}
\end{align*}
\]  

(6-1)

(6-2)

Where;

\[ u_n \] = the absolute temporal moment,

\[ \overline{u}_n \] = the normalized temporal moment,

\[ c(x,t) \] = the concentration at time, t, in location x, dimensionless \( C / C_0 \)

\[ t \] = flushing time in term of pore volume

\[ n \] = the order of the temporal moment, dimensionless

\[ x \] = location, L

For convenient comparison between the column tests, time and effluent concentration are normalized to do the MOM analysis. The residence time, \( RT \) can be obtain by eqn 6-3

86
Where;

\( IPW \) = injection pulse width, pore volume

\( RT \) = residence time, Pore volume,

\( \bar{u}_1 \) = 1st normalized moment, Pore volume.

### 6.4 Fate and Transport Modeling

A two-site adsorption/desorption model was adopted, which can be described by coupling instantaneous sorption (I) and kinetic sorption (II) with the advection-dispersion-sorption equation (Bales et al., 1991; McCaulou et al., 1994; Corapcioglu and Haridas 1985) as shown in eqn. 6-4 below.

\[
\theta \frac{\partial C}{\partial t} + \rho_b \left( \frac{\partial S^I}{\partial t} + \frac{\partial S^{II}}{\partial t} \right) = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}
\]  

(6-4)

Where;

\( \theta \) = porosity

\( C \) = HOP aqueous concentration in the aqueous, mg·L\(^{-1}\)

\( S^I \) = contaminant concentrations sorbed on instantaneous sites, mg·g\(^{-1}\)

\( S^{II} \) = contaminant concentrations sorbed on reversible kinetic sites, mg·g\(^{-1}\)

\( \rho_b \) = bulk density, g·cm\(^{-3}\)

\( t \) and \( x \) = time (min) and distance (cm), respectively

\( D \) = the dispersion coefficient, cm\(^2\) min\(^{-1}\)

\( v \) = the average linear flow velocity, cm·min\(^{-1}\)
Instantaneous sorption is represented by the sorption isotherm equation (Eqn 6-5a) where \( K^I \) is the equilibrium partition coefficient for the instantaneous sites (mg·L\(^{-1}\)). The model being used here utilizes linear relationships between the sorbed and aqueous phases rather than the non-linear Freundlich isotherms that was measured in the batch tests. However, because the column studies were not conducted under equilibrium conditions, the combination of linear instantaneous sorption and kinetic sorption is deemed appropriate. Reversible kinetic sorption was applied to describe contaminant absorption to and desorption from the absorbent (Eqn 6-5b), where \( k_{1}^{II} \) is first-order sorption rate coefficient of the kinetic sorption sites (min\(^{-1}\)), and \( k_{-1}^{II} \) is first order desorption rate coefficient of the kinetic sorption site (min\(^{-1}\)).

\[
\rho_b \frac{\partial S^I}{\partial t} = \theta \cdot K^I \frac{\partial C}{\partial t} \tag{6-5a}
\]

\[
\rho_b \frac{\partial S^{II}}{\partial t} = \theta \cdot k_{1}^{II} \cdot C - \rho_b \cdot k_{-1}^{II} \cdot S^{II} \tag{6-5b}
\]

The CXTFIT software package (Toride et al., 1995) was used to estimate breakthrough parameters associated with the two-site adsorption process. The governing transport equation is similar to that of the two-site model developed by Bales et al. (1991) with slight differences regarding the equilibrium and kinetic sites definitions, which are listed in eqn 6-6 below.

\[
\left(1 + \frac{f \rho_b K_d}{\theta}\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} - \frac{\alpha \rho_b}{\theta} \left[(1 - f)K_d C - S^{II}\right] - \frac{R_d}{\theta} + \frac{R_p}{\theta} \tag{6-6a}
\]

\[
\rho_b \frac{\partial S^I}{\partial t} = \theta \cdot f \cdot K_d \frac{\partial C}{\partial t} \tag{6-6b}
\]

\[
\rho_b \frac{\partial S^{II}}{\partial t} = \rho_b \cdot \alpha \cdot \left[(1 - f) \cdot K_d \cdot C - S^{II}\right] \tag{6-6c}
\]

Where;
\( K_d \) = the partition coefficient for sorption, L\(^3\)M\(^-1\)

\( \alpha \) = a first-order mass transfer rate, min\(^{-1}\)

\( f \) = the fraction of instantaneous sites

The two site adsorption model reduces to one-site fully kinetic adsorption model if \( f = 0 \) (only kinetic sites are present). Three dimensionless coefficients, retardation factor (\( R \)), mass transfer coefficient (\( \omega \)), and partition coefficient between equilibrium and kinetic sites (\( \beta \)) are defined to describe the inter-parameter relationship in CXTFIT (Torid et al., 1995).

\[
R = 1 + \frac{\rho_b \cdot K_d}{\theta} \quad (6-7a)
\]

\[
\beta = \frac{\theta + f \cdot \rho_b \cdot K_d}{\theta + \rho_b \cdot K_d} \quad (6-7b)
\]

\[
\omega = \frac{\alpha \cdot (1 - \beta) \cdot R \cdot L}{v} \quad (6-7c)
\]

\( R \), \( \beta \), and \( \omega \) can be estimated by fitting mathematical solutions of the theoretical transport models to experimental breakthrough curves through CXTFIT inverse modeling. Once \( R \), \( \beta \) and \( \omega \) are fitted, \( f \) can be calculated using eqn 6-8a (Toride et al. 1995) and sorption/desorption rate coefficients, \( k_1^{\text{II}} / k_1^{\text{I}} \) can be obtained from eqn 6-8b and 6-8c derived by Pang et al., 2002.

\[
f = \frac{\beta \cdot R - 1}{R - 1} \quad (6-8a)
\]

\[
k_1^{\text{II}} = \frac{\omega \cdot v}{L} \quad (6-8b)
\]

\[
k_1^{\text{I}} = \alpha = \frac{\omega \cdot v}{(1 - \beta)RL} \quad (6-8c)
\]

Where;
$L = \text{characteristic length, cm}$

6.5 Results and Discussion

6.5.1 Bromine Tracer Result

Br was used as a conservative tracer in this study to simulate the aqueous flow in the porous media. Figure 6-2 illustrates the normalized effluent concentration, $C / C_0$, versus the numbers of pore volumes treated. The MRFs and RTs obtained from temporal moment analysis are summarized in Table 6-1. As can be seen from Figure 6-1a, the bromide breakthrough curves (BTCs) were not axially symmetric and the time which took the BTCs to reach 100% was delayed. This phenomenon is often referred to as tailing and the effect increases with flow rate increasing. Because bromide has minimal sorption to the GAC, tailing in this case is the result of the flow rate which provided insufficient exposure time to ensure diffusion of bromide into the porous grains. In terms of residence time Br showed shorter RT (0.89 pore volume) under faster flow rate (10.2 ml min$^{-1}$), which is consistent with the finding showed in Figure 6-2a. The Br, which is a commonly used conservative tracer, exhibited good mass recovery fractions for all experimentally tested columns, with all MRFs higher than 90%, though not reaching the theoretical value of 100%. The sources of unaccounted mass might be due to sorption, dissolved bromide in the column, and dilution of bromide to below measurable levels. Compared to the quantity of TCE adsorbed, the comparatively small amount of Br adsorption can be ignored. The calculated value of the dispersion coefficient $D$ was optimized in CXTFIT using Br breakthrough data. Table 6-2 lists the corresponding dispersion coefficients over a range of flow rates. For different flow rates at constant CD concentrations, $D$ increased linearly with increasing flow rate (Table 6-2). This is consistent with the fact that $D$ is a function of flow velocity ($D = D_{\text{diffusion}} \cdot \tau + \alpha \cdot v$) when the aqueous diffusion is constant (Fetter, 1999). Linear
Figure 6-2a Breakthrough curve of Br under different flow rates

Figure 6-2b Breakthrough curve of Br for different CD concentrations
Table 6-1 Results of temporal moment analysis of conservative tracer and contaminant

<table>
<thead>
<tr>
<th>Flow rate (ml min⁻¹)</th>
<th>CD Conc (g L⁻¹)</th>
<th>Target chemical</th>
<th>Mass Recovery Fraction (MRF)</th>
<th>Residence Time (RT)</th>
<th>Pore volume</th>
</tr>
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<tr>
<td>10.2</td>
<td>50</td>
<td>Br</td>
<td>0.93</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TCE</td>
<td>0.63</td>
<td>23.91</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>50</td>
<td>Br</td>
<td>0.95</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TCE</td>
<td>0.61</td>
<td>29.94</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>Br</td>
<td>0.98</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TCE</td>
<td>0.55</td>
<td>45.27</td>
<td></td>
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<tr>
<td>4.0</td>
<td>20</td>
<td>Br</td>
<td>0.99</td>
<td>1.12</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>TCE</td>
<td>0.60</td>
<td>63.07</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>0</td>
<td>Br</td>
<td>0.99</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TCE</td>
<td>0.47</td>
<td>138.31</td>
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</tr>
</tbody>
</table>

Regression of the three 50g L⁻¹ CD column studies gave the dispersion equation as $D = 0.214 + 0.35 v$ ($R^2 = 0.999$). Unfortunately, there is no obvious trend in the calculated bromide dispersion coefficients for the column tests performed at various CD concentrations (0, 20, 50 g L⁻¹), but at the same velocity (4.0 ml L⁻¹).

Table 6-2 Dispersion coefficients under different flow rates and CD concentrations

<table>
<thead>
<tr>
<th>Flow velocity (ml/min)</th>
<th>10.2</th>
<th>4.0</th>
<th>1.0</th>
<th>4.0</th>
<th>4.0</th>
</tr>
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<tr>
<td>CD concentration (g·L⁻¹)</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Dispersion coefficient (cm²·min⁻¹)</td>
<td>11.88</td>
<td>4.422</td>
<td>0.421</td>
<td>4.645</td>
<td>3.075</td>
</tr>
</tbody>
</table>

The calculated value of the dispersion coefficient $D$ was optimized in CXTFIT using Br breakthrough data. Table 6-2 lists the corresponding dispersion coefficients over a range of flow rates. For different flow rates at constant CD concentrations, $D$ increased linearly with increasing flow rate (Table 6-2). This is consistent with the fact that $D$ is a function of flow velocity ($D = D_{diffusion} \cdot \tau + \alpha \cdot v$) when the aqueous diffusion is constant (Fetter, 1999). Linear regression of the three 50g L⁻¹ CD column studies gave the dispersion equation as $D = 0.214 + 0.35 v$ ($R^2 = 0.999$). Unfortunately, there is no obvious trend in the calculated bromide dispersion coefficients for the column tests performed at various CD concentrations (0, 20, 50 g L⁻¹), but at the same velocity (4.0 ml L⁻¹).
dispersion coefficients for the column tests performed at various CD concentrations (0, 20, 50 g/L), but at the same velocity (4.0 ml L⁻¹).

6.5.2 Effect of CD Concentration

In order to determine the effect of CD concentration on contaminant transport, column studies were conducted using a series of solutions of varying CD concentrations (0, 20, and 50 g·L⁻¹) but with constant TCE aqueous concentration and flow rate (4.0 ml min⁻¹). The results are shown in Figures 6-3a and 6-3b. Figure 6-3 depicts normalized TCE concentration versus time in pore-volumes. As can be seen from Figure 6-3a, TCE broke through earlier as CD concentration increased. This can be explained by the solubility enhancement of CD. To be more specific, the degree and elution time of TCE depend on the relative aqueous solubility and the affinity between adsorbates and the adsorbents; consequently, higher CD concentration would lead to early elution due to the solubility enhancements. Temporal moment analyses of the results were listed in Table 6-1, which quantified the effect of CD concentrations. There were apparently strong linear relationships between CD concentration and both retention time and mass recovery of the three column tests (RT = -0.78 C_CD + 62.3, R² = 0.99 and MRF = 0.0032 C_CD + 0.48, R² = 0.99).

To draw a more direct comparison on the basis of relative solubility for the varying CD concentrations, the time axis can be rescaled by multiplying by the apparent solubility enhancement factor. Figure 6-3b shows the results of this rescaling. Comparing the times at which tracers reach half their input concentration is often useful because the effects of non-ideal behaviors such as rate-limited dispersion and sorption are less pronounced. As shown in Figure 6-3b, TCE breakthrough curves exhibited similar scaled times at which they reach 50% of the input concentration, which is consistent with the batch test results presented in chapter 5.
The differences in the BTCs of the rescaled time showed the effects of non-equilibrium dispersion and sorption. As shown in Figure 6-3b, higher CD concentration led to earlier
appearance of TCE in the elution and delay in achieving full breakthrough. This can be explained as (1) the flow rate provided non-equilibrium condition such that TCE had insufficient time to fully interact with the GAC and (2) diffusion processes were slower as CD concentration increased due to the greater viscosity of the CD solutions, indicating that cyclodextrin increased the time needed for TCE to reach equilibration between GAC and liquid phases.

6.5.3 Effect of Flow Rate

![Figure 6-4. Breakthrough behavior of TCE under different flow rates](image)

The normalized effluent TCE concentration, $C / C_0$ versus the number of pore volumes under different flow rates is presented in Figure 6-4. The lowest flow rate, (1.0 ml·min$^{-1}$), illustrated a more symmetrical BTC, showing more ideal conditions were achieved under the longer exposure time provided at this flow rate. As the flow rate increased, the first appearance of TCE eluent was relatively earlier and exhibited relative greater delay in achieving full breakthrough, suggesting non-equilibrium processes are more significant at higher flow rates. To further
quantify the impact of flow rates on TCE sorption processes the 1-D calibrated model CXTFIT was used.

Figure 6-4 also shows the CXTFIT-simulated breakthrough curves for three flow rates which fit the experimental data well ($R^2 > 0.90$). Data were more scattered at later time intervals. This may be attributed to larger measurement errors in the GC/MS analysis at high concentrations. The dimensionless coefficients, (retardation factor ($R$), mass transfer coefficient ($\omega$), and partition coefficient between equilibrium and kinetic sites ($\beta$)) were obtained by CXTFIT optimization and other kinetic sorption parameters. The values of the constants $f_k^I$ and $k_{-1}^I$ were calculated from equation 6-9. Figure 6-5 illustrates the relationship between pore water velocity and chemical non-equilibrium parameters. As $v$ increased, $R$ was found to decrease. This is considered to be an indicator of non-equilibrium conditions (Pang, et al, 2002). This phenomenon can be explained in terms of retention time; a longer retention time at lower pore water velocity leads to a longer contact time, while shorter retention times may occur at higher superficial velocities. This relationship has been observed previously (Schulin et al., 1987; Ptacek and Gillham, 1992; Pang et al., 2002). The magnitude of $\beta$ and $\omega$ reflect the degree of chemical non-equilibrium (Pang et al., 2002). As shown in Figure 6-5, an inverse relationship between $v \sim \beta$ was found in this study, which can be explained by the definition of $\beta$. This finding is consistent with Toride et al.,(1995), who reported that only equilibrium sites exist when $\beta$ is equal to one (27) but conflicts with Pang et al.,(2002) who observed a positive trend between $v \sim \beta$ for the transport of metals.

The dimensionless mass transfer coefficient denoted by $\omega$, which functionally can be considered as the ratio of residence time ($L/v$) to reaction time ($1/(\alpha \cdot (1 - \beta) \cdot R)$). In this study,
ω and velocity were found to be inversely related. This is expected because when velocity increased sorption processes had relatively less time to act and the degree of mass transfer was far from equilibrium. In this study, \( f \) was found to be inversely related to \( v \), which is consistent

Figure 6-5. Relationship between pore velocity and chemical nonequilibrium parameters
with the definition of $f$. Since a larger pore velocity enhances mass transport and drives more chemical toward the surface of adsorbent media (Akratanakul et al., 1983; Pang et al., 2002), as expected, the sorption and desorption coefficients $k_{1}^{I}$ and $k_{-1}^{I}$ both increased with the increase of $v$.

**6.5.4 Mixtures Effects**

The breakthrough behavior of a HOP mixture in CD solution was evaluated by dissolving a set of HOPs (TCE, PCE, ethylbenzene, $o$-xylene, and naphthalene) in a 50 g·L$^{-1}$ CD solution and performing column experiments. The normalized effluent concentrations, $C/C_0$, and the number of pore volumes of the tested compounds are presented in Figure 6-6. TCE was found to breakthrough earlier than the other compounds. As can be seen in Figure 6-6, these three compounds showed distinct breakthrough times, with ethylbenzene first, then PCE and finally $o$-xylene. This result is attributed to the solubility enhancement effect of CD. In order to get a full understanding of the breakthrough behavior of the tested mixture, the value of solubility enhancement factor and apparent solubility for 50 g·L$^{-1}$ CD solutions were calculated based on eqn 4-10 and 5-8 and results are summarized in Table 6-3. The detailed parameters needed to calculate apparent solubility of naphthalene in this tested CD concentration is currently not available, therefore $S_{A(Naphthalene)}$ was estimated based on the values reported in McCray et al. (2000). Due to the solubility enhancement of CD, the apparent solubility of the tested compounds showed an order of TCE > Ethylbenzene > PCE > $o$-xylene > naphthalene (Table 6-3). As a result, the retardation factor should be in the opposite order, TCE < Ethylbenzene < PCE < $o$-xylene < naphthalene, which is consistent with the breakthrough behavior illustrated in Figure 6-6.
### TABLE 6-3  Solubility in water and CD solution of tested compounds

<table>
<thead>
<tr>
<th>Parameters</th>
<th>TCE</th>
<th>PCE</th>
<th>Ethylbenzene</th>
<th>o-xylene</th>
<th>Naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K'_{AI2}$</td>
<td>0.088</td>
<td>0.059</td>
<td>0.018</td>
<td>0.022</td>
<td>NA</td>
</tr>
<tr>
<td>$K_{AI2}$</td>
<td>0.441</td>
<td>0.682</td>
<td>0.308</td>
<td>0.210</td>
<td>NA</td>
</tr>
<tr>
<td>$E$</td>
<td>5.043</td>
<td>11.65</td>
<td>16.86</td>
<td>9.465</td>
<td>40†</td>
</tr>
<tr>
<td>$S_w$ (mg·L⁻¹)*</td>
<td>1150</td>
<td>150</td>
<td>153</td>
<td>152</td>
<td>31</td>
</tr>
<tr>
<td>$S$ (mg·L⁻¹)</td>
<td>5799</td>
<td>1747</td>
<td>2580</td>
<td>1439</td>
<td>1240</td>
</tr>
</tbody>
</table>

NA = not available

† Gao et al (2009)

† Estimated from values reported in McCray et al. (2000)

*Solubility in water; McCray et al. (2000)

---

**Figure 6-6. Breakthrough behavior of mixture in the presence of CD**
6.6 Conclusions

In this chapter the breakthrough behavior of trichloroethylene (TCE) in cyclodextrin solutions in columns packed with Norit C GRAN activated carbon were assessed. The effects of two variables including CD concentration (0, 20, 50 g L⁻¹) and flow rate (1-10 ml·min⁻¹) on HOP transport in CD solutions were investigated.

Comparison of original breakthrough curve under different CD concentrations to the solubility-enhancement-rescaled ones showed (1) all 3 curves exhibited similar scaled times at which they reach 50% of the input concentration, which is consistent with the batch test results presented in chapter 5, and (2) cyclodextrin increased the time needed for TCE to reach equilibration between GAC and liquid phases. Breakthrough curve under low flow rate illustrated a more symmetrical shape; as the flow rate increased, the first appearance of TCE eluent was relatively earlier and exhibited relative greater delay in achieving full breakthrough, suggesting non-equilibrium processes are more significant at higher flow rates. The breakthrough behavior of TCE, PCE, ethylbenzene, o-xylene and naphthalene was found to depend on the apparent solubility in HPCD solutions and the one with larger solubility was found to breakthrough earlier.

6.7 References


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CHAPTER 7. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The purpose of research described in this dissertation was to examine the separation of hydrophobic organic pollutants (HOPs) from post-flush cyclodextrin (CD) solutions. To that end, experimental and theoretical studies were conducted into the partitioning behavior of HOPs in air-water-CD and granular activated carbon (GAC)-water-CD systems. The following observations have been gleaned from these studies:

(1) In aqueous CD solutions, Henry’s constants decreased by a power law relationship with increasing CD concentration due to the solubility enhancement caused by CD molecules.

(2) In batch studies, the temperature dependence of air-water partitioning coefficient with the presence of CD was well described by the van’t Hoff equation for all HOPs, including trichloroethylene (TCE), perchloroethylene (PCE) and benzene, toluene, ethylbenzene and o-xylene (BTEX).

(3) The CD-water partition coefficients of HOPs obtained from a three-phase equilibrium model decreased linearly with increasing temperature.

(4) The fraction of HOP mass present in CD-complexes proportionally rise as CD concentration increased; as temperature increases, the HOP mass fraction present in CD-complexes decreases, with most of the displaced mass moving to the air phase.

(5) In aqueous HPCD solutions, the adsorption capacity of GAC decreased with increasing CD concentration due to an apparent solubility enhancement, resulting in a trend of decreasing fraction adsorbed in GAC phase.

(6) Statistical analysis showed that there was no significant difference between the rescaled traditional Freundlich isotherm derived from CD solutions and the one in CD-free solution.
(7) $K_f$ decreased as HPCD concentration increase and n maintain constant at different CD concentration. There was a linear relationship between the natural logarithms of $K_f$ and solubility enhancement factors with coefficient of 0.99.

(8) In GAC column studies, TCE in different HPCD solutions exhibited similar scaled times at which the effluent reached 50% of the input concentration; CD increased the time needed for TCE to reach equilibration between GAC and liquid phases.

(9) Also in column studies, TCE solutions flowing at higher experimentally tested flow rates had insufficient time to interact with GAC such that non-equilibrium processes were more significant at higher flow rates.

(10) The breakthrough behavior of TCE, PCE, ethylbenzene, o-xylene and naphthalene in GAC column studies was found to depend on the apparent solubility in HPCD solutions

7.2 Future Research Directions

It is of obvious interest to examine partitioning phenomena at environmentally relevant temperatures. Unfortunately, we were unable to obtain stable incubation temperatures below 35°C using our particular apparatus. By coupling a cooler incubator with GC/MS/CTC autosampler, Henry’s law constants of HOPs in CD solutions could be obtained over a larger temperature range. In addition, studies have been performed on Henry’s law constants and adsorption isotherm determination of several HOPs, but in the application of air stripper and adsorption to wastewater treatment, mixtures of HOPs are generally encountered. Using a greater diversity of HOPs and higher concentrations, sufficient quantities of HOP molecules could be studied in CD solutions to determine competition effects, as well as determine a more extensive mass distribution of HOPs among phases in complex systems. Combining the
partitioning behavior of single solute and multi-solute systems would be informative and practically applicable from the perspective of treatment of HOPs in the real world.
APPENDIX
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VITA

The author was born in Shandong, China, in April, 1977. She earned the degree of Bachelor of Science from the Department of Chemistry at Qingdao University in 2001, and then she went to the Graduate School of Beijing Institute of Technology (BIT) majoring in environmental engineering from 2001 to 2004. She received a Master of Engineering degree in environmental engineering from BIT in 2004. From May, 2004, to December, 2004, she worked as an environmental engineer at Beijing SPC Environmental Protection Tech Engineering Co., Ltd, P.R. China. In January, 2005 the author joined the School of Renewable Natural Resources at Louisiana State University (LSU) for a master’s degree which she received in 2007. In May 2007 she started work toward obtaining a doctoral degree in Civil Engineering Department at LSU and is due to receive it in December of 2010.