



Arsenic mobilization in an oxidizing alkaline groundwater: Experimental studies, comparison and optimization of geochemical modeling parameters

Saeedreza Hafeznezhani^{a,*}, Jacquelyn R. Lam^a, Yang Xiang^b, Matthew D. Reynolds^c, James A. Davis^d, Tiffany Lin^a, Jennifer A. Jay^a

^a Department of Civil and Environmental Engineering, UCLA, 5732 Boelter Hall, Box 951593, Los Angeles, CA 90095-1593, United States

^b Xiamen University, State Key Laboratory of Marine Environmental Science, 422 Siming S Rd, Siming, Xiamen, Fujian, 361006, China

^c Drumlin Environmental, LLC, 97 India Street, Portland, ME 04101, United States

^d Earth Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, United States

ARTICLE INFO

Article history:

Received 28 August 2015

Received in revised form

20 July 2016

Accepted 21 July 2016

Available online 22 July 2016

Keywords:

Arsenic

Mobilization

Groundwater contamination

Remediation

Geochemical modeling

Surface complexation modeling

Acidification

Adsorption

Natural attenuation

PHREEQC

FITEQL

ABSTRACT

Arsenic (As) mobilization and contamination of groundwater affects millions of people worldwide. Progress in developing effective in-situ remediation schemes requires the incorporation of data from laboratory experiments and field samples into calibrated geochemical models.

In an oxidizing aquifer where leaching of high pH industrial waste from unlined surface impoundments led to mobilization of naturally occurring As up to 2 mg L⁻¹, sequential extractions of solid phase As as well as, batch sediment microcosm experiments were conducted to understand As partitioning and solid-phase sorptive and buffering capacity. These data were combined with field data to create a series of geochemical models of the system with modeling programs PHREEQC and FITEQL. Different surface complexation modeling approaches, including component additivity (CA), generalized composite (GC), and a hybrid method were developed, compared and fitted to data from batch acidification experiments to simulate potential remediation scenarios. Several parameters strongly influence the concentration of dissolved As including pH, presence of competing ions (particularly phosphate) and the number of available sorption sites on the aquifer solids. Lowering the pH of groundwater to 7 was found to have a variable, but limited impact (<63%) on decreasing the concentration of dissolved As. The models indicate that in addition to lowering pH, decreasing the concentration of dissolved phosphate and/or increasing the number of available sorption sites could significantly decrease the As solubility to levels below 10 µg L⁻¹. The hybrid and GC modeling results fit the experimental data well (NRMSE<10%) with reasonable effort and can be implemented in further studies for validation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. Background

Arsenic (As), considered one of the most serious inorganic contaminants in drinking water can adversely impact human health and is recognized as a prominent environmental cause of cancer mortality worldwide (Smedley and Kinniburgh, 2002; Welch et al., 2000; Smith et al., 1992).

Arsenic is a ubiquitous trace element in the environment and can be mobilized from solid phases through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Following the World Health Organization (WHO) guideline in 1993, the US Environmental Protection Agency (US-EPA) reduced the maximum contaminant level (MCL) for As in drinking waters from 50 to 10 µg L⁻¹ in January 2001 (EPA, 2002; WHO, 2011).

While use of As containing compounds has decreased in recent decades and elevated levels of As in groundwater can generally be attributed to naturally occurring sources, anthropogenic activities such as agricultural and mining operations, industrial processes

* Corresponding author.

E-mail address: saeedreza@ucla.edu (S. Hafeznezhani).

and associated waste disposals can still cause or facilitate favorable conditions for mobilization of As from geologic sources into groundwater. Arsenic is the second most common contaminant of concern in National Priorities List (NPL), occurring at 47% of all Superfund sites in the US (EPA, 2002). High levels of As in the groundwaters of Bangladesh and West Bengal originate from natural sources with mobilization stimulated by anthropogenic inputs of natural organic matter (NOM) (Neumann et al., 2010; Harvey et al., 2006).

Arsenic speciation and fate is controlled by the pH and redox potential (Eh) of the system, the presence of ligands such as NOM and competing ions, and the mineral present at the site. Arsenic in groundwater is primarily present as oxyanions of As(V) (arsenate), with pKa's of 2.2, 6.9 and 11.5 or As(III) (arsenite), with pKa's of 9.3 and 14.2 (Stollenwerk, 2003).

Arsenic mobilization from solid to aqueous phases can occur in both reducing and oxidizing environments. Many studies have focused on reducing conditions, under which both As and Fe may be reduced and mobilized by microbial activity, as is occurring in Bangladesh (Radloff et al., 2011; Ravenscroft et al., 2009; Van Geen et al., 2006; Oremland and Stolz, 2005; Zheng et al., 2004; Anawar et al., 2002), Vietnam (Mai et al., 2014; Larsen et al., 2008; Postma et al., 2007; Berg et al., 2001), Cambodia (Lawson et al., 2013; Omoregie et al., 2013; Quicksall et al., 2008; Rowland et al., 2007; Polya et al., 2005), West Bengal, India (Neidhardt et al., 2014; Lawson et al., 2013; Islam et al., 2004; McArthur et al., 2004). Fewer studies have addressed oxidizing conditions, in which As(V) may be mobilized by desorption at high pH (Nicolli et al., 2012; Currell et al., 2011; Scanlon et al., 2009; Bhattacharya et al., 2006; Smedley et al., 2005), and others have investigated As solubility under variable redox conditions (O'Day et al., 2004).

Adsorption and coprecipitation on solid phases has been recognized as the principal factor in controlling As mobility in the environment (Wang and Mulligan, 2006). Sorption of As on Fe (III) (hydr)oxides is known as the most important process for limiting As solubility and has been investigated extensively. Due to their abundance in natural systems, high surface area and ability to adsorb As in large capacities, ferrihydrite (also referred to as amorphous hydrous ferric oxides or HFO) appears to be the most important solid phase responsible for removing As from the groundwater (Appelo and De Vet, 2003; Stollenwerk, 2003). The mechanism for specific adsorption has been described as ligand exchange reactions between ions in solution and surface functional groups leading to formation of both monodentate and bidentate inner-sphere complexes (Appelo and Postma, 2005; Sherman and Randall, 2003; Wilkie and Hering, 1996).

Efficiency of As adsorption onto Fe (III) oxides depends on a variety of factors such as the amounts and sorption capacity of minerals present, pH, concentrations and oxidation state of As, and concentration of other dissolved species that compete with As for adsorption sites (Stollenwerk et al., 2007). Ferrihydrite which has an amphoteric surface has strong affinity for adsorption of arsenate in pH range of 4–8. Adsorption studies at varying pH levels on ferrihydrite have shown that arsenate adsorption is higher at low pH values due to the net positive charge of the surface attracting negatively charged As(V) species (Raven et al., 1998). At high pH, arsenate adsorption becomes limited due to increased repulsion between the both negatively charged arsenate species and surface sites while arsenite can be retained in much larger amounts at such pH values due to its neutral charge (Masue et al., 2007; Dixit and Hering, 2003). Arsenic sorption can significantly be limited by presence of competing anions such as phosphate, silicates, bicarbonate and sulfate (Neupane et al., 2014; Kanematsu et al., 2012; Kanel et al., 2005; Dixit and Hering, 2003; Hongshao and Stanforth, 2001; Manning and Goldberg, 1996).

Efforts at applying geochemical modeling to simulate contamination and remediation scenarios in natural systems is challenging due to the complexity of interactions between groundwater and the solid matrix of the aquifer (Sharif et al., 2011). The majority of studies available on adsorption and surface complexation of trace contaminants have been conducted on pure mineral phases under controlled laboratory conditions. However, applicability of these findings to an environmental setting is limited due to the heterogeneous nature of aquifer media and the interactions among the various solid compositions.

Surface Complexation Models (SCM) for retention of trace elements such as As on natural heterogeneous solid phases can be categorized by two main approaches: (1) component additivity (CA) and (2) generalized composite (GC) (Davis et al., 1998). In the CA approach, it is assumed that the overall retention of solutes on a complex mineral assemblage can be described by combining the sorption results on the individual specific solid phases composing the sorbent mixture. This is possible by using databases developed from independent adsorption studies on the individual pure phases. The modeler needs to first adequately analyze the studied solid phase to characterize the composition of mineral mixture. Therefore in the CA approach the emphasis is usually on collecting mineralogical data for appropriate identification and quantification of solid phases responsible for sorption, without fitting the constants with experimental data.

In the GC approach, a generic solid surface is defined and assumed to represent the sorptive behavior of the entire mineral assemblage and site-specific surface characteristics are determined by conducting variety of experiments and fitting of data. Therefore, the GC approach focuses on investigating the site-specific holistic sorption characteristics of solid phases as a function of pH, concentration of adsorbing ion, and influence of competing ions. The stoichiometry and surface complex formation constants are then determined by statistical methods and fitting the experimental data.

While the CA approach seems to be more sound in theory, applying it to heterogeneous solid surfaces has limitations. First, in many situations sufficiently characterizing the composition of the sediments may not be possible or practical. Second, due to heterogeneity of natural sediment surfaces, the different mineral phases could interact and behave very differently than expected based on the findings from studies of isolated pure phases under controlled conditions. Presence of secondary minerals, impure mixture of phases, interactions with NOM, organic coating and clay minerals makes application of SCMs to natural sediments more challenging. (Biswas et al., 2014; Jessen et al., 2012; Hiemstra et al., 2010). Because of the difficulty in describing the actual surface charge of complex solid mixtures, applying the pH-dependent electrostatic correction terms required in the commonly used SCMs is not accurate for describing the adsorption on natural particles (Davis et al., 1998).

Also, the surface complexation mass-action reaction constants that are usually adopted from reference databases are developed from adsorption studies with constant background electrolyte concentrations in solution and will have limitations when applied to adsorption of solutes from the more complex natural groundwater systems. The intrinsic surface acidity constants are derived from titration experiments in simple electrolyte solutions and based on the assumption that only the functional groups control the acidity properties of the surface. However in natural systems, such as aquifers with calcareous lithology, presence of various ions in solution and dissolution of phases such as carbonates invalidate this assumption.

Sharif et al. (2011) signified the inherent uncertainty in using the CA approach and the need for properly determining the surface

Download English Version:

<https://daneshyari.com/en/article/6334808>

Download Persian Version:

<https://daneshyari.com/article/6334808>

[Daneshyari.com](https://daneshyari.com)