METHODS FOR SCALING AND COMPARING ADSORPTION DATASETS

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METHODS FOR SCALING AND COMPARING ADSORPTION DATASETS

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A Thesis

Submitted to

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Requirements for the

Degree of

Master of Science

Auburn, Alabama
August 9, 2008

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Date of Graduation

THESIS ABSTRACT

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Master of Science, August 9, 2008
(B.S., University of Mississippi, 2006)

65 Typed Pages

Directed by Mark O. Barnett

The presence of reactive groundwater contaminants are a great concern to many government agencies and private entities. The fate and transport of these contaminants is determined by their interactions with subsurface solids and hence a thorough understanding of these processes is necessary for the remediation of contaminated sites. There is an abundance of adsorption literature; however, these studies vary in their goals and methods. Some studies are general in nature, dealing with the general chemistry of adsorption in a well-controlled laboratory setting while others examine a specific problem at a contaminated site, using the soils and conditions at the site. This inherent difference, along with inadequate reporting of experimental conditions, makes it difficult to take information from one study and compare it confidently to others. Proper comparisons are an important part of studying these systems. Furthermore, developing predictive reactive-transport models requires the ability to scale the reactions to various systems.

As models capable of predicting the fate and transport of groundwater contaminants are developed, the need to compare adsorption data in a reliable manner is important. In this thesis, various approaches for comparing adsorption data were examined to determine the best method for designing and analyzing the results of adsorption experiments. The interactions of arsenate and goethite were examined as a representative system although results can be extended to other systems. A study of model-generated data was first executed to examine the basic theoretical principles of dataset comparison. These principles were then tested on a suite of experimental data from our laboratory and from the literature.

The results indicated that the most important factor in the comparison of sorption datasets is the total adsorbate-adsorbent ratio (e.g. mol As/mol Fe). If this value is too low, the system will be limited only by the amount of adsorbate present and accurate comparisons between datasets cannot be made. Additionally, it was found that normalization techniques can have a marked effect on comparisons, especially between systems with differing adsorbent types (i.e. natural and synthetic goethite). It is nearly always better to use the specific surface area of the adsorbent as a scaling parameter rather than the reactive mass of the adsorbent (in this case, Fe content). The incorporation of these techniques will improve the methods for scaling and comparing adsorption data in future studies.

ACKNOWLEDGEMENTS

The author would like to acknowledge the excellent instruction, support, and guidance of his advisor, Dr. Mark Barnett. Additional thanks to Dr. Dongye Zhao and Dr. T. Prabhakar Clement for their knowledge and support during the author’s term at Auburn University. The author would like to thank Jinling Zhuang for his technical assistance and training in the environmental laboratory at Auburn University. This work was supported by an ERSP research project from the Office of Science (BER), U.S. Department of Energy Grant no. DE-FG02-06ER64213.

Style manual or journal followed: Auburn University Graduate School: Guide to Preparation and Submission of Theses and Dissertations.

Computer software used: Microsoft Office 2003: Excel, Word; EndNote; VisualMINTEQ

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

INTRODUCTION

1.1 Problem Statement

The Department of Energy, along with many other public and private entities, are interested in the fate and transport of groundwater contaminants including metals, radio-nuclides, and chlorinated solvents. The interactions of these groundwater contaminants with subsurface solids are complex and as such are the subject of a wide variety of studies. Many research projects have studied and reported these interactions and processes in the laboratory. However, extrapolating these results to the field scale in order to predict the fate of the contaminants has been met with only moderate success. The ability to make reliable predictions regarding reactive contaminants will be beneficial in making remediation decisions and assessing risks to the public.

One of the first and most basic steps in improving the ability to scale subsurface interactions is establishing a method to compare experimental datasets. The work that has been completed to study groundwater contaminant reactions has utilized a variety of experimental conditions, soils, sediments, and overall approaches to their work. These differences create a need for a method that enables researchers and practitioners to normalize their data and compare them with other data from other experiments. The ability to compare data is dependent on the ability to identify the most important governing factors in the reactions, the parameters on which the reaction scale, and the experimental conditions which affect the reactions. Previous researchers have attempted this as needed for their work. However, no consensus has been reached and no standard set for the method one should follow to properly normalize and compare these subsurface reactions.

1.2 Objective

The primary objective of this work is to improve the ability to make reliable predictions of the fate and reactive transport of groundwater contaminants in field-scale applications. A highly toxic oxyanion, arsenate [As (V)], is used throughout this research as a representative contaminant. Its adsorption reactions with iron oxyhydroxides, specifically goethite, will be used as a means to thoroughly study the scaling of subsurface interactions. These scaling behaviors were investigated through a series of theoretical calculations, a review of previous literature, and new experiments. The results of adsorption studies were normalized and compared in many different manners in order to get to the root of the scaling issues.

1.3 Organization

This report is organized according to the guidelines for a publication-style thesis as outlined in the *Guide to Preparation and Submission of Theses and Dissertations* by the Auburn University Graduate School. Chapter 2 contains a review of the relevant literature, Chapter 3 is a draft manuscript fully covering the research completed for this thesis, and Chapter 4 contains conclusions drawn from this research. Additionally, samples of each of the calculations performed in this research were also completed and are attached as Appendix A.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background Information

The presence of reactive groundwater contaminants is a great concern to many government agencies and private entities. These contaminants include: solvents, heavy metals, organic compounds, radio-nuclides, and many more. The metalloid oxyanions arsenate, As(V), and arsenite, As(III), have received special attention due to their worldwide presence and highly toxic nature. Arsenic-contaminated sites present a danger to the environment and to the public that access the groundwater contained there.

2.1.1 Sources of Contamination

Arsenic is present in many parts of the world, most notably, in West Bengal, Bangladesh, and the western United States, but also in South America and other locations worldwide (Smedley and Kinniburgh 2002). Many of these locations are affected due to the presence of natural arsenic minerals and the conditions that trigger their release into groundwater. The development of high pH (<8.5) conditions and reducing conditions at near-neutral pH's have been shown to mobilize As even in locations with modest amounts of As in aquifer materials (Smedley and Kinniburgh 2002). The presence of competitive ions can also affect the interactions between As and subsurface minerals significantly and either prevent the uptake of As or trigger its release into the groundwater. There are also many anthropogenic sources of arsenic such as industrial processes located around the globe (Han, Su et al. 2003). Arsenic finds it way into groundwater through its use in metal mining, processing, and smelting operations (Smith, Naidu et al. 1998) and its use as a pesticide for both wood preservation and agricultural applications (Welch, Westjohn et al. 2000).

2.1.2 Health Concerns

The primary means of arsenic exposure to humans is through the ingestion of water, food, and, for children, contaminated soil. A typical exposure rate is 50 μg/day of total arsenic and 3.5 μg of that is inorganic arsenic species which is considerably more toxic (ATSDR 2007). The effects of an acute exposure to arsenic can range from minor pain, stomach irritation, fatigue, shortness of breath and nerve damage for low level exposure (300-30,000 μg/L in water) to death for higher level exposures (60,000 μg/L in water) (ATSDR 2007). The damage from chronic exposure to arsenic at low levels is also a major concern. Characteristics of long-term toxic exposure to arsenic include skin lesions, warts on the hands and feet, skin cancer, and blood vessel changes. The prolonged exposure to arsenic can also increase the risk for cancer of the liver, bladder, and lungs (ATSDR 2007).

2.1.3 Treatment Technology and Methods

The EPA has recognized several technologies for the treatment of As-contaminated water and they are summarized here (USEPA 2000). Similar to traditional water treatment processes, coagulation with ferric or aluminum salts is often utilized to remove dissolved and suspended arsenic. These processes have been studied extensively and are well understood. This technology is often paired with an oxidation step when treating water containing arsenite, As(III), due to the enhanced coagulation removal of the oxidized form, arsenate [As(V)]. Coagulation is followed by a settling step or microfiltration to remove the flocs which have formed (USEPA 2000).

Ion exchange is another, more expensive, treatment method for arsenic-contaminated waters. This technology employs a synthetic resin containing an initial ion which is removed and replaced with the arsenate or arsenite ion. The resins can be regenerated for repeated use, however, their capacity wanes and fouling occurs reducing the resins' effectiveness. Also, the regenerate solution must be disposed of, which adds more expense. Selective membrane technology is also employed for arsenic removal but faces the same expense and fouling issues as ion exchange resins. These technologies include reverse osmosis (RO) and electrodialysis reversal (EDR) (USEPA 2000).

Other important technologies aim to exploit the interactions of arsenic and iron oxides as a means of water treatment. This includes the study of arsenic removal by adsorption with iron oxide-coated sand, goethite-coated sand, and granular ferric oxide in a fixed bed apparatus.

2.2 Iron Oxide Interactions in the Subsurface

2.2.1 Presence of Iron Oxides in the Subsurface

The focus on iron oxides, an important factor that controls the mobility of As in the subsurface, is due to its high sorption capacity and its presence in soils around the world. In fact, much of the motivation for present modeling work is the recognition that amorphous iron oxides are universally prevalent in clays, soils and sediments; thus their interaction with groundwater constituents must be well understood for reactive transport to be modeled effectively (Jenne 1968; Pierce and Moore 1982). The presence of amorphous iron oxides, including hydrous ferric oxide (HFO) and ferrihydrite, as discrete minerals and as coatings on soil and sediment has been thoroughly noted in the literature (Buffle 1990; Wilkie and Hering 1996; Dixit and Hering 2003). Iron oxide-coated sand has been recognized as a significant presence in the subsurface environment and has been labeled as a dominant factor controlling As adsorption behavior (Edwards and Benjamin 1989; Scheidegger, Borkovec et al. 1993; Hiemstra and Van Riemsdijk 1999; Lombi, Wenzel et al. 1999; O'Reilly, Strawn et al. 2001; Cheng, Barnett et al. 2004; Swartz, Blute et al. 2004; Ying and Axe 2005). The formation and transformation of iron oxides has also been a focus of some attention. In addition to amorphous forms, crystalline forms of iron oxide, including hematite and goethite, are common in soil (Buffle 1990). Iron oxide minerals often precipitate at oxic-anoxic boundaries and form amorphous ferrihydrite; over time these minerals transform into crystalline structures such as goethite (Dixit and Hering 2003). Due to the fact that goethite is widespread in the subsurface (Schwertmann and Cornell 1991), much work has been devoted towards the study of its interactions with groundwater contaminants (Grossl and Sparks 1995; Zhao and Stanforth 2001; Dixit and Hering 2003; Lakshmipathiraj, Narasimhan et al. 2006; Gimenez, Martinez et al. 2007).

2.2.2 Arsenic Interactions with Iron Oxides

The work that has been done to elucidate the interactions of arsenic and iron oxides in the subsurface is spread out over many decades and many areas of focus. There are studies that describe arsenic’s interactions with amorphous iron oxide forms (Pierce and Moore 1980; Pierce and Moore 1982; Fuller, Davis et al. 1993; Waychunas, Rea et al.

1993; Waychunas, Fuller et al. 1996; Wilkie and Hering 1996; Raven, Jain et al. 1998; Goldberg and Johnston 2001; Goldberg 2002; Dixit and Hering 2003; Zeng, Fisher et al. 2008) as well as crystalline forms (Hingston, Posner et al. 1971; Lumsdon, Fraser et al. 1984; Fendorf, Eick et al. 1997; Matis, Zouboulis et al. 1997; Hiemstra and Van Riemsdijk 1999; Grafe, Eick et al. 2001; Zhao and Stanforth 2001; Dixit and Hering 2003; Lakshmipathiraj, Narasimhan et al. 2006; Gimenez, Martinez et al. 2007; Manasse and Viti 2007; Stachowicz, Hiemstra et al. 2007). In addition, much of this work has been well reviewed and summarized by Smith et al. (1998) and Sadiq (1997).

Arsenic is present primarily as the oxyanions arsenate, As (V), and arsenite, As(III), in groundwater. Table 2.1 shows reactions and constants for the aqueous species of arsenate and arsenite (Dixit and Hering 2003). These are multiprotic acids with pKa's of 2.3, 6.8, and 11.6 for arsenate species H_3AsO_4, $H_2AsO_4^-$, and $HAsO_4^{2-}$, respectively. The pKa's for the arsenite species H_3AsO_3 and $H_2AsO_3^-$ are 9.2 and 12.7, respectively (Goldberg and Johnston 2001). Arsenic is present as arsenate, As (V), in oxidizing conditions and as arsenite, As (III), in reducing conditions. Figure 2.1 shows the redox potential and dominant species at various pH's (Smedley and Kinniburgh 2002). Much of the focus on arsenic chemistry is placed on its inorganic complexes due to the higher toxicity of the inorganic species and the low propensity for arsenic to form organic complexes in soil (Sadiq 1997). Instead, the focus concerning arsenic complexation is on the reactions with iron oxides.

TABLE 2.1: Reactions and constants for the aqueous species of arsenate, As (V), and arsenite, As (III). (Dixit and Hering 2003)

As (V) Protonation and Complexation	**log K**
$AsO_4^{3-} + 3H^+ = H_3AsO_4$	20.60
$AsO_4^{3-} + 2H^+ = H_2AsO_4^-$	18.35
$AsO_4^{3-} + H^+ = HAsO_4^{2-}$	11.60
As (III) Protonation and Complexation	
$AsO_3^{3-} + 3H^+ = H_3AsO_3$	34.74
$AsO_3^{3-} + 2H^+ = H_2AsO_3^-$	25.52
$AsO_3^{3-} + H^+ = HAsO_3^{2-}$	13.41

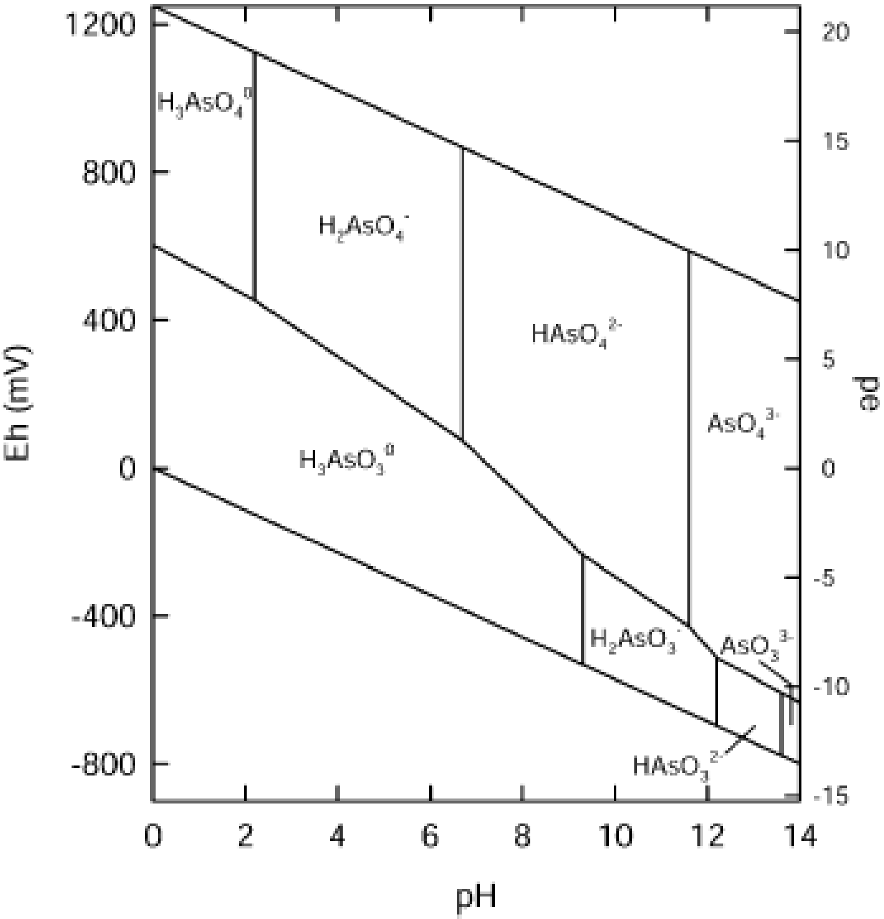

FIGURE 2.1: Eh-pH diagram for aqueous As species in the system As- O_2- H_2O at 25°C and 1 bar total pressure. (Smedley and Kinniburgh 2002)

Iron oxides, amorphous and crystalline, have a high affinity for arsenic and are able to bind the oxyanions in large quantities. Studies have shown that adsorption is the primary means of arsenic uptake over coprecipitation (Lumsdon, Fraser et al. 1984; Fuller, Davis et al. 1993; Waychunas, Rea et al. 1993; Sadiq 1997) and that arsenate is adsorbed more strongly than arsenite (Wilkie and Hering 1996). Arsenate has been shown to form inner-sphere complexes on amorphous and crystalline iron oxides (Fendorf, Eick et al. 1997; Goldberg and Johnston 2001). These complexes are monodentate at low arsenic loadings and bidentate at high arsenic loadings (Waychunas, Rea et al. 1993). Arsenite forms both inner and outer-sphere complexes (Goldberg and Johnston 2001). The formation of these complexes has been confirmed by numerous spectroscopic studies using various techniques, including wide angle X-ray scattering (WAXS), extended X-ray absorption fine structure (EXAFS), and infrared spectroscopy (Lumsdon, Fraser et al. 1984; Waychunas, Rea et al. 1993; Waychunas, Fuller et al. 1996; Fendorf, Eick et al. 1997). The reactions and constants shown in Table 2.2 have been used to model the interactions of arsenate and arsenite with goethite using a surface complexation model (Liger, Charlet et al. 1999; Dixit and Hering 2003).

TABLE 2.2: Reactions and constants for surface complexation reactions involving arsenic and goethite. (Liger, Charlet et al. 1999; Dixit and Hering 2003)

Surface Hydroxyl Protonation	**log K**
$>FeOH + H^+ = >FeOH_2^+$	7.47†
$>FeOH - H^+ = >FeO^-$	-9.51†
† Liger et al. (1999)	
As (V) Protonation and Complexation	
$>FeOH + AsO4^{3-} + 3H^+ - H_2O = >FeH_2AsO_4$	31.00
$>FeOH + AsO_4^{3-} + 2H^+ - H_2O = >FeHAsO_4^-$	26.81
$>FeOH + AsO_4^{3-} + H^+ - H_2O = >FeAsO_4^{2-}$	20.22
As (III) Protonation and Complexation	
$>FeOH + AsO_3^{3-} + 3H^+ - H_2O = >FeH_2AsO_3$	39.93
$>FeOH + AsO_3^{3-} + 2H^+ - H_2O = >FeH_2AsO_3^-$	32.40

The widespread presence of goethite in the subsurface environment (Schwertmann and Cornell 1991; Dixit and Hering 2003) and its particular promise as an adsorbent (Lakshmipathiraj, Narasimhan et al. 2006) has led many to study what governs its interactions with arsenic. Arsenic surface complexes on crystalline oxides have been shown to be more ordered than their counterparts on amorphous surfaces (Waychunas, Rea et al. 1993). The adsorption of arsenic is affected to various degrees by ionic strength, pH, and coexisting ions. McBride (1997) studied the ionic strength effect and found that the type of complex is an important factor in ionic strength dependence. Inner-sphere complex formation increases with or is unaffected by ionic strength, while outer-sphere complex formation decreases with increases in ionic strength (McBride 1997). The pH dependence of arsenic adsorption varies based on the oxidation state of the adsorbing ion. Figure 2.2 shows how the adorption of arsenate and arsenite onto goethite varies with pH. Arsenate adsorbs significantly across a wide range of pH values but reaches maximum adsorption at low pH, 4-5 (Manning and Goldberg 1996; Dixit and Hering 2003; Lakshmipathiraj, Narasimhan et al. 2006). Arsenite adsorption is at a maximum and fairly constant in the range of pH values from 5-9 (Wilkie and Hering 1996; Dixit and Hering 2003; Lakshmipathiraj, Narasimhan et al. 2006). Arsenic adsorption can also be affected significantly by the presence of ions that compete for surface sites. Phosphate is chemically very similar to arsenate and has a large effect on its interactions with goethite and other iron oxides. Thus there have been many studies to elucidate this effect (Hingston, Posner et al. 1971; Jain and Loeppert 2000; Zhao and Stanforth 2001; Dixit and Hering 2003; Zeng, Fisher et al. 2008). Competition from phosphate will decrease the adsorption of arsenate and arsenite, with arsenite being affected to a greater extent (Jain and Loeppert 2000; Dixit and Hering 2003). However, the order and duration of the anions' exposure to the surface affects the adsorption behavior. Hongshao and Stansford (2001) found that arsenate and phosphate adsorb equally when added simultaneously, but differently when the addition was staggered one way or the other.

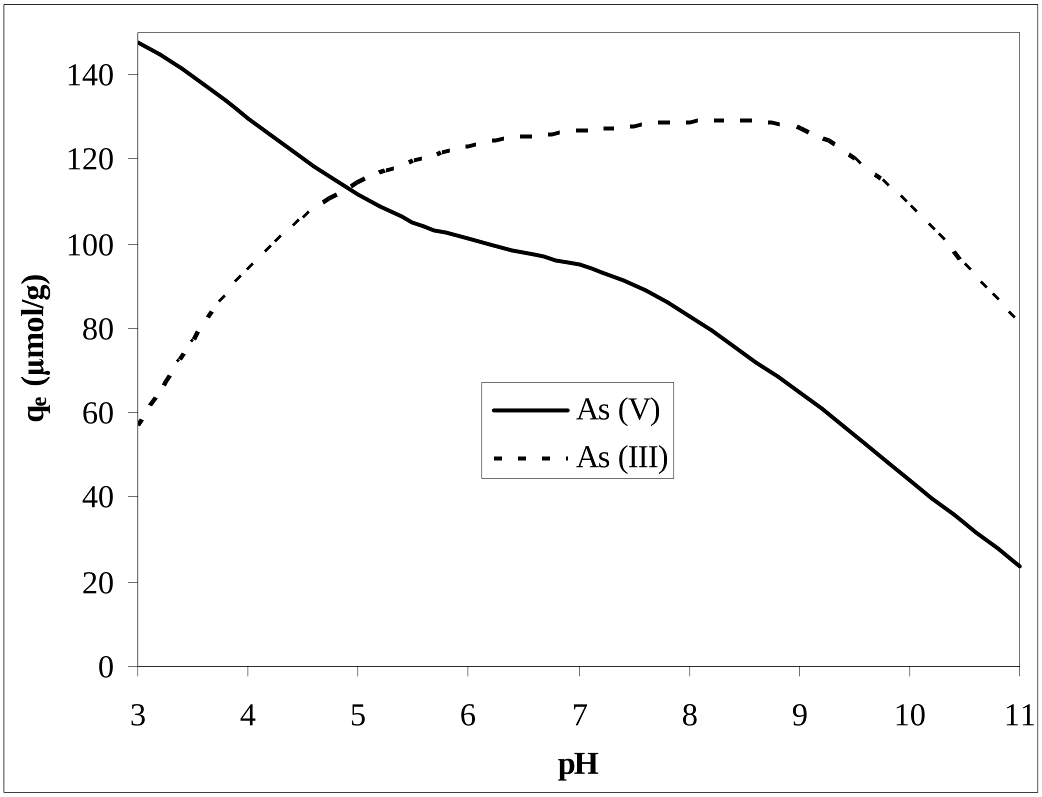

FIGURE 2.2: Model-generated adsorption edges for the adsorption of arsenic on goethite using the constants given in Tables 1 & 2. I=0.01M; C_T(As)=100µM; 0.5 g L^{-1} goethite. (Dixit and Hering 2003)

2.3 Status of Adsorption-Scaling Literature

There is an abundance of literature concerning the adsorption of groundwater contaminants onto iron oxides. These studies vary in their goals, determined by the funding agency, and this affects the way the study is completed. The differences and deficiencies in adsorption experimentation has been well summarized by E.A. Jenne (Jenne 1998). Some studies are general in nature, dealing with the chemistry in a well-controlled laboratory setting while others attack a specific problem at a contaminated site, using the soils and conditions at the site in their work. This inherent difference, along with inadequate reporting of experimental conditions, has led to a situation in which it is difficult to take information from one study and apply it confidently to others. Developing predictive reactive-transport models requires the ability to scale the reactions to various systems. The first step in identifying scaling parameters is being able to compare adsorption data from different systems.

2.3.1 Typical Study Details

Designing experiments for the laboratory that reflect field conditions can be difficult. Therefore, many adsorption studies have adjusted parameters such as solid-solution ratio to facilitate their laboratory limitations. In the field, there are often high solid-solution ratios and low adsorbate-adsorbent ratios (Wilkie and Hering 1996). These conditions make analysis in the laboratory and comparisons in the literature difficult due to the small amount of solution and low level of contaminants. Additionally, care must be taken when deviating from field conditions because some deviations may affect the mechanisms of the reactions being studied. Reports in the literature have indicated that different complexes are formed at low adsorbate-adsorbent ratios than at high ratios. For example, monodentate complexes are formed at low arsenic loadings while bidentate complexes are formed at higher arsenic loadings (Waychunas, Rea et al. 1993; Wilkie and Hering 1996). Despite its importance, the adsorbate-adsorbent ratio has been used as a key parameter for comparison in very few studies. Dixit and Hering (2003) used the ratio as a basis for comparing pH edges and determining crossover pH. Similarly, Wilkie and Hering (1996) compared data with identical chemical conditions recognizing the importance of having similar adsorbate-adsorbent ratios when adsorption is near 100%. Wilkie and Hering (1996) also noted the inadequacy of pH control and parameter reporting in previously published work.

2.3.2 Normalization and Plotting Techniques

As is the case with the scaling of experimental conditions between laboratory and field settings, little effort has been directed at properly normalizing the results of adsorption experiments for comparison. Most studies that use comparisons do not normalize the results at all or normalize only to the mass of the adsorbent. This technique often produces results that appear sufficient and prevents further examination to determine a more accurate technique. However, the mass of adsorbent is not necessarily directly related to the reactive capacity. Some published results employ a different technique and indicate that surface area may be a better parameter with which to normalize adsorption data (Pablan, Turner et al. 1998; Gimenez, Martinez et al. 2007). Normalization to the surface area is not common in the literature. Success with this normalization technique indicates that the amount of sorption sites on a particular adsorbent surface is more related to the surface area than the mass of the sorbent. Pablan et al. (1998) suggests that an effective surface area, a portion of the overall surface area, exists and could be a useful parameter in predicting sorption in various surfaces. Furthermore, a recent study of uranium adsorption to iron oxide-coated sand has concluded that surface area may be a better normalization parameter than iron content (Logananthan 2008, to be submitted). Proper normalization along with proper plotting techniques could aid significantly in comparisons between systems with different adsorbents.

Proper plotting technique can make comparisons between adsorption datasets easier. Plots of log K_D have been shown to be less sensitive to the solids concentration and thus relatively independent of solid-solution ratio (Jenne 1998; Pablan, Turner et al.

1998). Still, most comparisons are made using the traditional sigmoidal plots of % adsorbed and q_e (normalized or not). Jenne (1998) noted the difficulty in comparing data plotted this way due to the sensitivity to metal and solids concentration. If data are compared in sigmoidal plots, the experimental systems must be identical which is very tough to achieve. Thus, the literature contains comparisons which are accompanied by rationalizations and explanations to account for the differences that exist.

2.4 Importance for the Development of Predictive Models

The lack of the ability to adequately scale adsorption reactions from laboratory to field-scale is a major concern to reactive transport modelers and must be overcome. The ability to predict the fate and transport of harmful groundwater contaminants with minimal laboratory experiments, scaling the results to the field conditions, and plugging those parameters into model is a primary aim of many industries and government agencies who confront groundwater contamination. A reliable model will save time, money, and human resources enabling a much more efficient cleanup of the world's contaminated sites. The literature contains abundant information on the chemistry of groundwater contaminant interactions with subsurface solids, yet very little useful information on how to apply the chemistry to solve problems. The first step in being able to extrapolate adsorption data is to identify the factors which govern the scaling of these reactions and processes. This step is crucial and is largely missing in previous work.

CHAPTER THREE

METHODS FOR SCALING AND COMPARING ADSORPTION DATASETS

3.1 Abstract

As models capable of predicting the fate and transport of groundwater contaminants are constructed, the need to compare adsorption data in a reliable manner is important. In this work, various approaches for comparing adsorption data were studied to determine the best method for designing and analyzing the results of adsorption experiments. The interactions of arsenate and goethite were examined as a representative system. A study of simulated data was first executed to examine the basic principles of dataset comparison. These principles were then tested on a suite of experimental data, both new and from the literature. The most important factor in the comparison of sorption datasets was found to be the total adsorbate-adsorbent ratio. If this value is too low, the system will be limited only by the amount of adsorbate present and accurate comparisons cannot be made. Additionally, it was found that normalization techniques can have a marked effect on comparisons, especially between systems with differing adsorbent types (i.e. natural and synthetic goethite). It is nearly always better to use the specific surface area of the adsorbent as a scaling parameter rather than the reactive mass of the adsorbent (in this case, Fe content). The incorporation of these methods and techniques will improve the methods of comparing adsorption data in future studies.

3.2 Introduction

The presence of reactive groundwater contaminants is a great concern to many government agencies and private entities. These contaminants include solvents, heavy metals, organic compounds, and radionuclides. The metalloid oxyanions arsenate, As(V), and arsenite, As(III), have received special attention due to their worldwide presence and highly toxic nature. Arsenic-contaminated sites present a danger to the public and the environment.

Arsenic is present in many parts of the world including, most notably, West Bengal, Bangladesh, and the western United States, but also South America and other locations worldwide (Smedley and Kinniburgh 2002). Many of these locations are affected due to the elevated presence of naturally occuring arsenic and the conditions that trigger their release into groundwater. The development of high pH (<8.5) conditions and reducing conditions at near-neutral pH's have been shown to mobilize As, even in locations with modest amounts of As in aquifer materials (Smedley and Kinniburgh 2002). Modeling the reactive transport of arsenic is of utmost importance and relies on the ability to predict the interactions of arsenic with major subsurface constituents.

The focus on iron oxides as an important factor in the mobility of As and other contaminants in the subsurface is due both to its abundant presence in soils and sediments around the world and its natural affinity for As. In fact, much of the motivation for the present modeling work is the recognition that amorphous and crystalline iron oxides are universally prevalent in clays, soils and sediments; thus their interaction with groundwater constituents must be well understood (Jenne 1968; Pierce and Moore 1982). The presence of amorphous iron oxides, including hydrous ferric oxide (HFO) or ferrihyrdite, as discrete minerals and as coatings on soil and sediment has been widely reported in the literature (Buffle 1990; Wilkie and Hering 1996; Dixit and Hering 2003). Iron oxide coating on host minerals have also been recognized as a significant presence in the subsurface environment and labeled as a dominant factor controlling As adsorption (Edwards and Benjamin 1989; Scheidegger, Borkovec et al. 1993; Hiemstra and Van Riemsdijk 1999; Lombi, Wenzel et al. 1999; O'Reilly, Strawn et al. 2001; Cheng, Barnett et al. 2004; Swartz, Blute et al. 2004; Ying and Axe 2005) In addition to amorphous forms, crystalline forms of iron oxide, including hematite and goethite, are common in soil (Buffle 1990). Iron oxide minerals often precipitate at oxic-anoxic boundaries and form amorphous ferrihydrite; over time these minerals transform into crystalline structures such as goethite (Dixit and Hering 2003). Due to the fact that goethite is widespread in the subsurface (Schwertmann and Cornell 1991), much work has been devoted towards the study of its interactions with As (Grossl and Sparks 1995; Zhao and Stanforth 2001; Dixit and Hering 2003; Lakshmipathiraj, Narasimhan et al. 2006; Gimenez, Martinez et al. 2007). The complex mixtures and transformations of iron oxides in the subsurface necessitates the creation of a reliable means of scaling to predict the interactions between iron oxides and groundwater contaminants such as arsenic.

The interactions of arsenate and arsenite with iron oxides, amorphous and crystalline, have been studied extensively to elucidate the effect of pH, competitive ions, and oxidation/reduction conditions on the sorption processes as well as the mechanism and form of the resulting complexes (Hingston, Posner et al. 1971; Pierce and Moore 1980; Pierce and Moore 1982; Fuller, Davis et al. 1993; Waychunas, Rea et al. 1993; Wilkie and Hering 1996; Fendorf, Eick et al. 1997; Raven, Jain et al. 1998; Lombi, Wenzel et al. 1999; Grafe, Eick et al. 2001; Zhao and Stanforth 2001; Goldberg 2002; Yang, Barnett et al. 2002; Dixit and Hering 2003; Williams, Barnett et al. 2003; Gupta, Saini et al. 2005; Yang, Barnett et al. 2005; Lakshmipathiraj, Narasimhan et al. 2006; Gimenez, Martinez et al. 2007; Manasse and Viti 2007). The literature has also been reviewed and summarized to consolidate the work thus far (Sadiq 1997; Smith, Naidu et al. 1998). These studies found that iron oxides have a high capacity to adsorb arsenic and that this adsorption is highly dependent on pH. Arsenate adsorbs most effectively at low pH (~4), while arsenite adsorbs optimally at near-neutral pH (Pierce and Moore 1982). Both monodentate and bidentate inner-sphere complexes are formed on the iron oxide surface as confirmed by wide angle X-ray scattering (WAXS), extended X-ray absorption fine structure (EXAFS), and infrared spectroscopy (Lumsdon, Fraser et al. 1984; Waychunas, Rea et al. 1993; Waychunas, Fuller et al. 1996; Fendorf, Eick et al. 1997). The competition for surface sites between arsenic and other ions, particularly phosphate, is also an important point of interest in the study of arsenic's subsurface interactions with iron oxides. Several studies have shown that the presence of phosphate as a co-solute increases arsenic's mobility and competes with arsenic for adsorption sites (Hingston, Posner et al. 1971; Woolson, Axley et al. 1973; Peryea 1991; Jain and Loeppert 2000).

Alongside the supply of arsenic adsorption data has grown an inclination and need to compare the results of the numerous studies. The work completed thus far has contained many different sets of experimental conditions and surface types, leading to a wide range of methods being employed for comparing the data. Some researchers have noted the importance of selecting appropriate datasets for comparisons, using adsorbate-adsorbent ratios as a basis (Wilkie and Hering 1996; Dixit and Hering 2003). However, for all comparisons, the researcher often has limited access to vital information concerning the previous study. It has been noted previously that data is often collected in a range of adsorbate-adsorbent ratios that make comparisons between data sets difficult or of little use (Wilkie and Hering 1996; Dixit and Hering 2003). Much of the published literature contains data collected near 100% adsorption or far away from field conditions. These characteristics of the published data restrict their use for comparison to systems which are exactly the same. The present state of the literature data lacks a means to reliably compare adsorption data.

The main objective of this work is to examine the different methods employed for the comparison of adsorption data, using both theoretical (i.e., model) and experimental data by: 1) Generating theoretical adsorption curves and making comparisons to extract relevant principles such as the best graphical method, experimental design considerations, and normalization techniques; 2) Testing these principles through comparisons of datasets from the literature and our laboratory; and 3) Drawing conclusions regarding the best methods for designing experiments used for comparison, processing adsorption data, and comparing with previously published results.

3.3 Methods

These objectives were accomplished through a series of model and experimental studies. First, theoretical equilibrium isotherms were generated through the use of a published surface complexation model. Using these equations, theoretical adsorption edges were produced for various conditions and plotted using several common methods. The model adsorption edges were compared in order to examine how varying conditions affect the graphical presentation of the data. Next, these principles were tested by plotting actual experimental data, from our laboratory and the literature, to see if the theoretical results are mirrored in existing data.

3.3.1 Modeling

The theoretical comparison study was completed by calculating adsorption curves and comparing the results in various manners. For the model, the three plane model (TPM) was applied through Visual Minteq (ver. 2.52) with the existing goethite database (goethite021.mdb) for low and high affinity sites (Weng, Temminghoff et al. 2001). A set of isotherms was generated for a range of pH values (3-10). At 25°C and I= 0.01M, Freundlich constants were fit to the isotherm for each pH value to determine an equilibrium isotherm ($q_e=K_fC_e^n$) for each pH value. These equations were then used for all the calculations at the corresponding pH values. The theoretical work was performed in this manner to simplify the extraction of relevant principles by eliminating uncontrolled factors associated with laboratory experiments and to enable us to assess a much wider range of solid-solution ratios. The equations were applied for a range of solid-solution ratios from traditional laboratory-scale to full field-scale values. This included varying the total adsorbate-adsorbent ratio from 1-1000 mmol As/ mol Fe. Adsorption data were normalized and plotted both as Kd (L/g Fe) and q_e (mmol As/ mol Fe), where Kd is the distribution coefficient and q_e is the amount of As adsorbed at equilibrium. These are two common plotting methods when comparing adsorption data. Plots of % adsorbed are not useful for comparison due to differences in arsenic concentrations, solid-solution ratios, and adsorbent properties which require the data to be normalized in some manner.

3.3.2 Literature Comparison

Experimental conditions for the datasets used in this comparison study are given in the respective publications (Dixit and Hering 2003; Gimenez, Martinez et al. 2007; Stachowicz, Hiemstra et al. 2007). These data were chosen due to their quality, the range of experimental conditions, the type of surface (e.g., natural goethite, synthetic goethite, coated sand), and/or the similarity of the experimental conditions to the ones used here. The literature data were normalized both on the basis of the theoretical iron content of goethite of 0.6285 g iron/g goethite and the surface area reported in each study. The adsorbent properties and pertinent experimental conditions are given in Table 3.1.

TABLE 3.1: Summary of experimental conditions and sorbent properties for the experiments in this study and from literature sources. M1, M2, DH1-4, S, & G are pH edge datasets for testing comparison techniques. M1-low, M1-med, and M1-high are experimental datasets used to study normalization techniques.

Dataset	**Reference**	**Media**	**Surface Area (m^2/ g FeOOH)**	**Fe Content (mol Fe/ g)**	**As:Fe_T (mmol As/mol $Fe)_T$**
Synthesis Method 1 †	M1 (●)	Coated Sand	178	6.83E-05	19.5
Synthesis Method 2 †	M2 (○)	Coated Sand	104	8.56E-06	15.6
Dixit & Hering (10 µmol/L)	DH1 (■)	Synthetic Goethite	54	1.13E-02	1.8
Dixit & Hering (25 µmol/L)	DH2 (▲)	Synthetic Goethite	54	1.13E-02	4.4
Dixit & Hering (50 µmol/L)	DH3 (×)	Synthetic Goethite	54	1.13E-02	8.9
Dixit & Hering (100 µmol/L)	DH4 (–)	Synthetic Goethite	54	1.13E-02	17.8
Stachowicz et al.	S (+)	Synthetic Goethite	98	1.13E-02	14.8
Giminez et al.	G (*)	Natural Goethite	2	1.13E-02	17.8
Low Iron Sand	M1-low (●)	Coated Sand	279	7.15E-06	Varied
Medium Iron Sand	M1-med (■)	Coated Sand	148	3.26E-06	Varied
High Iron Sand	M1-high (▲)	Coated Sand	113	5.69E-05	Varied

† This study

3.3.3 Experimental

For comparison, additional experimental data were also measured. The chemicals used in this work were reagent grade and all solutions were prepared fresh using deionized water (DIW) (18MΩcm) from a Milli-Q water system. The coated sands used here were prepared according to previously published protocols (Schwertmann and

Cornell 1991; Scheidegger, Borkovec et al. 1993; Cheng, Barnett et al. 2004; Cheng, Barnett et al. 2006) . The sand produced using a homogeneous suspension method, abbreviated here as 'M1', had an iron content of 68.3 μmol Fe/ g sand and a surface area of 283 m^2/g Fe (178 m^2/g FeOOH). The sand produced using a heterogeneous suspension method, abbreviated here as 'M2', had a lower iron content of 8.56 μmol Fe/g sand and a surface area of 165 m^2/g Fe (104 m^2/g FeOOH). The specific surface area of the sands was measured by BET surface area analysis (ASAP 2020, Micrometrics).

As(V) stock solutions were prepared by dissolving $Na_2HAsO_4.7H_2O$ (s) in DIW. All reaction solutions contained 0.01 M $NaNO_3$ to control the ionic strength. The As(V) concentrations of the solutions used in pH edge experiments with the homogeneous and heterogeneous suspension system sands were 13.3 μM and 1.33 μM, respectively. The pH of the reaction solutions for the adsorption edges was adjusted by the addition of HNO_3 or NaOH as required to achieve the desired pH. The batch experiments were conducted in 50 mL polypropylene centrifuge tubes (Corning), at room temperature (~22 °C), and were shaken for 24 hours to equilibrate. This reaction time was determined to be sufficient by preliminary kinetic tests (not shown).

To further study normalization methods, three goethite-coated sands of varying Fe content and surface area were produced using the homogeneous suspension method (M1-low, M1-med, M1-high). The sands had iron contents of 7.15, 32.6, and 56.9 μmol Fe/ g sand and specific surface areas of 444, 235, and 178 m^2/g Fe (279, 148, 113 m^2/g FeOOH), respectively (shown in Table 3.1). Adsorption isotherm experiments were performed with As(V) concentrations from 0-100 μM for each sand. The solution pH was maintained at 7±0.2, the temperature was 22 ± 2°C, and the ionic strength was maintained by adding 0.01M $NaNO_3$.

After reaction, the solution equilibrium pH was measured using an Orion model (410A+) pH meter and filtered through a 0.45 μm syringe filter (Whatman). Analysis of the filtrate was performed within 24 hours using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS; Perkin-Elmer 3110 PC).

3.4 Results and Discussion

3.4.1 Modeling

Figures 3.1A and 3.1B illustrate the difficulties that arise when performing batch adsorption experiments at one condition and trying to extrapolate the results to significantly different conditions. Here the systems have the same total As but widely varying solid-solution ratios, which results in large differences in $(As/Fe)_T$. The distribution coefficients from systems with the same As(V) concentration but different $(As/Fe)_T$ can vary by several orders of magnitude as seen in Figure 3.1A. This variability is also seen when plotting q_e (As adsorbed/mass of sorbent) vs. pH (Figure 3.1B), but to a much lesser extent. Problems arise particularly when comparing adsorbate-limited systems (low As:Fe, ~1 mmol As/mol Fe), which is often the case in porous media, where As is low relative to iron. The differences in the results largely disappear when the systems are no longer limited by the amount of adsorbate present, as shown by the 100 and 1000 mmol As/mol Fe curves. These issues are critical when modeling in the field using the constant-K_D approach and could be a major reason for the trouble in reliably predicting field-scale reactive transport (Bethke and Brady 2000).

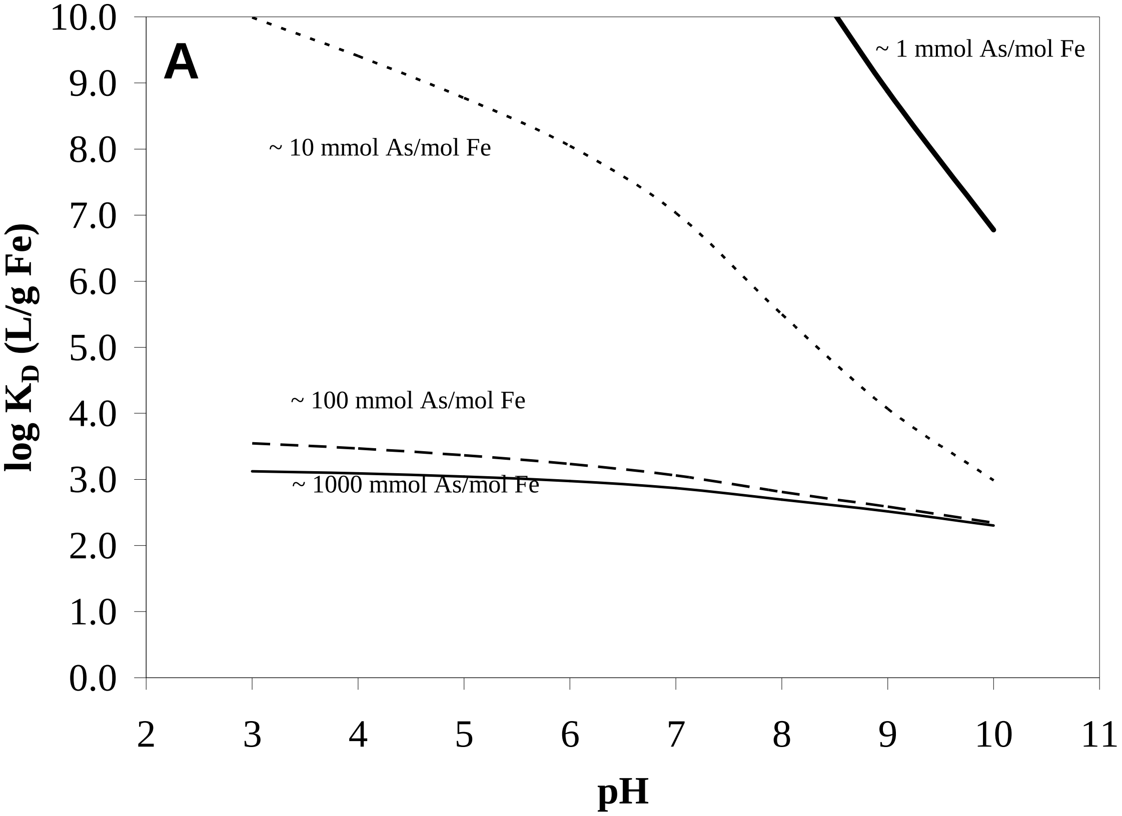

FIGURE 3.1A: Results from the model system. A) log K_D (L/g Fe) vs. pH for four $(As/Fe)_T$ values. (Typical field value: ~1mmol As/mol Fe; Typical laboratory value: 1-100 mmol As/mol Fe)

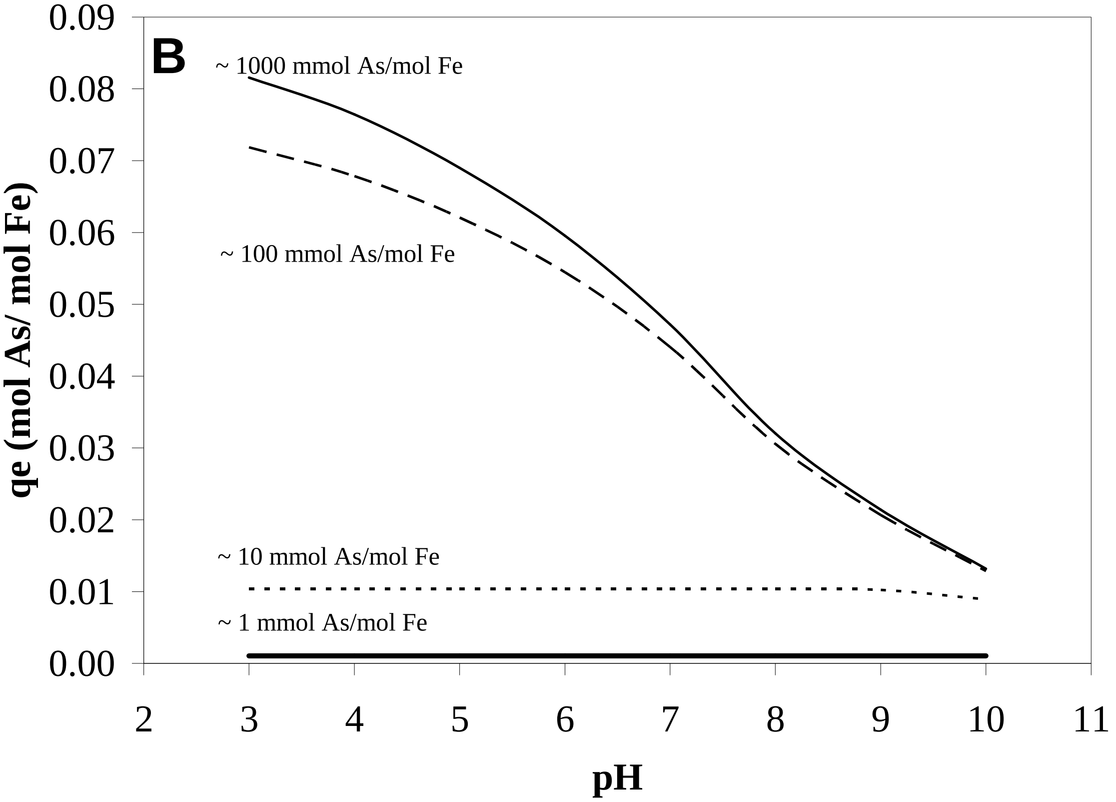

FIGURE 3.1B: Results from the model system. B) q_e (mol As/ mol Fe) vs. pH for four $(As/Fe)_T$ values. (Typical field value: ~1mmol As/mol Fe; Typical laboratory value: 1-100 mmol As/mol Fe)

Accounting for these factors by keeping the ratio of adsorbate to adsorbent constant and varying just the solid-solution ratio, the variability greatly declines. Figure 3.2 shows four systems with the same $(As/Fe)_T$ of 100 mmol As/ mol Fe but with different solid-solution ratios. These curves are more similar than those in Figure 3.1A with a difference of less than 1 log K_D unit per order of magnitude difference in solid-solution ratio. A slight difference in K_D with respect to solid-solution ratio is observed due to non-linear isotherms. Slight variances in the equilibrium point along the Freundlich isotherm curve produces differences in the slope between the four systems. Figure 3.2 shows that the difference in the systems is lower in the low pH range, when the isotherm is more linear, and increases in the upper pH range, where the isotherms are highly non-linear. The same calculations were performed assuming a linear isotherm and the pH edges were equal for all ratios (not shown).

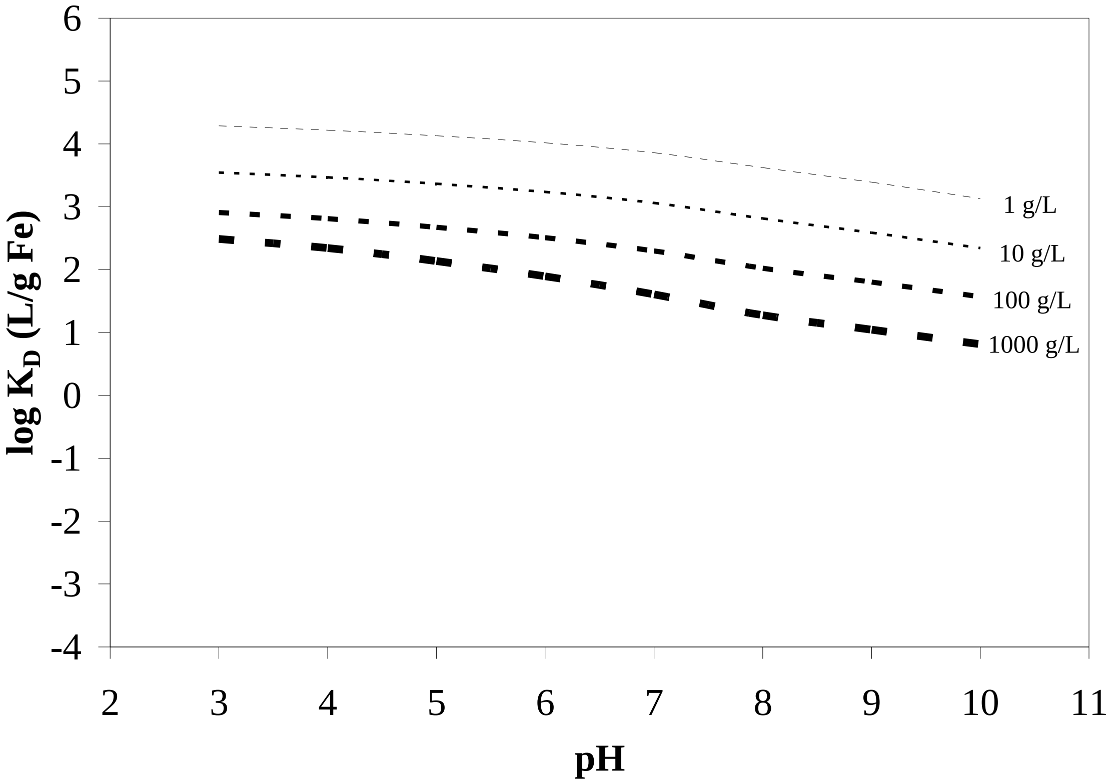

FIGURE 3.2: Results from the theoretical adsorption study. log K_D (L/g Fe) vs. pH for four different solid- solution ratios with a constant $(As/Fe)_T$ of 100 mmol As/mol Fe. Adsorbate-adsorbent ratio was maintained by varying As_T; 1, 10, 100 , and 1000 g/L contained 0.00667, 0.0667, 0.667, and 6.67 mM As, respectively.

3.4.2 Literature Comparison

A survey of the literature produced many studies of arsenate adsorption onto goethite or goethite-containing solids. These ranged from leaching studies in natural minerals to adsorption studies on laboratory-synthesized goethite. Three datasets were chosen for this comparison study: Dixit and Hering’s (2003) study of adsorption onto laboratory-synthesized goethite; the Stachowicz et al. (2007) study of arsenate adsorption on synthetic goethite with a high specific surface area (98 m^2/g); and the Giminez et al. (2007) study that used a natural goethite mineral with low specific surface area (2 m^2/g). These studies, along with our experiments on iron-coated sand, provided the needed range of data to test the results of the modeling study. The conditions of these experimental datasets, given in Table 3.1, show that these data have a range of $(As/Fe)_T$ from 1.8-19.5 mmol As/ mol Fe, approximately 1 order of magnitude. The range of conditions found in the literature illustrates the reality that laboratory data is not necessarily collected under the same conditions that are present in the field. Assuming a typical field solid-solution ratio of 3750 g/L (Phillippi, Loganathan et al. 2007), a soil Fe content of 0.1-50 g/kg (Goldberg, Lesch et al. 2005), a background arsenate soil concentration of 10 mg As/kg soil, and a groundwater arsenate concentration of 10-500 μg/L; yields the range of $(As/Fe)_T$ of 0.15– 84 mmol As/ mol Fe. The range of laboratory values is a small section of the possible field conditions.

Figure 3.3 shows the literature data normalized to Fe-content and plotted in two different ways corresponding to Figures 3.1A and 3.1B. To quantify the spread between the collected data, a line was fitted to each group of data and statistical values were extracted. The linear, least-squares fit was based on all the datasets combined (M1, M2, DH1-4, S, G). Likewise, the standard deviation was calculated for the combined datasets of each system (Fe normalized & surface area normalized). Figure 3.3A shows the data plotted as log K_D vs. pH. Most of the data is reasonably comparable (±1 standard deviation) when plotted this way, including datasets M1, M2, DH1-4 and S. There is, however, a larger difference between these datasets and the natural material, dataset G.

The difference between most of the data is about an order of magnitude in log $K_{D,}$ but this set of data drops far below the rest of the data, over an order of magnitude lower than the next lowest data set. The difference in the top groups (M1, M2, DH1-4 and S) is expected based on the spread of data in a similar range of Figure 3.1A, however, the discrepancy between those groups and the natural material could not be predicted with the simulated data. Figure 3.3B shows the data plotted in a different manner (qe vs. pH) and the results are as expected after looking at the model-predicted results in Figure 3.1B with respect to the absolute value and relative spread of the data. The adsorbate-limited datasets, DH1 and DH2, have values that are different from the rest of the datasets due to their lower $(As/Fe)_T$ values of 1.8 and 4.4 mmol As/ mol Fe, respectively. The adsorption in these datasets is ~ 100%, which inhibits their comparability with the other datasets. The group of datasets which are not adsorbate-limited are in a fairly tight group. However, if the data is inspected closely, it shows that there is a single difference of note amongst the non-adsorbate limited datasets. Again, this difference lies between the synthetic materials and the natural material. Datasets M1, M2, DH3, DH4, & S (synthetic) are closely grouped while dataset G (natural) is separated.

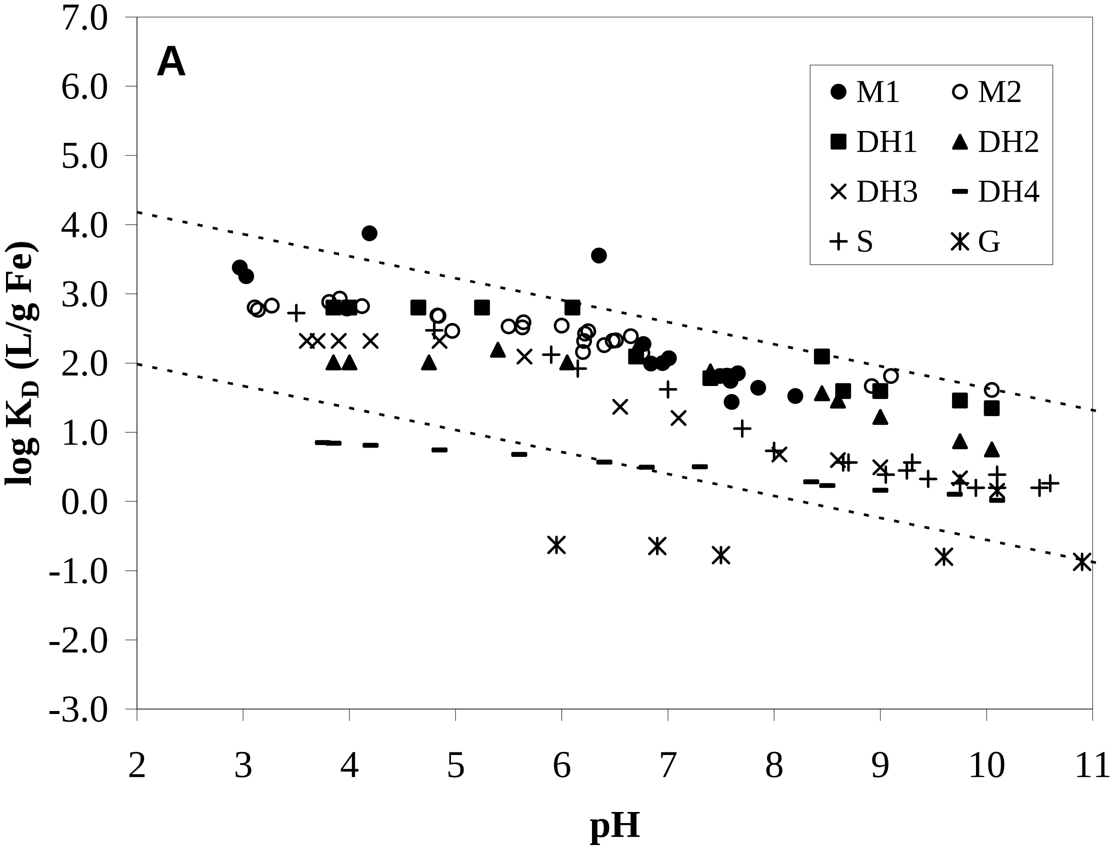

FIGURE 3.3A: Comparison of literature and experimental results normalized to Fe-content and plotted as A) log K_D (L/g Fe) vs. pH for data with various $(As/Fe)_T$ values. Dotted lines are ±1 standard deviation of the mean for the combined data.

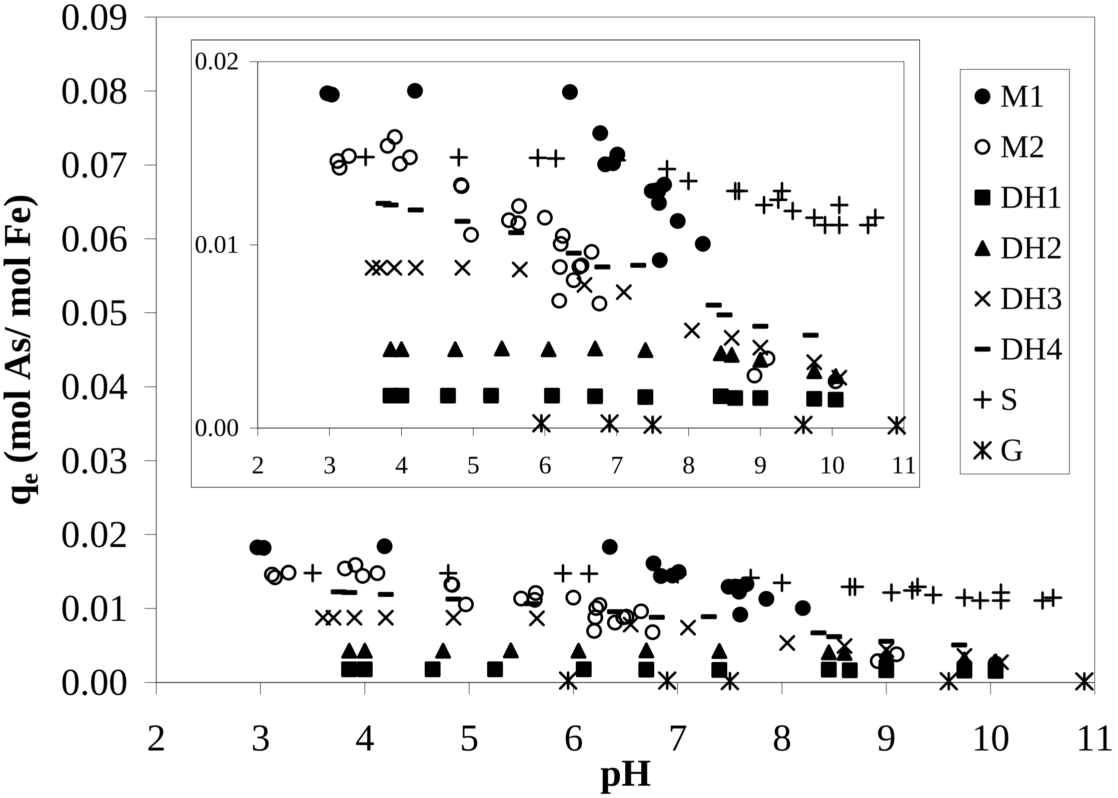

FIGURE 3.3B: Comparison of literature and experimental results normalized to Fe-content and plotted as B) q_e (mol As/ mol Fe) vs. pH for data with various $(As/Fe)_T$ values. The main scale in 3.3B matches the scale in Figure 3.1B; an inset is provided for clarity. Normalization factors are given in Table 3.1.

Figure 3.4 shows the literature data normalized to surface area and plotted in the same ways as in Figure 3.3. As far as data comparisons go, the data show the same principles as the model study. Figure 3.4A shows that all of the datasets, including the natural material, are more closely grouped than in Figure 3.3A. Figure 3.4B shows that the data may be more sensitive to adsorbate-limitation when normalized to specific surface area as there are larger differences between the datasets DH1, DH2, DH3, & DH4 in Figure 3.4B than in 3.3B. Looking at the data in Figure 3.4B and ignoring the adsorbate-limited datasets, DH1 and DH2, the difference in the non-limited sets is slightly larger than in Figure 3.3B (Fe-normalized). This has been seen in one previous study (Davis, Meece et al. 2004), where a drastic difference between the spread of the Fe-normalized data and the surface area-normalized data was not found. However, the exception in Figure 3.4B lies with the natural material which is not comparable when normalized to Fe but matches well with the other data when surface area is taken into account. This is an important consideration in the field where you can have widely varying specific surface area conditions.

A quantitative look at the spread of the data in Figures 3.3A and 3.4A showed a preference for surface area normalization. The standard deviation of the distribution coefficient for the Fe normalized data was 1.1 orders of magnitude compared to 0.87 for the surface area normalized data. These values show that the data is more consistent when normalized to surface area. The figures have lines that represent ± 1 standard deviation from the mean of the respective data to illustrate these results.

Figures 3.3 and 3.4 show that even for systems that have very similar experimental conditions and that are not adsorbate-limited, there will be some variance in the sorption edges. This variance may be due to many factors including adsorbent heterogeneities, unaccounted for competitive ions, and experimental error. These have been noted in previous studies when comparing datasets (Wilkie and Hering 1996; Hiemstra and Van Riemsdijk 1999; Dixit and Hering 2003; Ponthieu, Juillot et al. 2006; Gimenez, Martinez et al. 2007). This system, arsenate and goethite, illustrates many of the problems encountered when comparing data near the saturation of the adsorbent. Details and specific values such as adsorbent capacity, adsorption affinity, etc. will vary for other systems, but the basic considerations for comparing data still apply to all systems. Accounting for these issues is necessary when performing adsorption studies, and is best accomplished during the experimental design phase of the study.

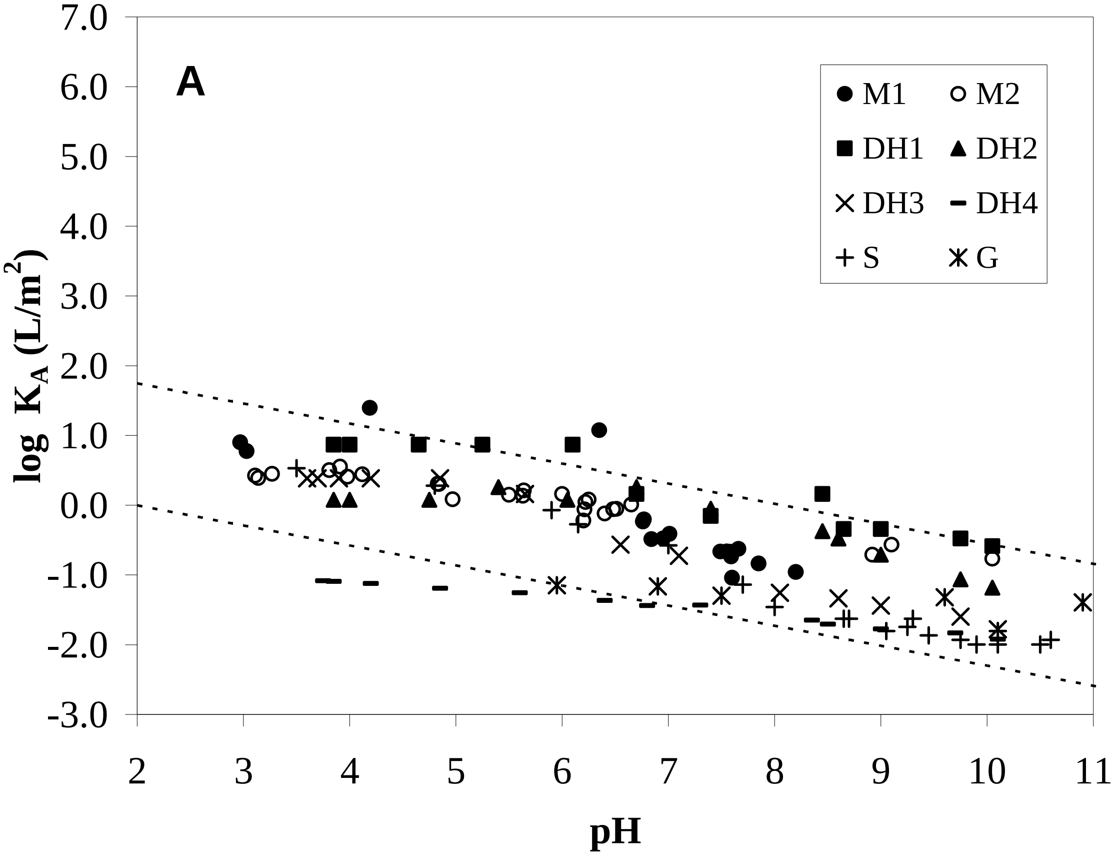

FIGURE 3.4A: Comparison of literature and experimental results normalized to surface area and plotted as A) log K_A (L/m^2) vs. pH for data with various $(As/Fe)_T$ values. Dotted lines are ±1 standard deviation of the mean for the combined data.

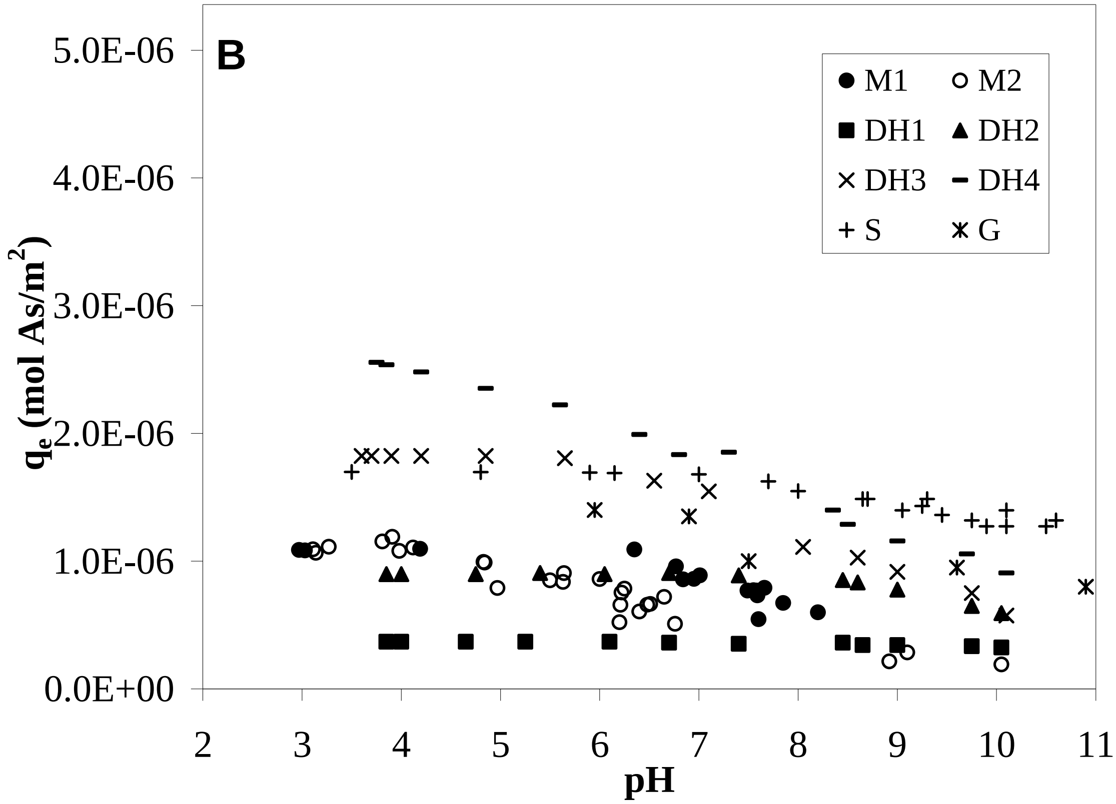

FIGURE 3.4B: Comparison of literature and experimental results normalized to surface area and plotted as B) q_e (mol As/ m^2) vs. pH for data with various $(As/Fe)_T$ values. The scale in 3.4B matches the scale in Figure 3.3B. Normalization factors are given in Table 3.1.

3.4.3 Normalization Technique

To further examine the factors governing the most appropriate technique used to normalize adsorption data, adsorption isotherms were constructed and normalized using the two different methods. Figures 3.5A and 3.5B show the isotherms normalized to Fe content and surface area, respectively. The maximum adsorption values range from 0.01 to 0.03 mol As/ mol Fe for the Fe-normalized isotherms. The highest specific adsorption belonged to the sand with the lowest Fe content while the medium and high Fe adsorbed at a similar level. Figure 3.5B, however, shows that when the isotherms are normalized to the specific surface area, the adsorption maximum is about the same for all three sands, ~1.1 μmol/ m^2. Our study of the literature data indicated that this is more often the case and that normalizing adsorption data to surface area is a more appropriate method when compared to normalization based on Fe content. In some cases there will not be a significant difference between the two methods, but most often the surface area method will be as good as or better than other methods. This advantage is particularly evident when one of the systems being compared contains natural materials with low specific surface area.

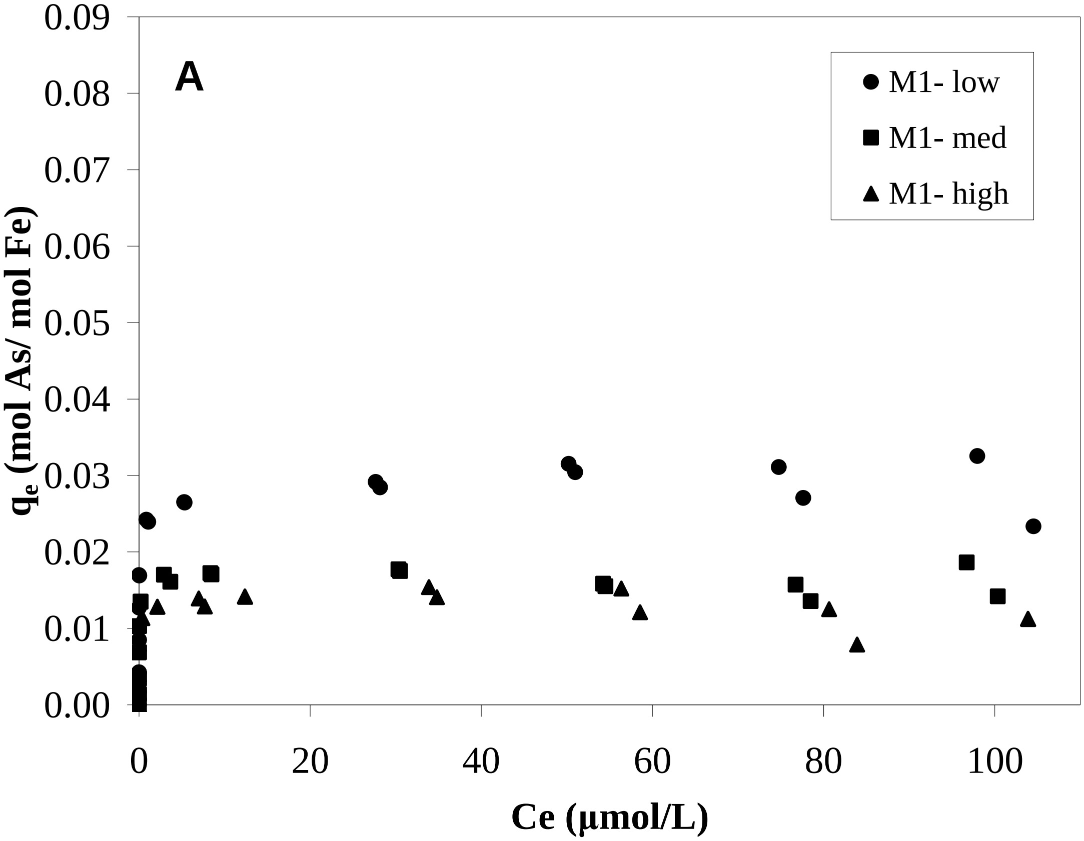

FIGURE 3.5A: Comparison of adsorption isotherms normalized to A) Fe content for three laboratory- synthesized Fe- coated sands. Experimental conditions: pH= 7±0.2; I=0.01M; T=~22°C. Normalization factors are given in Table 3.1.

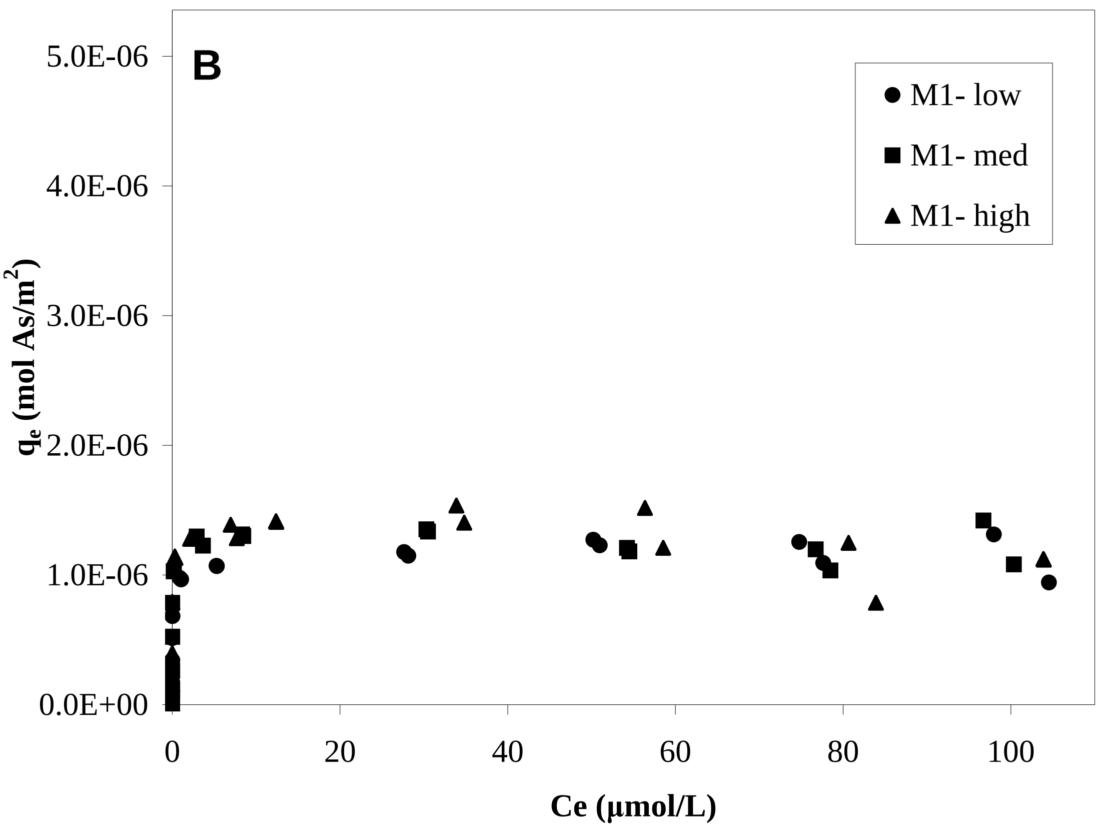

FIGURE 3.5B: Comparison of adsorption isotherms normalized to B) surface area for three laboratory- synthesized Fe- coated sands. Experimental conditions: pH= 7±0.2; I=0.01M; T=~22°C. Normalization factors are given in Table 3.1.

3.5 Conclusions

Model calculations were used to investigate the issues that arise when comparing adsorption data with various goethite adsorbents, experimental conditions, and on different scales. The majority of problems arise when systems are at or near their adsorption capacity. This condition often means that the system is limited by the amount of adsorbate present and experimental data may be of little use for comparisons. A survey and comparison of literature data shows that these problems frequently come into play even in well-controlled laboratory studies. Datasets should meet the following major criteria in order to make a valuable comparison with each other: 1) the systems should not be limited by the amount of adsorbate present. This makes presenting data as % adsorbed useful for isolated studies, but not appropriate for interstudy comparisons. 2) The datasets should have a similar adsorbate-adsorbent ratio; which will minimize the variance in the data due to non-linear isotherms. 3) The data should be normalized to the specific surface area of the adsorbent. In some cases normalization based on Fe content is acceptable, but rarely is this method more successful than the surface area method as a scaling parameter. 4) The literature survey also highlights the fact that laboratory data are frequently taken under conditions fairly dissimilar to those seen in the field. This discrepancy will make appropriate scaling, comparison, and normalization techniques of utmost importance in the future.

CHAPTER FOUR

CONCLUSIONS

The objective of the research described here was to examine the methods of comparing adsorption datasets for the purpose of scaling reactive transport models. The need for this work becomes evident when reviewing literature and noting the relative inability to meaningfully compare multiple adsorption studies. There are many harmful groundwater contaminants across the globe and much effort is devoted to the modeling and remediation of contaminated sites. The reactive transport of the groundwater contaminants is governed by the interaction of these contaminants with subsurface media and, often the specific presence of iron oxides in the soil. For this reason, the reactions between goethite and arsenic were used as a model system to study adsorption and the scaling behaviors of subsurface reactions. However, these results are applicable to other systems containing different media and contaminants.

Model-generated data were first used to identify the relevant theoretical parameters necessary to accurately compare adsorption datasets. The range of conditions at which these data were generated spans the gap from traditional laboratory-scale to typical field-scale conditions. The principles developed in this theoretical study were then applied to experimental data from the published literature and our laboratory. The results show that the majority of problems arise when systems are at or near their adsorption capacity. This condition often means that the system is limited by the amount of adsorbate present and experimental data may be of little use for comparisons. Specific conclusions are as follows: 1) experimental systems should not be limited by the amount of adsorbate present as this may be useful for isolated studies, but not for interstudy comparisons. 2) The datasets should have a similar adsorbate-adsorbent ratio, which will minimize the variance in the data due to non-linear isotherms. 3) The data should be normalized to the specific surface area of the adsorbent. In some cases normalization based on Fe content is acceptable, but rarely is this method more successful than the surface area method as a scaling parameter. 4) The literature survey also highlights the fact that laboratory data are frequently taken under conditions fairly dissimilar to those seen in the field. This discrepancy is of particular note and makes appropriate scaling, comparison, and normalization techniques of utmost importance. It is recommended that the preceding principles be noted and applied in future comparisons and noted when scaling parameters for use in reactive transport models.

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APPENDICES

APPENDIX A.

SAMPLE CALCULATIONS

Example 1

Example calculations to determine amount of arsenic (As) adsorbed per mass of adsorbent (iron oxide-coated sand, IOCS) from analytical data.

Given:

$10 gIOCS/L$
$6.83\times10^{-5} molFe/gIOCS$
$1.08 m^2/gIOCS$

From analytical measurements:

$C_o = 1 mgAs/L$
$C_e = 0.267 mgAs/L$

Solution:

Amount of arsenic adsorbed per gram of IOCS

$$q_e = \frac{(C_o - C_e)}{10 gIOCS/L}$$

$$q_e = \frac{(1-0.267) mgAs/L}{10 gIOCS/L} = 0.0733 mgAs/gIOCS$$

Amount of Arsenic adsorbed per m^2 of adsorbent

$$q_e = \frac{0.0733 mgAs/gIOCS}{(1.08 m^2/gIOCS)(74921.6 mgAs/molAs)} = \boxed{9.06\times10^{-7} molAs/m^2}$$

Amount of Arsenic adsorbed per mole of Fe

$$q_e = \frac{0.0733 mgAs/gIOCS}{(6.83\times10^{-5} molFe/gIOCS)(74921.6 mgAs/molAs)} = \boxed{0.0143 molAs/molFe}$$

Example 2

Example calculation for determining the distribution coefficient (K_d) from analytical data.

Given:

$6.83\times10^{-5} molFe / gIOCS$

$1.08m^2 / gIOCS$

From analytical measurements:

$$q_e = 0.0733 mgAs / gIOCS$$

$$C_e = 0.267 mgAs / L$$

Solution:

$$K_d = q_e / C_e$$

$$K_d = \frac{0.0733 mgAs / gIOCS}{0.267 mgAs / L} = 0.275 L / gIOCS$$

Distribution coefficient normalized to surface area.

$$K_d = \frac{0.275 L / gIOCS}{1.08 m^2 / gIOCS} = \boxed{0.254 L / m^2}$$

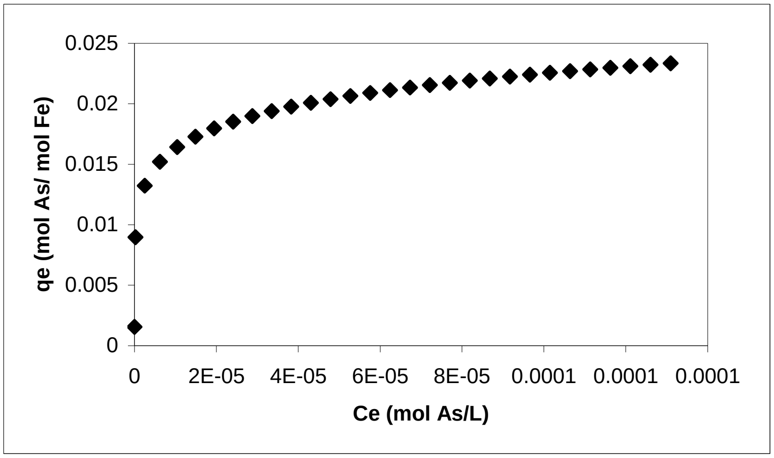
Distribution coefficient normalized to mass of adsorbent.

$$K_d = \frac{0.275 L / gIOCS}{(6.83\times10-5 molFe / gIOCS)(55.84 gFe / molFe)} = \boxed{72.1 L / gFe}$$

Example 3

Example determination of Freundlich constants from isotherm data.

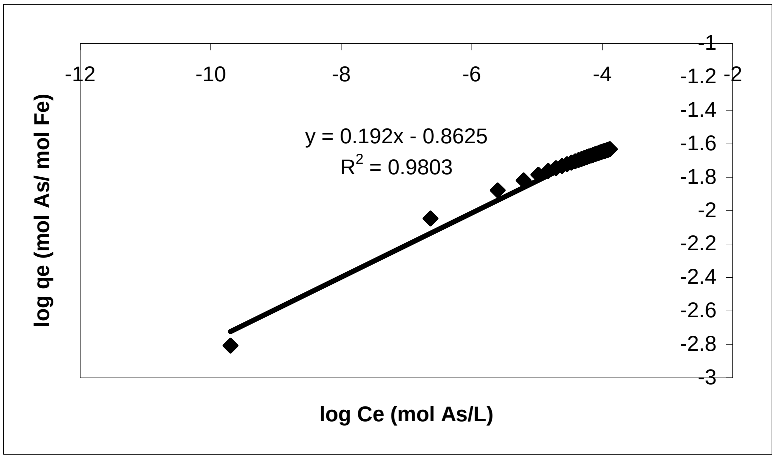
Isotherm data plotted traditionally:



Freundlich equation: $q_e = K_F C_e{}^n$

Linearized Freundlich equation: $\log q_e = \log K_F + n \log C_e$

Isotherm data plotted as log q_e vs. log C_e:



Determination of Freundlich parameters:

$$n = \boxed{0.192}$$

$$K_F = 10^{-0.863} = \boxed{0.137 L / molFe}$$

Example 4

Finding K_D using the Freundlich equation for a given set of conditions.

Using the predermined constants, a Freundlich equation can be written for this system at equilibrium:

$$q_e = 0.137 C_e^{0.192}$$

This equation, a set solids concentration, and a set value for the total amount of contaminant in the system allow us to calculate equilibrium concentrations in the aqueous and solid phases.

$$C_T = 10^{-4.17} = 6.67 \times 10^{-5} molAs/L$$

$$C_S = 6.43 \times 10^{-4} molFe/L$$

Two equations:

$$q_e = 0.137 C_e^{0.192}$$

$$q_e (6.43 \times 10^{-4} molFe/L) + C_e = 6.67 \times 10^{-5} molAs/L$$

Solve for the two unknowns:

$$q_e = 0.0207 molAs/molFe$$

$$C_e = 5.33 \times 10^{-5} molAs/L$$

Calculate K_D from q_e and C_e:

$$K_D = \frac{q_e}{C_e} = \frac{0.0207 molAs/molFe}{5.33 \times 10^{-5} molAs/L} = 388 L/molFe$$