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Short Communication

Dependence of particle concentration effect on pH and redox for arsenic removal by FeS-coated sand under anoxic conditions

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HIGHLIGHTS

- Solid-solution ratio (SSR) effect observed at pH 5, but not at pH 7 and 9.
- At pH 5, K_d increased with SSR, inverse to typical trend.
- SSR effect tied to change in As(III) removal mechanism which varied with pH and pe.

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ABSTRACT

FeS has been recognized as a good scavenger for arsenic under anoxic conditions. To create a suitable adsorbent for flow-through reactors such as permeable reactive barriers, it has been suggested that this material may be coated onto sand. However, previous work on FeS-coated sand has focused on batch reactors, while flow-through reactors usually have higher solid-solution ratios. To ascertain whether differences in the solid-solution ratio (SSR) are important in this system, batch sorption experiments were conducted as a function of pH using As(III) and FeS-coated sands at various solid-solution ratios. The results showed little variation in the distribution coefficient with SSR at pH 7 and 9. However, at pH 5, the results showed lower values of the distribution coefficient at lower SSRs, the reverse of typically reported SSR effects. Measured pe values showed a dependence on SSR, which, when coupled with chemical modeling of the Fe–As–S–H_2O system, suggested a change in the removal mechanism with SSR, from adsorption to a reduced Fe(II) oxyhydroxide phase (represented by $Fe_2(OH)_5$) to precipitation as As_2S_3 or AsS. On the other hand, at pH 7 and 9, arsenite adsorption is the most probable removal mechanism regardless of the pe. Thus, this study identified variations in pH and redox conditions, and the removal mechanisms that these parameters govern, as the reason for the apparent SSR effect.

1. Introduction

Iron sulfide (FeS) has shown promise for the removal of As(III) under anoxic conditions (Wolthers et al., 2005; Gallegos et al., 2008). To create an appropriate material for the removal of As(III) in flow-through reactor configurations such as permeable reactive barriers (PRBs), synthetic FeS may be coated onto the surface of a natural silica sand (Han et al., 2011a). FeS-coated sand showed a lower removal capacity than nanoparticulate (NP) FeS at pH values of 5 and 7; however, it showed a higher capacity at pH 9 (Han et al., 2011a). These differences were explained in terms of differences in states of aggregation, iron mineral composition and metal oxides that exist naturally on the sand surface (Han et al., 2011a). The redox condition may also be a critical factor in determining the sorption characteristics of FeS in different forms (Han et al., 2011b).

The previous work utilized batch systems, whereas the proposed use of FeS-coated materials is as a sorbent in a flow-through reactor. The issue of scaling batch data to flow-through systems is complex. One of the potential issues is the solid-solution ratio (SSR) effect, also known as the solid effect, or particle concentration effect (Phillippi et al., 2007). In moving from batch systems to column reactors, the particle concentration increases from under 100 to 500 g L^{-1} for granular reactants, or even lower

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for nanoscale particles, to a value ranging from 3000 to 5000 g L^{-1} for columns (Maraqa, 2001). Ideally, sorption isotherm parameters should be independent of the SSR for the same system composition (Chang and Wang, 2002; Dong et al., 2005; Leote et al., 2013). However, a dependence on the SSR has been observed in systems comprising sorbents as diverse as soils, estuarine and marine sediments, and well-characterized minerals, and sorbates ranging from metals and nutrients to organic compounds and actinides (Leote et al., 2013). The general pattern of the particle concentration effect is higher values of the distribution coefficient at lower SSRs (O'Connor and Connolly, 1980; Bajracharya et al., 1996; Benoit and Rozan, 1999; Porro et al., 2000; Chang and Wang, 2002; Chang et al., 2002; Phillippi et al., 2007; Wang et al., 2009; Utomo and Hunter, 2010; Leote et al., 2013). This phenomenon has been explained in terms of: (i) sorption sites with different affinities for the sorbate (Hemming et al., 1997); (ii) an erroneous inclusion of colloidal forms of the sorbate in measuring the dissolved fraction concentration (Benoit and Rozan, 1999); (iii) flocculation of the sorbent affecting specific surface area (Utomo and Hunter, 2010); (iv) competition between the sorbate and like-charged ionic species for sorbent sites (Chang et al., 2002); and (v) complexation among multiple sorbates (e.g., metal cations and ligands) and the sorbent (Phillippi et al., 2007). In fact, Phillippi et al. (2007) contend that if the appropriate nano- or molecular-scale phenomena can be accounted for, the apparent particle concentration effect has a well-defined basis for its occurrence.

To ascertain whether a SSR effect existed in the As(III)-FeS-coated sand system, sorption measurements of As(III) onto FeS-coated sands were conducted at various SSRs as a function of pH under anoxic conditions. Such an understanding may be critical in extrapolating data obtained in batch reactors generally conducted at low SSRs to flow-through reactors where, by virtue of their nature, have high SSRs.

2. Methods

The methods of synthesizing the FeS and the FeS-coated sand utilized in this study have been described previously (Butler and Hayes, 1998; Han et al., 2011a). To evaluate the particle concentration effect, a series of sorption isotherms were measured at three different SSRs at pH 5, 7 and 9. The test tubes were prepared with 1 g, 2 g, and 5 g of FeS-coated sand and 10 mL of the following buffers: 0.1 M $C_2H_3NaO_2$ buffer for pH 5, 0.1 M 3-(N-morpholino) propanesulfonic acid (MOPS) for pH 7, and 0.1 M N-cyclohexyl-2-aminoethanesulfonic acid (CHES) for pH 9, to give SSRs of 100, 200, and 500 g FeS-coated sand L^{-1}. The FeS-coated sand contained 1.42×10^{-5} mol FeS g^{-1} sand (1.25 mg FeS g^{-1} sand); thus, the three SSRs corresponded to 0.125, 0.250, and 0.625 g FeS L^{-1}. As(III) stock solution was spiked into each tube to achieve a concentration range of 1.3×10^{-6} M to 6.7×10^{-4} M. The prepared reaction tubes were then mixed with an end-over-end rotator for two days. After two days, the supernatant in tubes was filtered through a 0.1 μm nylon filter, diluted, and then acidified with HNO_3 and analyzed for arsenic by inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin–Elmer).

As(III)-sorption tests were also conducted using FeS-coated sand over the range of pH 2–12. One gram of FeS-coated sand, 9.9 mL 0.1 N NaCl solution, and 0.1 mL of 1.3×10^{-3} M $NaAsO_2$ stock solution were placed in 15 mL polypropylene tubes to achieve an As(III) concentration of 1.3×10^{-5} M As(III). Various amounts of 0.08 N HCl and 0.1 N NaOH solutions were added to each tube to adjust the pH and mixed using an end-over-end rotator. The change of ionic strength during the pH adjustment was assumed to be negligible (the maximum additions resulted in a change in ionic strength of less than 0.01 M). After two days of mixing, half of the supernatant was filtered with a 0.1 μm nylon filter and acidified for the analysis of As(III) and dissolved Fe (Fe_{diss}) concentration using ICP-MS. The other half of the supernatant was used for pH measurements.

In addition, Eh was measured as a function of solids concentration in the absence of arsenic to investigate the redox condition as a function of particle concentration in FeS-coated sand suspensions. The concentrations of FeS-coated sand were selected to correspond to the conditions for the redox measurements for nanoparticulate (NP) FeS reported in Gallegos et al. (2008). The FeS-coated sand was mixed with 10 mL of pH-buffered solution. After two days of equilibration, both the pH and Eh were measured in these suspensions. Eh was measured using an ORP (oxidation–reduction potential) combination electrode (Cole-Parmer). Once the readings stabilized, the potentials were recorded, corrected for the standard hydrogen electrode and temperature, and then converted to pe. All the experiments in this study were performed in an anaerobic glovebox, under a gas phase of 95% N_2/5% H_2, maintained using a Pd catalyst. All solutions were made up using deionized water and were purged using N_2.

3. Results and discussion

3.1. Isotherm measurements

Fig. 1 shows the results of the sorption experiments conducted at SSRs of 100, 200 and 500 g L^{-1} at pH values of 5, 7, and 9. The panels on the left side of Fig. 1 (Fig. 1a, c, e) show the quantity of As(III) removed from solution. The panels on the right side of Fig. 1 (Fig. 1b, d, and f) show the distribution coefficient, K_d, expressed as the ratio of mg As(III) sorbed g^{-1} sand to mg of As(III) L^{-1} remaining in the aqueous phase. The distribution coefficient is sometimes portrayed as a constant (Weber and DiGiano, 1996). However, in this system, as in others (e.g., Fox et al., 2006; Hyun et al., 2009), the distribution coefficient varied as a function of pH and concentration of the solute. At pH 7 and pH 9, the value of K_d is essentially independent of the SSR. But, at pH 5, K_d increased with the solids concentration, inverse to the commonly reported SSR effect of higher values of K_d at lower SSRs (O'Connor and Connolly, 1980; Bajracharya et al., 1996; Benoit and Rozan, 1999; Porro et al., 2000; Chang and Wang, 2002; Chang et al., 2002; Phillippi et al., 2007; Wang et al., 2009; Utomo and Hunter, 2010; Leote et al., 2013).

To understand this phenomenon in terms of the chemistry of the system, measurements were made of dissolved Fe concentrations and As(III) removal from solution over the pH range of 2–12 at a single SSR of 100 g L^{-1} (Fig. 2). Fig. 2 shows that at pH values lower than 7, the dissolved Fe concentration increased abruptly and the As(III) removal was almost 100%. Spectroscopic information has suggested that in FeS-coated sand systems, As(III) is removed through the formation of orpiment (As_2S_3) at pH 5 (Han et al., 2011b). At pH values above 7, As(III) removals dropped and then reached a local maximum near pH 9, close to the pK_{A1} of 9.24 for As(III). Spectroscopic information has indicated that As associated with the surface of the FeS-coated sand is in the form of arsenite in this pH region, indicating that the removal mechanism is adsorption (Han et al., 2011b). The adsorption reaction may take place on the surface of FeS, which consists of both >SOH and >FeOH, on the secondary surface of the oxidation products of FeS such as magnetite (Gallegos et al., 2008), or on the iron oxyhydroxide solid coating of the underlying natural sand (Han et al., 2011b). Since the dominant aqueous arsenic species changes from $H_3AsO_3^0$ to $H_2AsO_3^-$, coupled with the fact that the FeS or Fe oxide phases on the coated sand have a negative charge at alkaline pH values, the adsorption decreased above pH 9.24.

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