Journal of Colloid and Interface Science 333 (2009) 6–13

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Normalization, comparison, and scaling of adsorption data: Arsenate and goethite

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ARTICLE INFO

Article history:
Received 6 July 2008
Accepted 9 January 2009
Available online 15 January 2009

Keywords:
Adsorption
Arsenic
Arsenate
Goethite
Iron oxides
Scaling
Surface area
Normalization
Adsorbate-to-adsorbent ratio

ABSTRACT

Various approaches for analyzing adsorption data were examined to determine the best method for reporting and interpreting the results of adsorption experiments and ultimately extrapolating laboratory measurements to the field. The interactions of arsenate and goethite were used as representative adsorbate and adsorbent, respectively, although the general principles are applicable to other adsorbate–adsorbent systems as well. A modeling exercise was conducted first to determine the theoretical principles governing the comparison and scaling of adsorption data. These principles were then tested on a suite of experimental data, both new and previously published. Log K_D is significantly more sensitive to variations in adsorbate (As_T) or adsorbent (Fe_T) concentrations than either adsorbed concentration (q) or percentage adsorbed. The sensitivity of K_D relative to q occurs due to the non-linearity of the adsorption isotherm at a given pH, since as the equilibrium aqueous concentration approaches zero, q also approaches zero while K_D approaches infinity. Varying As_T and Fe_T while keeping As_T/Fe_T fixed yields more consistent values of percentage adsorbed, $\log K_D$, and q, although the adsorbate-to-adsorbent ratios used in laboratory studies often have a rather narrow range compared to those possible in the field. Specific surface area is also a better scaling parameter than the mass of adsorbent, especially between systems with differing adsorbents with markedly different specific surface areas (e.g., natural versus synthetic goethite). Our results have significant implications to contaminant transport modeling, as the constant K_D approach is the most common method of modeling contaminant transport, while contaminant concentrations in the field are typically low, precisely the conditions where K_D is most sensitive.

1. Introduction

The transport of reactive groundwater contaminants is of significant 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 particular attention due to their ubiquitous presence and toxicity. Arsenic-contaminated sites present a danger both to the public and the environment.

Arsenic is present in many parts of the world including, eastern India, Bangladesh, the western United States, South America, Vietnam, and other locations around the world [1]. Many of these locations are affected due to the elevated presence of naturally occurring As due to conditions that trigger their release into groundwater. The development of high pH (>8.5) conditions and reducing conditions at circumneutral pH, for example, have been shown to mobilize As, even in locations with modest amounts of As in aquifer materials [1]. Modeling the reactive transport of As, which depends on the ability to predict the interactions of As with major subsurface constituents, is thus of considerable importance.

Iron oxides are arguably the most important factor controlling the mobility of As in the subsurface due to the abundance of Fe in soils and sediments and its natural affinity for As. In fact, much of the motivation for the present modeling work is the recognition that amorphous and crystalline Fe oxides are universally prevalent in soils and sediments; thus their interaction with groundwater constituents must be well understood [2,3]. The presence of amorphous Fe oxides, including hydrous ferric oxide (HFO) or ferrihydrite, as discrete minerals and as coatings on soil and sediment has been widely reported in the literature [4–6]. Iron oxide coatings on host minerals have also been recognized as a predominant factor controlling As adsorption and mobility [7–11]. In addition to amorphous forms, crystalline forms of Fe oxide, including hematite and goethite, are common in soil [4]. Iron oxide minerals often precipitate at oxic–anoxic boundaries and form amorphous ferrihydrite; over time these minerals transform into crystalline structures such as goethite [6]. Due to the fact that goethite is widespread in the subsurface [12], much work has been devoted towards the study of its interactions with As [6,13–16]. The complex mixtures and transformations of Fe oxides in the subsurface necessitate the creation

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doi:10.1016/j.jcis.2009.01.017

of a reliable means of scaling adsorption reactions to predict the fate and transport of groundwater contaminants such as As.

The interactions of arsenate and arsenite with Fe oxides, amorphous and crystalline, have thus been extensively studied to elucidate the effect of pH, competitive ions, and oxidation/reduction conditions on the adsorption processes as well as the mechanism and form of the resulting complexes [3,5–7,13,15–29]. The literature has also been reviewed and summarized to consolidate the work thus far [30,31]. These studies have shown both that Fe oxides have a high capacity to adsorb As and that the adsorption is highly pH-dependent. Arsenate adsorbs most effectively at low pH (∼4), while arsenite adsorbs optimally at circumneutral pH [3]. Both monodentate and bidentate inner-sphere complexes are formed on the Fe oxide surface as confirmed by wide angle X-ray scattering (WAXS), extended X-ray absorption fine structure (EXAFS), and infrared spectroscopy [23,28,32,33]. The competition for surface sites between As and other ions, particularly phosphate, is also an important factor governing the interaction of As in the subsurface. Several studies have shown that the presence of phosphate as a co-solute increases the mobility of As via competition for adsorption sites [27,34–36].

With the proliferation of As adsorption data, there is a 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 and contrasting the data. Some researchers have noted the importance of selecting appropriate datasets for comparisons, using adsorbate-to-adsorbent ratios as a basis [5,6]. It has been noted previously that data is often collected in a wide range of adsorbate-to-adsorbent ratios, which make comparisons between datasets difficult or of marginal use [5,6]. Much of the published literature contains data collected near 100% adsorption or under very specific experimental conditions. The present state of the literature lacks a means to reliably compare adsorption data, for As in particular and adsorbates in general.

The main objective of this paper is to determine the best method to compare, normalize, and scale pH-dependent adsorption data, using both theoretical (i.e., model) and experimental data by: (1) generating theoretical adsorption curves to extract relevant principles such as the best graphical method, experimental design considerations, and normalization techniques; (2) testing these principles through comparisons of experimental datasets reported in the literature and from our laboratory; and (3) elucidating the best methods for designing experiments and processing adsorption data to facilitate inter-study comparisons. Arsenate and goethite were selected as example adsorbate and adsorbent, respectively, but the underlying principles are applicable to other adsorbate–adsorbent systems as well.

2. Methods

To accomplish these objectives, we conducted both model and experimental studies. First, theoretical equilibrium adsorption curves were generated through the use of a published surface complexation model. Next, these principles were tested by plotting actual experimental data, both from our laboratory and the literature, to determine to what extent the theoretical results are reflected in the existing data.

2.1. Modeling

The modeling study was conducted by calculating equilibrium adsorption curves and comparing the results in various manners. The model used was the CD-MUSIC three plane model as implemented in Visual Minteq (ver. 2.53) with the existing goethite database (goethite021.mdb and goethite110.mdb) [37,38]. This surface complexation model conceptualizes the adsorption reactions as ligand exchange reactions occurring between aqueous As species and specific goethite surface groups. The model considers adsorption resulting from pH-dependent changes in surface charge, surface potential, aqueous As speciation, and total As and goethite concentration. Further details of the model can be found in the original sources [37,38] and in Appendix A. The modeling was performed to determine the theoretical normalization and comparison principles under ideal conditions (e.g., free from experimental errors). An adsorption isotherm and several pH adsorption edges were generated for a range of adsorbate-to-adsorbent ratios ($\mathrm{As_T/Fe_T}$, the ratio of total (dissolved and solid) As to total Fe), which varied from values typical of traditional laboratory batch experiments to field-scale. Adsorption data were normalized and plotted as percentage of $\mathrm{As_T}$ adsorbed, adsorbed As concentration (q, $\mathrm{mol\,As\,mol^{-1}\,Fe}$), and as the log of the distribution coefficient, K_D ($\mathrm{L\,g^{-1}\,Fe}$), defined by

$$\frac{q}{C} = K_\mathrm{D}, \tag{1}$$

where C ($\mathrm{mol\,L^{-1}}$) is the equilibrium As aqueous-phase concentration. All three are common graphical methods for comparing adsorption data [2,6]. However, plots of percent $\mathrm{As_T}$ adsorbed versus pH, although common, are generally not regarded as a useful basis for comparison due to differences in As concentrations, solid-to-solution ratios, and adsorbent properties that require the data to be normalized in some manner [2].

2.2. Literature data

Experimental conditions for the datasets used in this comparison study are given in the respective publications [6,13,39]. These data were chosen due to our judgment of their quality, the range of experimental conditions used, the type of surface (e.g., natural versus synthetic goethite) 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 Fe content of goethite (0.6285 $\mathrm{g\,Fe\,g^{-1}}$ goethite) and the surface area reported in each study. The adsorbent properties and pertinent experimental conditions are given in Table 1.

Table 1
Summary of experimental conditions and adsorbent properties for the experiments.

Dataset	Abbreviation	Media	Surface area ($\mathrm{m^2\,g^{-1}}$ FeOOH)	Fe content ($\mathrm{mol\,Fe\,g^{-1}}$ material)	$\mathrm{As_T/Fe_T}$ ($\mathrm{mmol\,As\,mol^{-1}\,Fe}$)
Hartzog et al.[a]	HM	Coated sand	178	6.83×10^{-5}	19.5
Hartzog et al.[a]	HT	Coated sand	104	8.56×10^{-6}	15.6
Dixit & Hering (10 μM)	DH1	Synthetic goethite	54	1.13×10^{-2}	1.8
Dixit & Hering (25 μM)	DH2	Synthetic goethite	54	1.13×10^{-2}	4.4
Dixit & Hering (50 μM)	DH3	Synthetic goethite	54	1.13×10^{-2}	8.9
Dixit & Hering (100 μM)	DH4	Synthetic goethite	54	1.13×10^{-2}	17.8
Stachowicz et al.	S	Synthetic goethite	98	1.13×10^{-2}	14.8
Gimenez et al.	G	Natural goethite	2	1.13×10^{-2}	17.8

[a] This study.